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REVIEW ARTICLE

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Natural materials as sustainable adsorbents for per- and polyfluoroalkyl (PFAS) substances remediation in real water systems

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Abstract

The persistence of per- and polyfluoroalkyl substances (PFAS) in aquatic environments poses major challenges for water treatment, particularly in real water systems where dissolved organic matter, co-existing ions, suspended solids, variable pH, and co-contaminants can reduce adsorption performance. This review evaluates natural adsorbents for PFAS remediation, including biochar, clays, zeolites, agricultural residues, cellulose-based materials, chitosan derivatives, algae-based adsorbents, and hybrid composites. Emphasis is placed on adsorption performance in relation to adsorbent dosage, initial PFAS concentration, pH, contact time, removal efficiency, desorption behavior, and field applicability. The reviewed studies show that adsorption efficiency is strongly governed by surface functional groups, pore structure, surface charge, hydrophobic domains, and water matrix complexity. Dosage differences are critically interpreted as indicators of material efficiency and scalability, since high removal at high adsorbent loading does not necessarily represent superior performance. pH effects are also discussed with caution because some reported trends originate from controlled laboratory matrices rather than true real-water conditions. Kinetic data are often well described by pseudo-second-order models; however, such fitting should be interpreted as evidence of surface-controlled adsorption behavior rather than definitive proof of chemisorption without supporting characterization. Long-chain PFAS generally show stronger retention through combined hydrophobic and electrostatic interactions, whereas short-chain PFAS are more mobile, less hydrophobic, and more prone to desorption. Overall, natural adsorbents offer promising sustainable options for PFAS removal, but practical implementation requires improved adsorbent design, regeneration assessment, repeated adsorption-desorption testing, and pilot-scale validation under realistic water matrices across groundwater, surface water, wastewater, stormwater, and landfill leachate applications globally.

KEYWORDS
PFAS; real water; treatment; removal; mechanism

1. INTRODUCTION

PFAS represent a large class of synthetic organofluorine compounds characterized by extraordinary chemical stability and unique physicochemical properties, including resistance to heat, water, and oil (Panieri, Baralic, Djukic-Cosic, Buha Djordjevic, & Saso, 2022). These features have driven their extensive use in numerous industrial and consumer products, such as firefighting foams, food packaging, water-repellent coatings, textiles, and protective linings for industrial equipment (Gaines, 2023). However, the same stability that makes PFAS desirable in manufacturing also renders them extremely persistent in the environment, earning them the designation of “forever chemicals.” PFAS have been widely detected in surface water, groundwater, sediments, air, and even within biotic tissues, indicating their ubiquitous distribution (Ehsan, Riza, Pervez, & Liang, 2025). Human exposure pathways include the consumption of contaminated drinking water and food, the use of household products, and occupational exposure. Unlike other persistent organic pollutants (POPs), which are lipophilic and tend to accumulate in fatty tissues, PFAS exhibit a strong affinity for proteins, particularly serum albumin and liver fatty acid-binding proteins (Fan et al., 2025). Their strong binding to proteins enables prolonged retention in protein-rich organs, thereby extending biological half-lives. Long-term exposure has been associated with a wide range of adverse health effects, including endocrine disruption, impaired immune function, developmental abnormalities, and potential carcinogenicity. With global production continuing to rise and mounting evidence of health risks, PFAS have emerged as a priority pollutant requiring effective strategies for control and remediation.

The application of natural materials as adsorbents for PFAS removal has gained increasing attention as a promising and environmentally sustainable approach for water pollution management. Their importance becomes more evident when compared with conventional adsorbents, such as commercial granular activated carbon, ion exchange resins, and synthetic polymeric materials, which are often associated with high production costs, energy-intensive regeneration, limited selectivity toward short-chain PFAS, and the generation of concentrated PFAS-laden residuals after treatment. Although these conventional adsorbents have been widely used and can be effective for long-chain PFAS, their performance may decline in complex real water systems due to competition with dissolved organic matter, inorganic ions, and co-contaminants. In this context, natural adsorbents offer a strategic alternative because they are generally abundant, low-cost, renewable, and can be derived from locally available resources, including biomass waste, clay minerals, zeolites, lignocellulosic fibers, and agricultural residues (Gonçalves et al., 2025). Their use also aligns with circular economy and waste-to-resource principles by converting low-value natural or agricultural materials into functional adsorbents for water remediation. In addition, natural adsorbents can be physically or chemically modified to enhance surface area, porosity, surface charge, and functional group density, thereby improving their affinity toward both short- and long-chain PFAS (Kinoti, Karanja, Nthiga, M’thiruaine, & Marangu, 2022). Several studies have reported that acid- or amine-modified biochars exhibit stronger PFAS adsorption than their unmodified counterparts, highlighting the potential of surface engineering to improve adsorption efficiency. Another key advantage is their potential suitability for decentralized or resource-limited water treatment applications, where low-cost, accessible, and easily prepared materials are more practical than expensive synthetic adsorbents. Nevertheless, challenges remain, including adsorbent regeneration, the management of contaminated residuals, long-term stability, and reduced efficiency in complex water matrices (Pazol et al., 2024; Pervez et al., 2024). Therefore, adsorption technologies based on natural materials not only provide a cost-effective and sustainable remediation option but also represent an important pathway for improving the practical applicability of PFAS treatment in real aquatic systems..

This review examines the types of PFAS compounds and natural adsorbents applied for their removal in real water systems. Particular emphasis is placed on adsorption performance under diverse experimental conditions, including adsorbent dosage, initial PFAS concentration, pH, contact time, and removal efficiency. In this review, the term "real water systems" refers to environmentally relevant aqueous matrices, including groundwater, surface water, municipal and industrial wastewater, treated wastewater, stormwater runoff, landfill leachate, and mixed environmental matrices. These systems differ from synthetic laboratory solutions because they commonly contain dissolved organic matter, co-existing inorganic ions, suspended solids, variable pH and ionic strength, as well as other organic and inorganic co-contaminants that may influence PFAS adsorption behavior. The novelty of this review lies in its focus on studies conducted under such real water conditions rather than relying solely on simplified synthetic laboratory solutions. Adsorption performance is further examined in relation to mechanistic aspects, including adsorption pathways, kinetic and isotherm models, and desorption behavior to assess reusability. Accordingly, this review not only consolidates existing findings but also highlights new perspectives on the scalability and field applicability of natural adsorbent-based PFAS remediation. The insights presented are expected to provide a strong scientific basis for the development of selective, efficient, and sustainable adsorption technologies to address PFAS contamination in aquatic environments.

2. EXPERIMENTAL OF NATURAL ADSORBENTS FOR PFAS

Effective removal of per- and polyfluoroalkyl substances (PFAS) from real water systems is essential to mitigate their persistence, mobility, and potential risks to human health and aquatic ecosystems. Various natural adsorbents have been investigated for PFAS remediation, as summarized in Table 1. These materials, including biochar, activated carbon, clay minerals, algae-based materials, cellulose-based membranes, chitosan derivatives, protein-based adsorbents, and plant-derived biomasses, exhibit different removal performances depending on their surface chemistry, pore structure, functional groups, and affinity toward specific PFAS compounds. However, adsorption performance should not be evaluated solely based on removal percentage, because high removal efficiency may result from high adsorbent loading rather than intrinsically superior adsorption capacity. Therefore, the application rate or dosage of adsorbents is a critical parameter for assessing not only treatment efficiency but also material utilization, economic feasibility, and scalability.

As shown in Table 1, the adsorbent dosage used in previous studies varied considerably, ranging from very low amounts of 0.012–0.024 g for nanofibrous materials, such as nanofibrous Chlorella powder and cellulose-based electrospun nanofibrous membranes, to higher dosages exceeding 4 g/L for porous activated carbon (PAC) (Mantripragada, Deng, & Zhang, 2023; Mantripragada, Dong, & Zhang, 2023). This wide dosage range reflects major differences in adsorbent morphology, surface area, porosity, and density of active binding sites. Low-dose adsorbents with high PFAS removal efficiency indicate more efficient material utilization because a smaller amount of material can provide sufficient active sites for adsorption. For example, biochar derived from sawdust achieved PFOS removal at a relatively low dosage of 0.25 g/L over 24 h under acidic conditions (Mer, Arachchilage, Tao, & Egiebor, 2024), suggesting favorable interaction between the adsorbent surface and PFOS. Similarly, nanofibrous and membrane-based adsorbents may achieve rapid PFAS capture at low dosages because their fibrous morphology provides accessible surface sites and short diffusion pathways. In contrast, materials requiring higher dosages may still achieve high removal percentages, but their practical efficiency may be lower if the adsorption capacity per unit mass is limited (Dudarko et al., 2024).

The critical interpretation of dosage differences is particularly important for assessing the scalability of PFAS adsorption technologies. At laboratory scale, increasing adsorbent dosage can improve removal efficiency by increasing the number of available adsorption sites. However, at pilot or field scale, excessive adsorbent dosage may increase operational costs, material consumption, pressure drop in column systems, regeneration frequency, and the volume of spent adsorbent requiring safe disposal. This issue is especially relevant for real water systems, where dissolved organic matter, co-existing ions, suspended solids, and competing contaminants may occupy active sites and reduce PFAS uptake. Therefore, an adsorbent that performs well only at high dosages in simplified laboratory solutions may not necessarily be suitable for large-scale application. Conversely, adsorbents that maintain high removal efficiency at low dosages and short contact times are more promising for practical implementation because they offer better material efficiency and lower secondary waste generation (Niu et al., 2020). Dosage should also be interpreted in relation to the initial PFAS concentration and the type of PFAS targeted. Many experimental studies used relatively high PFAS concentrations compared with environmentally relevant levels, which may overestimate adsorption performance and limit direct translation to real water treatment. In addition, long-chain PFAS such as PFOA and PFOS are generally more readily adsorbed because of stronger hydrophobic interactions, whereas short-chain PFAS such as PFBS and GenX often require more specialized surface functionalities, such as cationic, amine-rich, or ion-exchange sites. Thus, differences in dosage cannot be interpreted independently from PFAS chain length, functional head group, water matrix composition, and adsorbent surface properties. A more meaningful comparison among adsorbents should consider removal efficiency together with adsorption capacity, contact time, dosage requirement, regeneration potential, and stability under realistic water conditions.

Experimental durations also varied widely, from as short as 0.25–1 h for highly reactive biochar or integrated NF-MAC systems to several months for plant-based systems such as soybean and wet cattail biomass (Sim et al., 2024). Short-duration adsorption systems may be more suitable for engineered treatment processes because they enable rapid PFAS capture and easier integration into existing water treatment units. In contrast, plant-based and biomass accumulation systems may provide more sustainable but slower remediation pathways, making them more appropriate for passive or nature-based treatment applications. The pH of the experimental systems also ranged broadly from acidic to alkaline conditions, which strongly influenced adsorption mechanisms. Acidic conditions generally enhanced adsorption of anionic PFAS by promoting electrostatic attraction with positively charged adsorbent surfaces (Dong, Min, Huo, & Wang, 2021; Dudarko et al., 2024; Mer et al., 2024). However, some modified adsorbents, including aminated composites and β-cyclodextrin-containing materials, maintained adsorption performance across wider pH ranges because hydrophobic interactions, host–guest inclusion, or ion-exchange mechanisms contributed to PFAS retention.

Comparison of adsorbent types reveals important strengths and limitations for practical PFAS remediation. Carbon-based adsorbents generally provide high surface area, developed porosity, and strong affinity for long-chain PFAS, but their application may be limited by regeneration challenges, material cost, and management of PFAS-laden residues. Biopolymer-based adsorbents, such as chitosan, cellulose, protein-based materials, and quaternized cotton, offer tunable surface charge, biodegradability, and potential selectivity toward anionic PFAS, although their stability and performance toward short-chain

PFAS require further validation. Mineral-based adsorbents, including natural clays and silica, are abundant and inexpensive but often require surface modification to improve adsorption affinity. Hybrid systems, such as nanofiltration–magnetic activated carbon integration and biochar–alginate composites, represent promising strategies because they combine separation efficiency, adsorption capacity, and improved operational flexibility. Overall, dosage differences across studies should be interpreted as indicators of material efficiency and practical feasibility, not merely as experimental conditions. Future studies should therefore report adsorption capacity, removal efficiency, dosage-normalized performance, regeneration behavior, and matrix effects to enable fairer comparison and more reliable scale-up assessment.

Table 1. Summary experimental design by using different natural adsorbent

Natural adsorbent	PFAS compound	Application rate	Experimental duration (h/d)	Reference
Silver-impregnated activated carbon (SIAC)	PFBS/PFOS	PFBS/PFOS of 500 mg/L and 5–6 mg SIAC	48 h	(Amirfakhri, Zobel, Lilla, Tomaszewski, & Stellpflug, 2025)
Electrospun polyacrylonitrile (ESPAN) nanofibers were coated with polyaniline (PANI)	PFAS	PFAS of 100 µg/L and 0.6 g/L PANI-ESPAN nanofibrous adsorbent	12 h	(Jahan, Tani, Patel, Zhao, & Zhang, 2025)
Quaternized cellulose nonwovens (QCNWs)	PFAS	PFAS of 40 mg/L and 10 mg QCNWs	24 h	(Y. Kang et al., 2025)
Silica	PFOA	PFOA of 0.1 mol/L and 0.012 mol/L silica	12 h	(Dudarko et al., 2024)
Sawdust biochar	PFOS	PFOS of 500 µg/L and 0.25 g/L Sawdust biochar	24 h	(Mer et al., 2024)
Organically modified clays (organoclays)	PFAS	PFAS of 1 mg/L and 10 mg organoclays	24 h	(Dong, Min, Zhang, Zhao, & Wang, 2024)
Nanofiltration (NF) - magnetic activated carbon (MAC) integration	PFAS	PFAS of 10-200 mg /L and 10 mg NF or MAC	1 h	(Sim et al., 2024)
Activated carbon (AC) and anion exchange resins (AERs)	PFAS	PFAS of 100 µg/L and >1 mg/L AC & AERs	-	(Lenka, Kah, Chen, Tiban-Anrango, & Padhye, 2024)
Nanofibrous Chlorella powder (the Algae)	PFAS	PFAS of 100 mg/L and 0.012 – 0.024 g Nanofibrous	0.5 h	(Mantripragada, Deng, et al., 2023)

		Chlorella powder (the Algae)		
Cellulose-based electrospun nanofibrous membranes with soy protein coating	PFAS	PFAS of 100 mg/L and 0.012 – 0.024 g cellulose-based electrospun nanofibrous membranes with soy protein coating	24 h	(Mantripragada, Dong, et al., 2023)
Albumin- and rice straw biochar-alginate beads	PFAS	PFAS of 1-3 g/L and 0.5-1.5 g/L albumin- and rice straw biochar-alginate beads	16 h	(Militao et al., 2023)
Chitosan / polyethyleneimine xerogel	PFAS	PFAS of 10 ppb to 600 ppm and ~22,5 mg Chitosan / polyethyleneimine xerogel	24 h	(Kebria et al., 2023)
Soybean plants	PFAS	PFAS of 10 μg/kg or 100 μg/kg and soybean plants	41 d	(W. Zhang, Tran, & Liang, 2022)
Protein solutions	PFOA	PFOA of 25 μL, 1 ppm and 2.2 μL, 160 μM protein solutions	14 h	(Hernandez et al., 2022)
Natural clay	PFOS/PFOA	PFOS/PFOA of 1 mg/L and 0.25 g/L natural clay	24 h	(Dong et al., 2021)
Wet cattail (Typha latifolia) biomass	PFOS/PFOA	PFOS/PFOA of 25 or 500 ng/L and wet cattail (Typha latifolia) biomass	120-210 d	(W. Zhang, Cao, & Liang, 2021)
Porous activated carbon (PAC)	PFOA	PFOA of 2 mg/L and 4 g/L PAC	6 h	(G. Liu et al., 2020)
Aminosilane nanocomposite	PFOS/PFOA	100 mL of water added PFOS/PFOA of 1 mg/L and 0.02 g/L Aminosilane nanocomposite	48 h	(Xing, Chen, Zhu, & Liu, 2020)
β-cyclodextrin-containing (β-CD)	PFOA	200 mL of water added PFOA of 200	24 h	(Yang, Ching, Easler, Helbling, & Dichtel, 2020)

		µg/L and 20 ml/L β-CD		
Biochar	PFOA/PFOS	PFOA/PFOS of 20-50 mg/L and 25-250 mg/L Biochar	0.25-7 h	(Niu et al., 2020)
Activated carbons (ACs)	PFOS	50 mL of water added PFOS of 35 ml and 5 mg Acs	24 h	(Meng, Fang, Maimaiti, Yu, & Deng, 2019)
Natural clay	PFOS/PFOA	PFOS/PFOA of 5, 50, & 500 µg/L and 5 mg/L natural clay	24 h	(Ray, Shabtai, Teixidó, Mishael, & Sedlak, 2019)
Grape Active Carbon	PFOS/PFOA	100 mL of water added PFOS/PFOA of 0.125 and 1 mg/L and 0.02 g/L grape active carbon	2 h	(Fagbayigbo, Opeolu, Fatoki, Akenga, & Olatunji, 2017)
Biochar corn straw	PFOS	50 mL of water added PFOS of 10 mg/L and 2 mg/L biochar corn straw	48 h	(Guo, Huo, Feng, & Lu, 2017)
Quaternized cotton	PFOS/PFOA	PFOS/PFOA of 0.46 mmol/L and 0.01 g Quaternized cotton	4 h & 12 h	(Deng et al., 2012)
Chitosan beads	PFOS/PFOA	200 mL of water added PFOS/PFOA of 0.093-0.744 mmol/L and 15.2–15.3 mg/L Chitosan beads	150 h	(Q. Zhang, Deng, Yu, & Huang, 2011)
Silica	PFOS/PFOA	0,500 g/L silica and 200 µg/L PFOS/PFOA	96 h	(Tang, Shiang Fu, Gao, Criddle, & Leckie, 2010)

3. EFFECT OF PH ON PFAS REMOVAL BY NATURAL ADSORBENTS

The pH of the aqueous system plays a decisive role in governing PFAS removal by natural adsorbents because it affects adsorbent surface charge, PFAS speciation, electrostatic attraction, and competitive interactions in solution. As summarized in Table 2, effective PFAS removal has been reported across a relatively wide pH range, although the optimum condition varies depending on adsorbent type, PFAS species, and water matrix composition. Silver-impregnated activated carbon (SIAC) removed 82.8% of PFBS and PFOS under near-neutral conditions at pH 6.5–7.5 (Amirfakhri et al., 2025). Similarly, electrospun polyacrylonitrile nanofibers coated with polyaniline (PANI-ESPAN) and quaternized cellulose nonwovens (QCNWs) achieved high removal efficiencies of >98% and

98%, respectively, at pH 6 (Jahan et al., 2025; Kang et al., 2025). In contrast, silica-based adsorbents achieved >90% PFOA removal under strongly acidic conditions at pH 3 (Dudarko et al., 2024), while sawdust biochar removed 66.9–71.4% of PFOS under similar acidic conditions (Mer et al., 2024). Organically modified clays showed high efficiencies of 95.5–99% at neutral pH 7 (Dong et al., 2024), and nanofiltration integrated with magnetic activated carbon (NF-MAC) also performed well at pH 7, with removal efficiencies of 86.1–96.6% (Sim et al., 2024). Conversely, activated carbon combined with anion exchange resins showed lower removal efficiency under strongly alkaline conditions, with PFAS removal reported at <80% at pH >10 (Lenka et al., 2024). These findings indicate that acidic to near-neutral pH conditions generally favor PFAS adsorption by enhancing electrostatic attraction between anionic PFAS and positively charged adsorbent surfaces, whereas strongly alkaline conditions may weaken adsorption due to surface deprotonation and electrostatic repulsion.

Composite and biopolymer-based adsorbents also demonstrate pH-dependent behavior. Albumin- and rice straw biochar-alginate beads maintained high PFAS removal efficiencies of 87–99% at pH 6–8 (Militao et al., 2023), while chitosan/polyethyleneimine xerogels showed relatively limited adsorption of 4.5–20.7% at pH 6.5 (Kebria et al., 2023). Natural clay exhibited broad removal performance across pH 3–11, while β-cyclodextrin-containing adsorbents showed variable removal within pH 3.9–7.9 (Niu et al., 2020). Grape-derived activated carbon achieved 88–95% removal at pH 4–9 (Fagbayigbo et al., 2017), and chitosan beads reached very high PFOS/PFOA removal across pH 3–9.5. It is important to note that the pH effects summarized in Table 2 are derived from studies with different levels of environmental realism. Some studies were conducted using true or near-real water matrices, such as natural water, wastewater, treated wastewater, or environmentally relevant aqueous samples. However, other studies were performed under partially controlled laboratory conditions using simplified matrices, including deionized water, synthetic PFAS solutions, single-contaminant systems, or pH-adjusted background electrolytes. Therefore, the pH trends reported in the literature should be interpreted with caution. Controlled laboratory matrices are valuable for identifying fundamental adsorption mechanisms because they allow the effects of pH, surface charge, and PFAS structure to be isolated.

Table 2. pH condition of natural adsorbents for PFAS removal

Natural adsorbent	PFAS compound	Removal (%)	pH	Reference
Silver-impregnated activated carbon (SIAC)	PFBS/PFOS	82.8	6.5-7.5	(Amirfakhri et al., 2025)
Electrospun polyacrylonitrile (ESPAN) nanofibers were coated with polyaniline (PANI)	PFAS	>98	6	(Jahan et al., 2025)
Quaternized cellulose nonwovens (QCNWs)	PFAS	98	6	(Y. Kang et al., 2025)
Silica	PFOA	>90	3	(Dudarko et al., 2024)
Sawdust biochar	PFOS	66.9-71.4	3	(Mer et al., 2024)
Organically modified clays (organoclays)	PFAS	95.5-99	7	(Dong et al., 2024)

Nanofiltration (NF) - magnetic activated carbon (MAC) integration	PFAS	86.1-96.6	7	(Sim et al., 2024)
Activated carbon (AC) and anion exchange resins (AERs)	PFAS	<80	>10	(Lenka et al., 2024)
Nanofibrous Chlorella powder (the Algae)	PFAS	72	4 & 6	(Mantripragada, Deng, et al., 2023)
Cellulose-based electrospun nanofibrous membranes with soy protein coating	PFAS	5-85	4 & 6	(Mantripragada, Dong, et al., 2023)
Albumin- and rice straw biochar-alginate beads	PFAS	87–99	6-8	(Militao et al., 2023)
Chitosan / polyethyleneimine xerogel	PFAS	4.5-20.7	6.5	(Kebria et al., 2023)
Natural clay	PFOS/PFOA	70-98	3-11	(Dong et al., 2021)
Aminosilane nanocomposite	PFOS/PFOA	65-78	8.2	(Xing et al., 2020)
β-cyclodextrin-containing (β-CD)	PFOA	5-90	3.9-7.9	(Yang et al., 2020)
Biochar	PFOA/PFOS	<50	2-10	(Niu et al., 2020)
Natural clay	PFOS/PFOA	95	7.5	(Ray et al., 2019)
Grape Active Carbon	PFOS/PFOA	88-95	4-9	(Fagbayigbo et al., 2017)
Chitosan beads	PFOS/PFOA	≤99.94	3-9.5	(Q. Zhang et al., 2011)
Silica	PFOS/PFOA	90	3-11	(Tang et al., 2010)

4. ADSORPTION MECHANISM OF NATURAL ADSORBENTS AGAINST PFAS

The adsorption of PFAS onto natural adsorbents is governed by multiple interaction mechanisms, including electrostatic attraction, hydrophobic interactions, ion exchange, and hydrogen bonding, as illustrated in Figure 1.

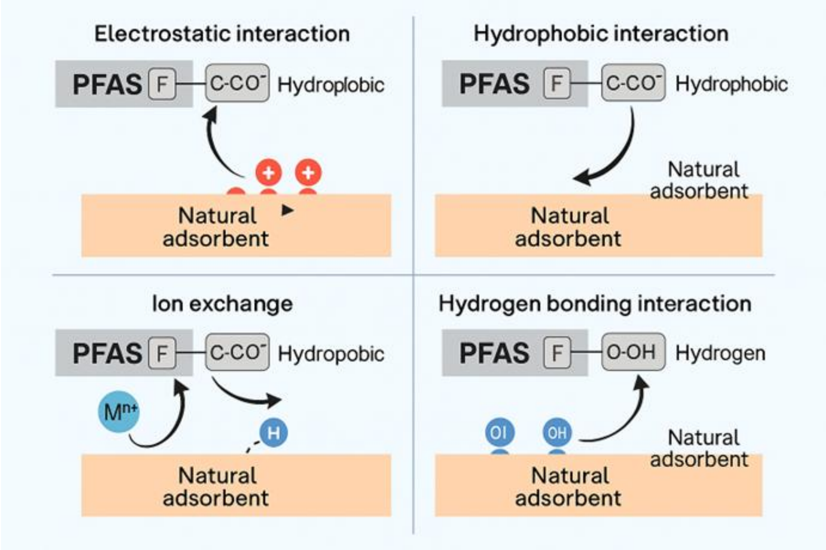

Figure 1. mechanism of PFAS in natural adsorbent

4.1 Electrostatic interaction

Electrostatic interaction is one of the key mechanisms governing PFAS adsorption onto natural adsorbents, particularly because most PFAS exist in aqueous systems as anionic species with negatively charged terminal groups, such as sulfonate ($-SO_3^-$) and carboxylate ($-COO^-$), attached to hydrophobic perfluorinated carbon chains (G. Kim, Mengesha, & Choi, 2024). These negatively charged head groups can interact with positively charged adsorption sites on natural or modified adsorbent surfaces. Therefore, the strength of electrostatic attraction is closely controlled by the surface charge of the adsorbent, solution pH, point of zero charge (pHpzc), ionic strength, and the presence of competing ions in the water matrix.

The influence of electrostatic interaction is clearly reflected in the pH-dependent adsorption behavior of many natural adsorbents. Under acidic to near-neutral conditions, adsorbent surfaces are more likely to become protonated, thereby increasing the density of positively charged sites available for PFAS binding. This condition enhances the attraction between anionic PFAS and the adsorbent surface. For example, silica showed high PFOA removal under strongly acidic conditions, while sawdust biochar, organoclays, natural clay, grape-derived activated carbon, and chitosan beads also demonstrated improved PFAS removal within acidic to near-neutral pH ranges. These trends indicate that protonated or positively charged surface sites play an important role in strengthening PFAS retention, particularly for compounds whose adsorption is strongly influenced by their ionic head groups.

In contrast, adsorption efficiency may decline under alkaline conditions because deprotonation of surface functional groups can reduce positive surface charge or even produce negatively charged adsorbent surfaces. When the solution pH exceeds the pHpzc of the adsorbent, electrostatic repulsion between anionic PFAS and negatively charged surfaces becomes stronger, resulting in weaker adsorption affinity (H.-H. Kim, Koster van Groos, Zhao, & Pham, 2024). This phenomenon helps explain why some adsorbent systems show reduced PFAS removal at high pH, especially when electrostatic attraction is the dominant binding mechanism. Therefore, pH does not merely act as an operational variable, but directly regulates surface charge and determines the extent to which PFAS can be retained by natural adsorbents.

Electrostatic interaction also contributes to differences in performance among adsorbent types.

Materials containing cationic or protonatable functional groups, such as amine-modified adsorbents, quaternized cellulose, quaternized cotton, chitosan-based materials, and polyaniline-coated nanofibers, generally provide stronger binding sites for anionic PFAS. This feature is particularly important for short-chain PFAS, which have weaker hydrophobic affinity than long-chain compounds and therefore depend more strongly on ionic or electrostatic interactions for effective removal. In this context, increasing the density of positively charged surface sites through chemical modification can improve adsorption capacity, selectivity, and material efficiency, especially in complex water matrices where PFAS must compete with other anions for available adsorption sites.

The presence of multivalent cations, such as Ca^{2+} and Mg^{2+}, may further influence electrostatic adsorption through a cation-bridging mechanism. These cations can act as intermediaries between negatively charged PFAS head groups and neutral or slightly negatively charged adsorbent surfaces, thereby enhancing PFAS retention under certain conditions (Iqbal et al., 2025). However, this effect is highly dependent on water chemistry. In real water systems, high ionic strength and abundant competing ions may either facilitate PFAS adsorption through bridging effects or suppress adsorption by screening electrostatic attraction and occupying active sites. Dissolved organic matter may also interfere with electrostatic binding by competing for positively charged adsorption sites or altering the surface properties of the adsorbent.

4.2 Hydrophobic interaction

Hydrophobic interaction is another major mechanism controlling PFAS adsorption onto natural adsorbents, particularly for long-chain compounds such as PFOA and PFOS. PFAS molecules consist of a hydrophilic ionic head group and a hydrophobic perfluorinated carbon tail. The perfluoroalkyl tail has low polarity and strong C–F bonds, which reduce its affinity for the aqueous phase and promote association with hydrophobic domains on adsorbent surfaces. Natural adsorbents with high carbon content, aromatic structures, and well-developed porous networks, such as biochar, activated carbon, grape-derived activated carbon, and carbonized biomass materials, therefore tend to exhibit stronger affinity toward long-chain PFAS than toward short-chain analogues (Huang et al., 2019). The role of hydrophobic interaction is particularly evident in the stronger adsorption of long-chain PFAS compared with short-chain PFAS. Longer perfluoroalkyl chains provide a larger hydrophobic surface area, allowing stronger van der Waals interactions and more favorable partitioning into non-polar domains of the adsorbent. This explains why PFOA and PFOS are generally removed more efficiently than short-chain compounds such as PFBS, PFBA, or GenX, which possess weaker hydrophobic affinity and rely more heavily on electrostatic attraction or ion-exchange mechanisms. In carbon-rich adsorbents, hydrophobic interaction may work together with pore-filling and π-associated interactions, thereby stabilizing PFAS molecules within micropores and mesopores. As a result, adsorbents with high surface area and suitable pore size distribution can achieve rapid and relatively strong PFAS retention, especially when the pore structure is accessible to the targeted PFAS molecules.

Hydrophobic interaction also helps explain why some carbon-based adsorbents maintain relatively good PFAS removal across wider pH ranges. Unlike electrostatic attraction, which is strongly affected by surface protonation and deprotonation, hydrophobic interaction is less directly controlled by pH. Therefore, when hydrophobic partitioning becomes dominant, adsorption may remain effective even under conditions where electrostatic attraction is weakened. However, pH can still indirectly influence hydrophobic adsorption by altering the surface chemistry of the adsorbent, changing the aggregation behavior of PFAS, and modifying the competition between PFAS and other organic substances in water. Thus, high removal efficiency under acidic or neutral conditions may result from the combined effects of electrostatic attraction and hydrophobic retention, whereas sustained removal under broader pH conditions often indicates a stronger contribution from hydrophobic domains and pore-associated adsorption.

The contribution of hydrophobic interaction should also be interpreted in relation to adsorbent dosage and material efficiency. Increasing the dosage of carbonaceous adsorbents can improve PFAS removal by providing more hydrophobic surfaces and pore sites. However, high removal at high dosage does not necessarily indicate superior material performance if the adsorption capacity per unit mass remains low. Materials that achieve efficient PFAS uptake at lower dosages are more desirable because they use the available hydrophobic domains more effectively, reduce material consumption, and generate less spent adsorbent. This consideration is important for scaling up PFAS treatment, as excessive adsorbent use may increase operational costs, regeneration demand, and the volume of PFAS-laden residuals requiring further management.

In real water systems, hydrophobic interaction may be weakened by dissolved organic matter, surfactants, suspended solids, and other co-contaminants. Natural organic matter can occupy hydrophobic adsorption sites, block pores, or form surface coatings that reduce PFAS access to active domains. Similarly, suspended particles and organic co-contaminants may compete with PFAS for non-polar regions of the adsorbent. These matrix effects are particularly important for wastewater, stormwater, landfill leachate, and mixed environmental waters, where organic loads are often higher than in simplified laboratory solutions. Therefore, hydrophobic adsorption observed in controlled experiments may not always be directly transferable to complex environmental matrices unless competitive effects and pore accessibility are carefully evaluated.

Overall, hydrophobic interaction provides a key explanation for the preferential adsorption of long-chain PFAS by carbon-rich natural adsorbents. Stronger retention is generally associated with longer perfluoroalkyl chains, higher adsorbent aromaticity, greater organic carbon content, and well-developed pore structures. Nevertheless, hydrophobic interaction alone is insufficient to explain all PFAS adsorption behavior, particularly for short-chain PFAS and highly competitive water matrices. The most effective natural adsorbents are therefore those that combine hydrophobic domains with electrostatic or ion-exchange sites, enabling simultaneous retention of both long-chain and short-chain PFAS under realistic water treatment conditions.

4.3 Ion exchange

Ion exchange constitutes another key mechanism governing the adsorption of PFAS onto natural adsorbents, particularly those containing exchangeable surface cations. During adsorption, PFAS anions bearing terminal sulfonate or carboxylate groups can displace these weakly bound ions through ligand exchange or electrostatic displacement, resulting in stable attachment to the adsorbent surface. The ion exchange capacity (IEC) of an adsorbent is a critical parameter controlling this process (Khan et al., 2022).

Solution chemistry strongly affects ion exchange interactions. Elevated concentrations of competing anions, such as sulfate or phosphate, were shown to reduce PFAS adsorption by occupying available sites, whereas multivalent cations facilitated “cation bridging” between PFAS molecules and adsorbent surfaces (Kasula, Ortbal, Kebede, Terry, & Esfahani, 2025). Long-chain PFAS anchored to hydrophobic regions of the adsorbent while their functional groups engaged in ion exchange, producing a dual-binding effect that strengthened adsorption and reduced desorption rates (S. B. Kang, Wang, Zhang, Kim, & Won, 2023). Moreover, surface modification of natural adsorbents with quaternary ammonium or other cationic groups substantially increased their ion exchange capacity, improving the removal of short-chain PFAS that primarily rely on ionic interactions.

4.4 Hydrogen bonding

Hydrogen bonding constitutes a complementary yet important mechanism in PFAS adsorption onto natural adsorbents, particularly when the adsorbent surface contains polar functional groups that can act as hydrogen bond donors or acceptors. Hydrogen bonding has been reported to act synergistically with hydrophobic interactions, particularly in the case of long-chain PFAS. The hydrophobic perfluorocarbon tail anchors the molecule to non-polar domains of the adsorbent, while the polar head group engages in hydrogen bonding with surface functionalities, resulting in stronger and more stable adsorption (Biswas & Das, 2021). This dual mechanism not only enhances adsorption capacity but also increases resistance to desorption under fluctuating environmental conditions. Surface modification has been shown to significantly improve hydrogen-bonding capacity. Treatments that introduce hydroxyl or amine functionalities such as grafting of polyethylenimine or oxidative processes that increase –OH content substantially enhanced the uptake of both short- and long-chain PFAS (Arnold, Singh, & Sydlik, 2025). Such modifications are particularly effective for short-chain PFAS, which rely more heavily on polar interactions and are less influenced by hydrophobic partitioning.

5. DESORPTION MECHANISM AND CHALLENGES

The desorption of PFAS from natural or engineered adsorbents constitutes a major challenge in water treatment applications because it determines whether adsorption can provide stable long-term immobilization or only temporary contaminant transfer. In contrast to adsorption, which immobilizes PFAS through electrostatic attraction, hydrophobic interaction, ion exchange, or hydrogen bonding, desorption occurs when these interactions become weakened under dynamic environmental conditions. The principal triggers of desorption include pH fluctuations, changes in ionic strength, the presence of competing ions, and dissolved organic matter, all of which can destabilize PFAS–adsorbent interactions and promote the release of bound PFAS back into aqueous systems. Short-chain PFAS, such as PFBA and PFBS, are particularly prone to desorption because they generally have weaker hydrophobic affinity and lower overall binding strength than long-chain analogues such as PFOA and PFOS (Khazaee et al., 2021). Their retention depends more strongly on electrostatic attraction and ion-exchange interactions, which are highly sensitive to changes in pH, ionic strength, and competing anions. This behavior has important implications for adsorbent design. Adsorbents intended for short-chain PFAS removal should not rely solely on hydrophobic domains or general surface porosity, but should incorporate more selective and stable binding sites, such as cationic functional groups, amine-rich surfaces, quaternary ammonium groups, ion-exchange sites, or hybrid structures capable of combining electrostatic attraction with confined pore retention. From a field-application perspective, the higher desorption tendency of short-chain PFAS means that laboratory removal efficiency alone is insufficient to confirm practical feasibility. Adsorbents must also be evaluated through repeated adsorption–desorption cycles, column tests, and long-term operation under real water matrices containing dissolved organic matter, co-existing ions, suspended solids, and variable pH. Without such validation, short-chain PFAS may be released during regeneration, matrix changes, or prolonged operation, thereby reducing treatment reliability and increasing the risk of secondary contamination. By contrast, long-chain PFAS are generally retained more strongly because of the combined contribution of hydrophobic and electrostatic interactions, although their desorption can still occur under highly competitive or chemically fluctuating conditions. Surface charge instability further contributes to desorption, especially for adsorbents with a point of zero charge (pHpzc) near neutral pH, where even small pH shifts can alter surface potential and weaken PFAS binding (Pimentel, Freire, Gómez-Díaz, & González-Álvarez, 2023). Ionic competition also complicates retention because multivalent cations such as Ca^{2+} and Mg^{2+} may initially stabilize PFAS adsorption through cation bridging, but under competitive aqueous conditions they may also contribute to displacement processes. Similarly, dissolved organic matter can occupy adsorption sites, modify adsorbent surface properties, and weaken PFAS retention, a phenomenon that is particularly relevant in natural water, wastewater, stormwater, landfill leachate, and other complex real water systems.

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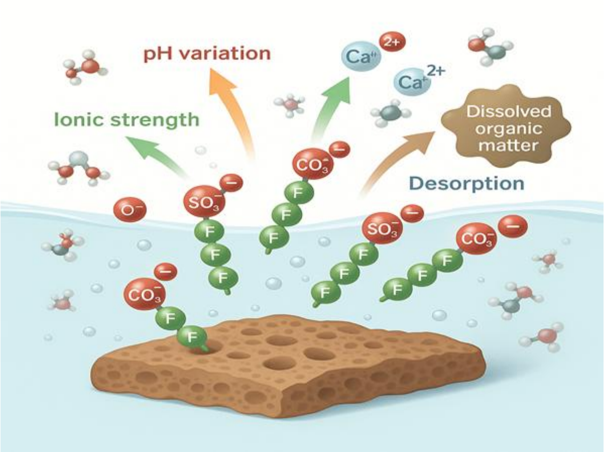

Figure 2. Schematic illustration of the desorption mechanisms of PFAS

Despite the promising adsorption performance observed under controlled laboratory conditions. Adsorbent regeneration is essential for cost-effectiveness, it frequently generates concentrated PFAS eluates that remain environmentally persistent and toxic, thereby transferring rather than resolving the contamination problem (F. Liu, Pignatello, Sun, Guan, & Xiao, 2024). Addressing these challenges requires strategies aimed at minimizing desorption and enhancing treatment durability. Promising directions include: (i) functionalizing adsorbent surfaces with chemical groups that promote irreversible PFAS binding, (ii) integrating adsorption with destructive technologies such as photocatalysis or electrochemical oxidation to prevent re-release, and (iii) validating adsorption–desorption dynamics through pilot and field-scale investigations under realistic water matrices. Such integrated approaches are considered essential for ensuring the long-term sustainability of adsorption-based PFAS remediation technologies.

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6. KINETIC AND ISOTHERM PROFILES

The adsorption behavior of PFAS is largely controlled by kinetic and isotherm characteristics, which provide important insights into mass transfer processes, adsorption rates, and equilibrium binding at adsorbent surfaces. In many reported studies, PFAS adsorption kinetics have been well described by the pseudo-second-order (PSO) model (Omo-Okoro et al., 2020). The PSO model assumes that the rate-limiting step involves electron sharing or exchange between functional groups on the adsorbent surface and the ionic moieties of PFAS. Nevertheless, adsorption frequently occurs in multiple stages, followed by a slower phase dominated by intraparticle diffusion into micropores (Pranić, Carlucci, van der Wal, & Dykstra, 2025). However, the interpretation of PSO fitting should be made with caution because model fit alone does not conclusively confirm a specific adsorption mechanism. A good agreement with the PSO model may indicate that surface-controlled interactions, such as electrostatic attraction, ion exchange, or other specific binding processes, contribute to the overall adsorption rate, but it should not be regarded as definitive evidence of chemisorption without additional supporting analyses. As illustrated in Figure 3, comparative kinetic modeling using pseudo-first-order (PFO), pseudo-second-order (PSO), and intraparticle diffusion approaches can help describe the adsorption rate and identify possible stages of PFAS uptake. Nevertheless, these models should be interpreted as empirical or semi-empirical tools rather than direct proof of a single adsorption mechanism. PFAS adsorption may involve multiple simultaneous processes, including external mass transfer, surface binding, pore diffusion, hydrophobic partitioning, and electrostatic interactions, which cannot be fully distinguished by kinetic model fitting alone. Therefore, confirmation of chemisorption requires complementary evidence, such as changes in surface functional groups, spectroscopic characterization, thermodynamic parameters, pH-dependent adsorption behavior, desorption resistance, or regeneration performance. Accordingly, PSO fitting remains useful for describing adsorption kinetics, but it should be interpreted together with mechanistic and characterization evidence rather than as standalone proof of chemisorption.

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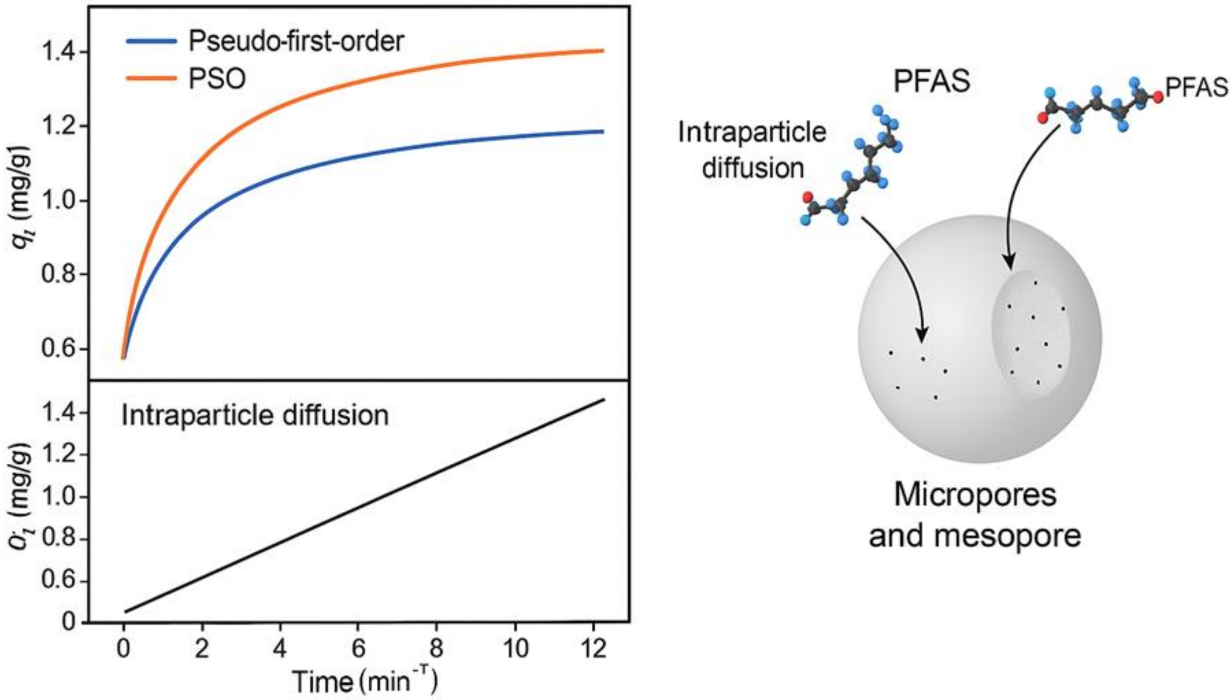

Figure 3. Kinetic profiles of PFAS adsorption modeled using PFO and PSO kinetics

Isotherm models complement kinetic evaluations by characterizing equilibrium adsorption capacities and surface heterogeneity. Among these, the Langmuir isotherm has been widely applied to describe PFAS adsorption, particularly for long-chain compounds such as PFOA and PFOS. As illustrated in Figure 4, the Langmuir curve exhibits a saturation plateau, indicating the monolayer adsorption limit on homogeneous sites. This feature is especially relevant for strongly hydrophobic, long-chain PFAS. The model assumes monolayer adsorption on uniform binding sites, consistent with strong interactions and limited desorption, and provides reliable estimates of maximum adsorption capacity (Beyioku, Gilboa, & Ronen, 2025). In contrast, the Freundlich isotherm has often yielded better fits under environmentally relevant conditions, reflecting the heterogeneous nature of adsorbent surfaces and the multilayer adsorption behavior commonly observed for short-chain PFAS. The Freundlich constants further capture adsorption intensity and surface heterogeneity, making this model particularly applicable in systems influenced by natural organic matter and competing ions. Beyond these classical approaches, the Dubinin–Radushkevich (D–R) isotherm has also been employed to differentiate between physical and chemical adsorption mechanisms, based on calculated mean free energy values (Omo-Okoro et al., 2020). Although less frequently applied, the D–R model provides additional insights into whether adsorption is governed by weaker van der Waals forces or stronger chemisorptive interactions.

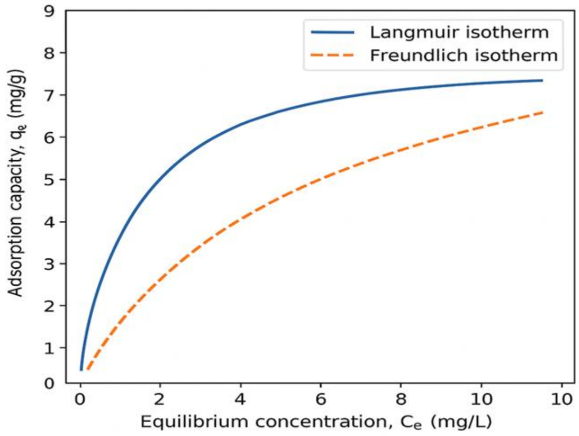

Figure 4. Comparison of Langmuir and Freundlich isotherm models describing PFAS adsorption

7. CHALLENGES AND FUTURE RECOMMENDATIONS

Despite the promising performance of natural adsorbents in PFAS remediation, several critical challenges still hinder their direct implementation in real water systems. A key limitation is the strong dependency of adsorption efficiency on pH conditions, where acidic or near-neutral environments generally enhance PFAS removal, but efficiency decreases significantly under alkaline conditions. For example, silica and biochar showed superior adsorption at acidic pH (Dudarko et al., 2024; Mer et al., 2024), whereas activated carbon combined with anion exchange resins exhibited lower removal rates under alkaline conditions (Lenka et al., 2024). This pH sensitivity creates practical obstacles because natural waters typically experience dynamic and fluctuating pH values. Another major challenge arises from the dominance of laboratory-scale batch experiments with simplified conditions that do not reflect the complexity of real aquatic environments. For instance, nanofibrous adsorbents required very low dosages to remove PFAS efficiently, while porous activated carbon needed higher concentrations (Mantripragada, Deng, et al., 2023; Mantripragada, Dong, et al., 2023). Moreover, most studies used single PFAS compounds at relatively high concentrations, rather than environmentally relevant trace levels and mixed PFAS systems. This limits the transferability of laboratory findings to field conditions.

Additionally, the lack of systematic studies on desorption and reusability makes it difficult to assess long-term sustainability. While carbon-based adsorbents such as PAC and NF-MAC have demonstrated rapid PFAS removal within short durations (Sim et al., 2024), their regeneration performance and stability under repeated use remain underexplored. Without robust desorption and reusability data, scaling up these systems could face significant operational and economic barriers. Looking forward, future research should prioritize experiments under realistic environmental conditions, including multi-PFAS mixtures, variable pH ranges, and the presence of co-contaminants. The development of surface-modified or hybrid natural adsorbents (e.g., biochar–alginate composites or NF-MAC systems) represents a promising pathway to overcome pH sensitivity and enhance adsorption selectivity (Militao et al., 2023; Sim et al., 2024). Equally important, pilot-scale and column-based investigations are urgently needed to bridge the gap between controlled laboratory experiments and real world applications. Incorporating advanced characterization techniques to elucidate adsorption mechanisms will further strengthen the scientific foundation for designing selective, efficient, and sustainable PFAS removal technologies.

8. CONCLUSION

This review demonstrates that natural adsorbents offer a promising and sustainable approach for the remediation of per- and polyfluoroalkyl substances (PFAS) in real water systems. The reviewed studies show that adsorption performance is strongly governed by the physicochemical properties of the adsorbents, including surface functional groups, pore structure, surface charge, and hydrophobic domains. In addition, solution chemistry, particularly pH, ionic strength, dissolved organic matter, and the presence of competing ions, plays a decisive role in controlling PFAS retention. Long-chain PFAS, such as PFOA and PFOS, are generally more strongly adsorbed because of combined hydrophobic and electrostatic interactions, whereas short-chain PFAS remain more difficult to remove due to their weaker hydrophobicity and higher mobility in aqueous systems. Kinetic and isotherm analyses further indicate that PFAS adsorption is commonly associated with pseudo-second-order kinetics and either Langmuir or Freundlich behavior, depending on the adsorbent characteristics, PFAS structure, and water matrix complexity.

Despite these promising findings, the practical implementation of natural adsorbents remains constrained by several unresolved issues. Desorption under fluctuating environmental conditions, limited regeneration efficiency, the production of PFAS-concentrated eluates, and reduced performance in complex water matrices remain major barriers to field-scale application. Therefore, the main conclusion of this review is that natural adsorbents can contribute significantly to PFAS remediation, but their long-term effectiveness depends on improving adsorption stability, selectivity, and resistance to matrix interference. Future research should be directed toward validating these materials under realistic water conditions, particularly through column and pilot-scale studies, while also incorporating regeneration assessment, techno-economic analysis, and life cycle evaluation. Such efforts are necessary to ensure that natural adsorbent-based PFAS remediation is not only effective at the laboratory scale but also sustainable, scalable, and applicable in real water treatment systems.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Pardin Lasaksi: Writing – original draft, Conceptualization. Marchel Putra Garfansa: Conceptualization, Supervision. Iswahyudi Iswahyudi: Writing – review & editing, Supervision.

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CONFLICT OF INTEREST

The author declares no conflicts of interest.

DATA AVAILABILITY STATEMENT

Data available by request.

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