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Review

A critical review of biochar for the remediation of PFAS-contaminated soil and water

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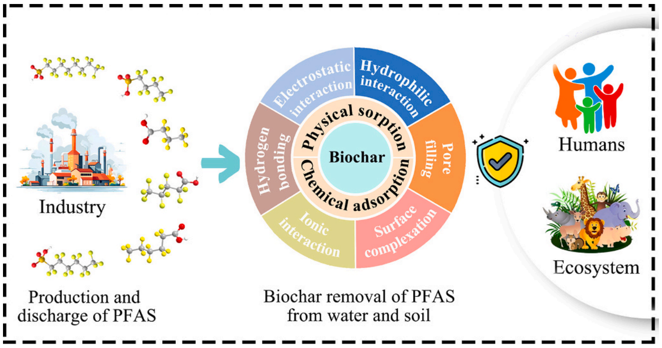
HIGHLIGHTS

- A comprehensive coverage of the remediation of PFAS by biochar is presented.
- Biochar's PFAS sorption mechanisms and key influencing factors are elucidated.
- Cases for remediation of PFAS contamination by biochar are discussed in detail.

GRAPHICAL ABSTRACT



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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) present significant environmental and health hazards due to their inherent persistence, ubiquitous presence in the environment, and propensity for bioaccumulation. Consequently, the development of efficacious remediation strategies for soil and water contaminated with PFAS is imperative. Biochar, with its unique properties, has emerged as a cost-effective adsorbent for PFAS. Despite this, a comprehensive review of the factors influencing PFAS adsorption and immobilization by biochar is lacking. This narrative review examines recent findings indicating that the application of biochar can effectively immobilize PFAS, thereby mitigating their environmental transport and subsequent ecological impact. In addition, this paper reviewed the sorption mechanisms of biochar and the factors affecting its sorption efficiency. The high effectiveness of biochars in PFAS remediation has been attributed to their high porosity in the right pore size range (>1.5 nm) that can accommodate the relatively large PFAS molecules (>1.02–2.20 nm), leading to physical entrapment. Effective sorption requires attraction or bonding to the biochar framework. Binding is stronger for long-chain PFAS than for short-chain PFAS, as attractive forces between long hydrophobic CF_2-tails more easily overcome the repulsion of the often-anionic head groups by net negatively charged biochars. This review summarizes case studies and field applications highlighting the effectiveness of biochar across various matrices, showcasing its strong binding with PFAS. We suggest that research should focus on improving the adsorption performance of biochar for short-chain PFAS compounds. Establishing the significance of biochar surface electrical charge in the adsorption process of PFAS is necessary, as well as quantifying the respective contributions of electrostatic forces and hydrophobic van der Waals forces to the adsorption of both short- and long-chain PFAS. There is an urgent need for validation of the effectiveness of the biochar effect in actual environmental conditions through prolonged outdoor testing.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) represent a class of organofluorochemicals that have been synthesized since the 1940s (Lyu et al., 2022). According to Evich et al. (2022), there are over 8000 distinct PFAS compounds. PFAS compounds are widely used across fields and industries, including firefighting foams, electronics manufacturing, and consumer goods like water-resistant clothing and electric vehicle batteries (Evich et al., 2022; Glüge et al., 2020; Zhang et al., 2024). The ubiquity, potential toxicity, and propensity for bioaccumulation of PFAS across diverse environmental matrices and biological organisms have garnered global attention due to their far-reaching implications for environmental health and safety (Kemper et al., 2024; Liu et al., 2023a; Sonne et al., 2023).

Environmental concerns regarding the utilization of PFAS emerged toward the end of the 20th century (Gaines, 2023). It was recognized that perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA)—among the most extensively employed PFAS compounds due to their exceptional resistance to biodegradation—were pervasive in diverse biological and environmental components (Wee and Aris, 2023). Furthermore, these compounds exhibited the potential for biomagnification in food webs (Miranda et al., 2023). The health impacts of many PFAS compounds remain the subject of ongoing research (Pelch et al., 2022; Wee and Aris, 2023). Establishing a definitive link between exposure to specific PFAS chemicals and the manifestation of adverse health effects can be a protracted process, particularly for recently identified PFAS compounds (Wee and Aris, 2023; U.S. HHS, 2016). The typical structure of PFAS is detailed in Table S1.

Exposure to PFAS can occur through inhalation, oral ingestion, and dermal contact (ATSDR, 2021; U.S. EPA, 2023). The consumption of contaminated drinking water and food is recognized as a primary source of PFAS accumulation in the human body (U.S. EPA, 2023). PFAS has been found in human lungs, brain, liver, bone, and kidneys (Koelmel et al., 2023; Lin et al., 2023; Pérez et al., 2013; Zhao et al., 2023). Exposure to PFAS is linked to various health concerns (U.S. HHS, 2016). PFAS compounds have persistent, bioaccumulative, and toxic properties (Han et al., 2023), which are underscored by their unique ability to bind with proteins and cell membranes, forming hydrogen bonds—a characteristic not shared by all persistent organic pollutants (Zhao et al., 2023). Epidemiological studies have consistently demonstrated a correlation between exposure to PFAS and a spectrum of adverse health outcomes. These include increased serum lipid levels, elevated cholesterol, obesity, disruptions in hormonal regulation, heightened blood pressure, and a diminished immune response (U.S. EPA, 2023).

Exposure to PFAS typically occurs through contaminated soil and water, where the stable fluorocarbon bond enables persistent pollution

(Abunada et al., 2020; Sørmo et al., 2023). Soil-borne PFAS stems from various sources, including firefighting foam use at training facilities, PFAS-containing biosolid application on farmland, irrigation with PFAS-contaminated water, and industrial emissions releasing PFAS-laden effluents (Abunada et al., 2020; Høisæter et al., 2019; Lee et al., 2014; Fig. 1). PFAS can persist in soil through processes such as sorption, partitioning, and various chemical reactions. Research has shown that PFAS toxicity can adversely affect soil enzyme activity, microorganism cellular structural integrity, and induce the mineralization of soil organic matter (Bolan et al., 2021; Li et al., 2024b; Cai et al., 2020, 2019; Qiao et al., 2018).

Certain PFAS compounds exhibit water solubility, making them prone to leaching and thus migrating into various aquatic environments, including groundwater and surface water, with some of them being drinking water sources (Robey et al., 2020; Abunada et al., 2020; Fig. 1). Survey data reported by Hu et al. (2016), revealed that approximately 6 million U.S. residents had PFAS levels in their drinking water exceeding the recommended values established by the U.S. Environmental Protection Agency (EPA). Up to 26,000 sites may be contaminated with PFAS (Darlington et al., 2018). If soil hot spots are not remediated, they can result in PFAS contamination of nearby water bodies to an extent that exceeds environmental quality thresholds for centuries (Ruyle et al., 2023).

In 2016, the U.S. EPA recommended that the concentration of combined PFOA and PFOS in drinking water should not exceed 70 ng L^{-1} (U.S. EPA, 2016). However, in 2022, it revised these standards to more stringent levels, setting the Interim Updated Lifetime Health Advisory standards for PFOA and PFOS at 0.004 ng L^{-1} and 0.02 ng L^{-1}, respectively (U.S. EPA, 2022). In April 2024, the U.S. EPA's newly released National Primary Drinking Water Regulation legally mandated enforcement of maximum contaminant concentrations of 4 ng L^{-1} for PFOA and PFOS in drinking water and the completion of monitoring of public water systems within three years (by 2027) (U.S. EPA, 2024). These concentrations are exceedingly low, emphasizing the urgent need for effective measures to reduce current environmental PFAS concentrations and further PFAS release into the environment.

The introduction of PFAS compounds into the environment through non-point source pathways presents significant challenges to the cost-effectiveness of remediation and associated strategies due to the complex nature of the environmental matrices they inhabit (Naidu et al., 2020; Rafiei and Nejadhashemi, 2023). As a result, a proactive mitigation approach involves addressing PFAS-contaminated point sources, which include facilities such as factories, wastewater treatment plants, fire training facilities, and landfills (Andrews et al., 2021; Ehsan et al., 2023; Joerss et al., 2022). It is crucial to implement targeted measures in areas with elevated PFAS concentrations. For example, employing advanced treatment methodologies at wastewater treatment plants, such as adsorption, biological remediation technologies (e.g., aerobic/anaerobic digestion, biofiltration), and other methods, can effectively reduce the emission of PFAS pollutants (Chen et al., 2012; Kibambe et al., 2020; Lenka et al., 2021).

In addition to addressing PFAS point sources, remediating sites contaminated with PFAS compounds is crucial for mitigating associated risks. Effective methods for the remediation of PFAS from soil encompass soil washing (Høisæter et al., 2021), incineration (Kumar et al., 2023), smoldering (Duchesne et al., 2020), ball milling (Battye et al., 2024), and stabilization techniques (Bui et al., 2024). In practice, soil washing demands optimization based on soil types, soil-to-detergent ratios, and PFAS contact time to ensure cost-effectiveness (Bui et al., 2024; Nguyen et al., 2022). Incineration requires high destruction levels and minimal by-product generation, resulting in steep energy and operational costs (Garg et al., 2023; Zhang et al., 2023a). Recently, smoldering combustion has emerged as an effective method for remediating PFAS-contaminated soils (Duchesne et al., 2020; Fournie et al., 2023). However, it requires additional fuel, like granular activated carbon, to maintain temperatures for PFAS degradation and manage by-products, including hydrogen fluoride (Duchesne et al., 2020; Fournie et al., 2023; Kang et al., 2023). Fournie et al. (2023) found that adding calcium oxide to the smoldering combustion process to promote calcium and fluorine mineralization offers a potential solution to this issue. Recent research has also demonstrated that pyrolysis at temperatures of 400 °C or above can effectively eliminate PFAS from sewage sludge (Hušek et al., 2024).

For combustion destruction, ball milling is a simple, reliable method suitable for on-site use (Battye et al., 2024; Turner et al., 2021). However, optimizing ball milling requires addressing challenges related to

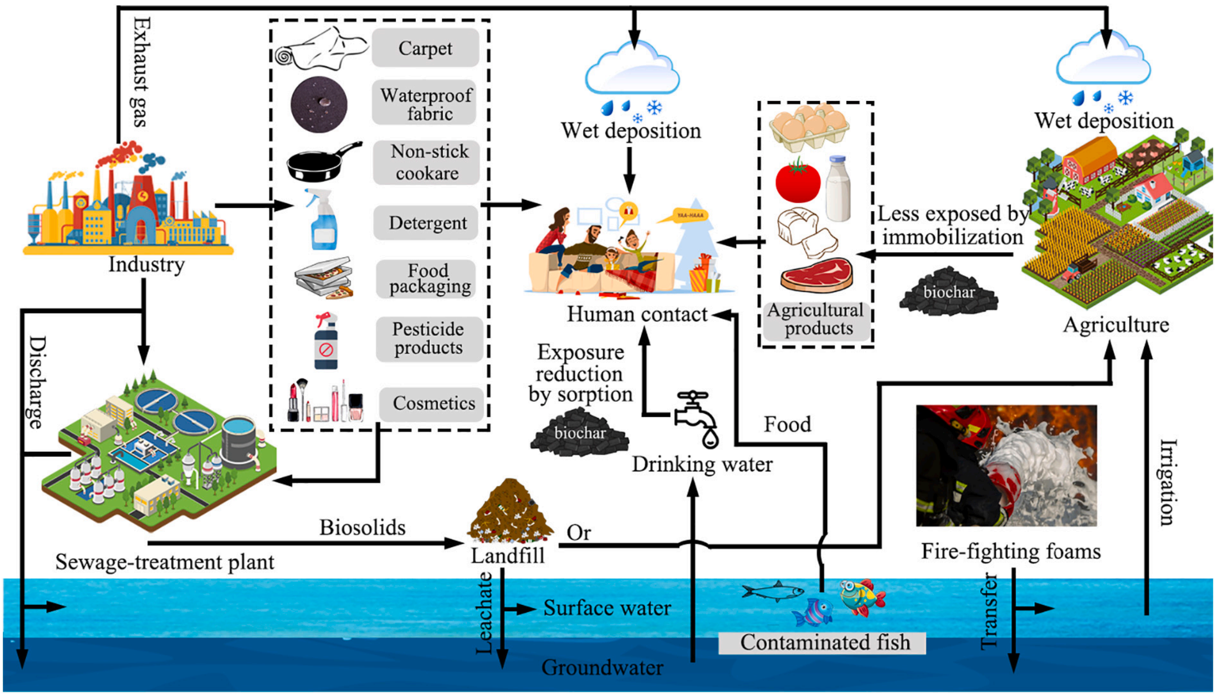

Fig. 1. Human exposure pathways for PFAS and the potential positive impacts of biochar on exposure pathways.

soil particle sizes, moisture content, and mixing ratios (Battye et al., 2024; Turner et al., 2021). Phytoremediation may partially mitigate the environmental risks of PFAS-contaminated soil (Evangelou and Robinson, 2022). Plants reduce PFAS mobility through hydraulic control, organic carbon addition, runoff and erosion reduction, and exclusion from aerial portions. However, PFAS persists due to its inherent stability (Gobelius et al., 2017; Lyu et al., 2022). Therefore, the research focuses on PFAS stabilization in soil.

In recent years, numerous emerging treatment technologies have been employed to destroy or degrade PFAS in aqueous solutions. These methods primarily encompass ultrasonic decomposition (Singh Kalra et al., 2021), photochemical reactions (Verma et al., 2024), electrochemistry (Sharma et al., 2022), plasma degradation (Alam et al., 2023), and UV-activated sulfite-iodide degradation (Li et al., 2023). Despite these advances, many of these technologies remain in the laboratory research phase, predominantly due to concerns regarding potential byproducts, high energy consumption, and high costs (Singh et al., 2021; Yadav et al., 2022). Consequently, the widespread application of these technologies in the field remains limited (Singh et al., 2021). Adsorption is widely acknowledged as an efficacious technique for treating PFAS in water and soil to prevent human exposure (Du et al., 2014). Commonly utilized adsorbents for the elimination of PFAS compounds include ion-exchange resins, nanomaterials, activated carbon, and metal-organic frameworks (Gagliano et al., 2020; Pauletto and Bandosz, 2022; Verma et al., 2021; Yadav et al., 2022). However, in soil, the use of adsorbents is restricted to carbon-based materials (Bui et al., 2024; Zhang and Liang, 2022a). Nevertheless, these methods have inherent limitations, such as high material costs, stringent operational demands, and low maintenance cost-effectiveness (Wanninayake, 2021). Thus, there is a burgeoning interest in the exploration of cost-effective methods, including the application of biochar (Zhang et al., 2021).

Biochar, an organic material rich in carbon derived from the pyrolysis of various biomass feedstocks (including agricultural and forest remnants, green wastes, biosolids, or manure) (Chen et al., 2024, 2023; Li et al., 2024a; Masud et al., 2023), has emerged as an intriguing option for PFAS remediation. Due to its highly porous structure, high ionic affinity, and significant surface area, biochar may serve as an effective adsorbent for PFAS compounds. Biochar may effectively reduce the mobility and bioavailability of PFAS in the environment through hydrophobic and electrostatic interactions (Hassan et al., 2020). The distinctive physicochemical attributes of biochar, including its relatively long-term stability and adsorption capacity (Wen et al., 2023) position biochar as an appealing alternative for PFAS remediation. Moreover, biochar holds potential for sustainable implementation as it can be derived from diverse sources of organic waste or agricultural residues (Van Nguyen et al., 2022), while removing CO_2 removal due to its recalcitrance and associated environmental co-benefits such as reduced N_2O emissions (Lehmann et al., 2021; Xie et al., 2024).

The C-sink services of biochar production and use can be certified (subtracting CO_{2eq} emission expenditures along all transport, production, processing, and C-sink installation pathways), registered in a global C sink registry, and traded (EBC, 2012-2023; Schmidt et al., 2019) which would further reduce costs. An additional benefit, in terms of mitigation of PFAS contamination, can be achieved through pyrolysis and biochar production if the feedstock source itself is contaminated with PFAS. This is usually the case for biosolids and digestates, and hence, thermal destruction of the PFAS load within these feedstocks is possible if the pyrolysis is run at a sufficiently high temperature, i.e., $\geq$600 °C (Sørmo et al., 2023).

By employing biochar as a remediating agent, a promising opportunity arises to mitigate the associated risks to human health and ecosystems by reducing PFAS concentrations in contaminated soils and water (Wang et al., 2023a). However, further research and optimization efforts are necessary to gain a comprehensive understanding of sorption mechanisms, assess their long-term effectiveness, and develop efficient application technologies for PFAS removal using biochar. The main aim of this review article is to focus on anionic PFAS and explore the following key aspects: (i) elucidating the nature and sorption mechanisms of PFAS in biochar; (ii) examining the factors influencing the sorption efficiency of biochar; (iii) presenting case studies and field applications; and (iv) discussing challenges and future directions to provide a comprehensive assessment of biochar's application in removing PFAS complexes.

2. Properties and sorption mechanisms of biochar

Different biochars can exhibit distinctive properties that contribute to their potential for effectively sorbing and immobilizing PFAS compounds. These properties include a high specific surface area, notable porosity, substantial ion exchange capacity, significant carbon content, and diverse functional groups (Krebsbach et al., 2023a; Park et al., 2020; Saeidi et al., 2020).

2.1. Physical sorption

The specific surface area of biochar is influenced by the variety of raw materials and production conditions. Typically, biochar's specific surface area spans from 1.5 to 500 $m^2\ g^{-1}$, and its extensive porous structure offers a plethora of binding sites conducive to the adsorption of PFAS (Chen et al., 2019). PFAS molecules adhere to the surface of biochar through van der Waals forces, electrostatic interactions, and hydrogen bonding occurring within pores or on the exterior surface. Research by Karbassiyazdi et al. (2023) underscores the significant role of hydrogen bonding in PFAS adsorption onto activated charcoal, influenced by factors such as source, charcoal type, and functional groups. For instance, amide groups on perfluorooctane amido betaine (PFOAB) and perfluoroctaneamido ammonium iodide (PFOAAmS) act as hydrogen bonding acceptors, strengthening interactions with charcoal possessing hydrogen-donor biochar functionalities (-COOH or -OH) during sorption (Xing et al., 2011; Zhi and Liu, 2018).

Oxygen-containing functional groups (C—O) on biochar facilitate hydrogen bond formation with PFAS, and notably, the introduction of iron promotes the protonation of C-O-C and C═O on biochar, enhancing hydrogen bond formation during PFAS sorption (Fang et al., 2014; Liu et al., 2023b). Certain cationic PFAS (e.g., PFOAAmS) possess positively charged quaternary ammonium groups that facilitate their adsorption onto the negatively charged surfaces of biochar through electrostatic attraction (Zhi and Liu, 2018). The surface charge of biochar, influenced by solution pH, results in a positively charged surface below the zero charge point (pH_{pzc}), enabling the sorption of negatively charged PFAS (e.g., anionic PFAAs like PFOA and PFOS) via electrostatic interactions (Hassan et al., 2020; Lyu et al., 2022). Additionally, the presence of positively charged groups, such as nitrogen groups (amine groups) on the biochar surface, accelerates the rate of PFAS adsorption by enhancing electrostatic interactions (Hassan et al., 2020; Liu et al., 2022). The adsorption and rejection of PFAS by biochar depend on the solution pH, refer to Section 3.1 for more details.

2.2. Hydrophobic partitioning

Biochar adsorbs hydrophobic PFAS compounds by facilitating their partitioning between the aqueous phase and the carbon-rich biochar matrix (Saeidi et al., 2020). Hydrophobic interactions are the main adsorption mechanism controlling anionic PFAS binding to biochar (related studies in Table S3). This phenomenon relies on the inherent affinity of hydrophobic parts of the PFAS compounds for the organic carbon within biochar. Hydrophobic interactions can be qualitatively conceptualized as processes resulting in the aggregation of hydrophobic moieties, thereby generating attractive forces between hydrophobic entities (Zhang et al., 2019). Notably, hydrophobicity is crucial for the sorption of long-chain PFAS compounds such as PFOS (Deng et al., 2015;

Militao et al., 2021; Nguyen et al., 2023).

The hydrophobicity of biochar is predominantly influenced by the amount of condensed aromatic "black carbon" in the matrix relative to the amount (or lack) of surface functional groups (Bostick et al., 2018; Goranov et al., 2020). These factors are determined by aspects such as feedstock type and pyrolysis conditions (Krebsbach et al., 2023; Wiersma et al., 2020). For example, the hydrophobicity of biochar is closely associated with specific surface functional groups, namely alkane, and olefin, with their prevalence influencing the material's hydrophobic characteristics (Fan et al., 2022). Biochar produced at lower temperatures exhibits a heightened presence of aliphatic compounds within its pores, resulting in increased hydrophobicity (Fan et al., 2022). Conversely, biochar generated at elevated temperatures manifests heightened hydrophobicity primarily due to the prevalence of aromatic, condensed moieties, characterized by functional groups such as =C-H, CH, and CC (Chen et al., 2016; Fan et al., 2022; Zimmerman and Mitra, 2017). Since aromatic surfaces are more planar than aliphatic ones (Ahmed et al., 2018; Cornelissen et al., 2004), PFAS can approach them much more closely, allowing stronger van der Waals dispersive interactions that weaken with the 6th power of separation distance (Dzyaloshinskii et al., 1961). The C/H ratio serves as a key indicator for evaluating the aromaticity of biochar, notably, an augmentation in the degree of aromatization of biochar correlates with enhanced hydrophobicity (Chen et al., 2016; Fan et al., 2022).

Biochar facilitates the adsorption of PFAS compounds by effectively partitioning them between the aqueous phase and the organic carbon-rich matrix of biochar (Singh, 2022). The efficiency of adsorption is contingent not only upon the hydrophobicity of the adsorbent but also exhibits a correlation with the hydrophobicity of the adsorbent PFAS. For instance, Hakimabadi et al. (2023) observed that PFOS demonstrated a higher affinity for carbon adsorbents compared to 6:2 fluorotelomer sulfonic acid (6:2 FTS). This discrepancy was attributed to the increased hydrophobicity of the (-CF_2-CF_2-) moiety in PFOS when contrasted with the hydrogenated carbon structure (i.e., -CH_2-CH_2-). Furthermore, the presence of an additional -CF_2- unit in perfluoropentanoic acid (PFPeA) compared to PFBA led to heightened sorption of PFPeA. This augmented adsorption can be rationalized by the enhanced hydrophobicity associated with the additional fluorinated moiety. In addition, the -SO_3 headgroup of PFBS exhibited greater hydrophobicity than the -COO headgroup of PFPeA, resulting in a higher adsorption capacity for PFBS compared to PFPeA (Hakimabadi et al., 2023; Krafft and Riess, 2015; Parker et al., 2022). Biochar may also sorb PFOS compounds through hydrophobic interactions facilitated by C-O-C groups (Militao et al., 2023).

2.3. Surface complexation

The surface of biochar usually hosts a variety of functional groups, including phenolic (-OH), aldehyde (-CHO), hydroxyl (-OH), carboxyl (-COOH), and ketone groups (C=O) (Khalid et al., 2020). These functional groups exhibit differing sensitivities to pyrolysis temperature (Keiluweit et al., 2010). Functional groups are more prevalent at lower and intermediate pyrolysis temperatures (300–450 °C) and decrease as the temperature rises, with a noticeable decrease above 600 °C and near absence at 750 °C (Janu et al., 2021). These functional groups play a crucial role in the interaction with PFAS compounds through surface complexation (Krebsbach et al., 2023). This mechanism involves the formation of chemical bonds or ion exchange reactions between biochar surface functional groups and PFAS molecules dissolved in the solution. The fluorine atom (F^-) in PFAS can displace the hydroxyl ion (OH^-) and subsequently form complexes on biochar surfaces. An analysis of the FTIR spectra of biochar before and after PFAS adsorption reveals that carboxylic ester functional groups may significantly contribute to electrostatic interaction and complex adsorption of PFAS substances (Wahab et al., 2010; Zhang et al., 2021).

3. Factors affecting the sorption strength of biochar

Both the source material and the pyrolysis regime profoundly affect the properties of biochar. Consequently, their properties can vary considerably. However, biochar sorption of PFAS is generally controlled by two main factors: 1) physical characteristics (porosity), which determine the capacity (Fig. 2); and 2) chemical characteristics (matrix properties), which determine the affinity of biochar for the PFAS sorbate.

Specific surface area and pore volume are important for a biochar sorbent's capacity as these parameters are related to the number of active adsorption sites and pore-filling capacity (Ahmad et al., 2014; Hale et al., 2016). For example, it has been found that pores in non-activated wood-based chars often are too narrow (<1.5 nm) to accommodate bulky PFAS molecules (Krahn et al., 2023; Sørmo et al., 2024). A general rule of thumb is that pores need to be 2–3 times molecular diameter to effectively capture a contaminant (Zimmerman et al., 2004). Maximal pore diameter $D_{max} = 0.96$ nm for PFPeA, 1.54 nm for perfluorodecanoic acid (PFDA) (Krahn et al., 2023), where the pore volume (PV) of wood-based biochars was almost exclusively in the pore range < 3 nm, while the pore volume and surface area of wood-based biochars can result in too low of porosity suitable to accommodate relatively large PFAS compounds (Sørmo et al., 2024). The resulting effect is that most PFAS restricted from diffusing into and accessing sorption sites inside micropore structures due to size exclusion effects and steric hindrances. Sørmo et al. (2024) discovered that biochar exhibits a significant adsorptive capacity for PFAS molecules with diameters >1.02 to 2.20 nm, particularly when the biochar possesses high porosity and a pore size exceeding 1.5 nm.

Total carbon and black carbon contents have previously been used as a general predictor for the sorption strength of charcoals and soils to both PFAS and halogenated organic compounds (Cornelissen et al., 2005; Fabregat-Palau et al., 2021; Hale et al., 2016; Kupryianchyk et al., 2016; Zareitalabad et al., 2013). The amount of condensed aromatic carbon (ConAC) in a biochar is likely linked to the biochar's surface hydrophobicity and could thus be considered a factor describing the affinity of a biochar sorbent for a PFAS sorbate bound by hydrophobic interactions (Goranov et al., 2024). When predicting sorbent effectiveness, ConAC and SSA/PV should be considered jointly, as ConAC reflects sorption affinity (hydrophobic effects between sorbate and biochar surface), while SSA/PV determines sorption capacity (available sites and pore filling). These indicators are correlated, as a high SSA is usually produced at the same high temperatures that favor the formation of biochars with high contents of condensed aromatic carbon (Hale et al., 2016; Zimmerman and Ouyang, 2019). High-temperature pyrolysis (>700 °C) is often preferred for producing effective biochar sorbents for PFAS.

The presence of positively charged mineral surfaces in biochar is another key factor influencing its affinity for PFAS. Previous studies have shown that PFAS that contain negatively charged head groups can bind to positively charged surfaces of iron oxides through ionic interactions (Lu et al., 2016). Zhang et al. (2022) also observed indications of this effect in iron-enriched charcoal from metal smelting processes. Biochar surfaces typically exhibit a low point of zero charge (PZC), resulting in a negative charge due to the deprotonation of surface functional groups at the alkaline pH of the biochar (Ahmad et al., 2014). Mineral phases have variable PZCs and might create niches with positive charges that could be involved in the electrostatic attraction of the PFAS functional groups. Biochar modification with specific minerals or metal salts to enhance sorption, particularly through electrostatic interactions, has been thoroughly investigated for heavy metals. However, similar research on polar organic contaminants and surfactants remains limited (Liu et al., 2023b; Xu et al., 2017).

Various factors influencing biochar adsorption efficiency for PFAS, including pH, ionic strength, temperature, contact time, and co-existing contaminants, are outlined by Zhang et al. (2023b) and depicted in

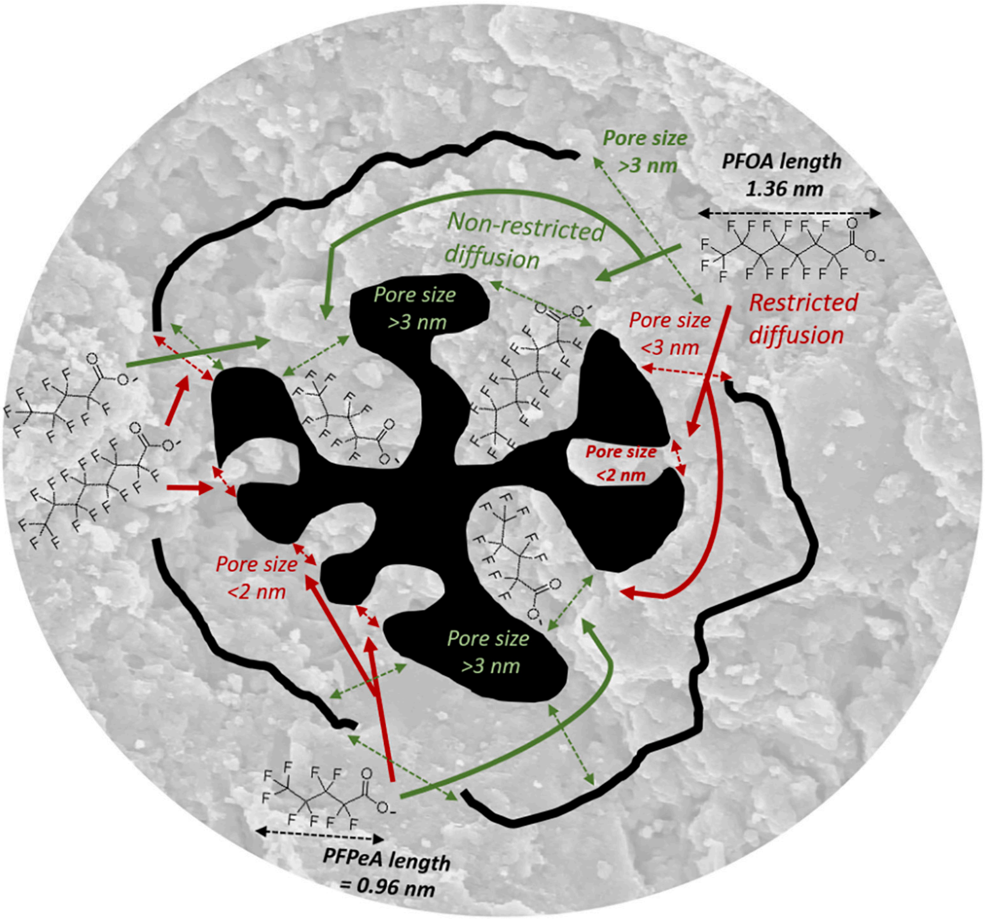

Fig. 2. Illustration of how the diffusion of PFOA and PFPeA into the pores of biochar sorbents is regulated by pore size.
Reprinted with permission from Sørmo, PhD thesis, NMBU 2023, thesis number 2023:77, ISBN 978-82-575-2109-7.

Fig. 3. The significance of comprehending and optimizing these factors in achieving efficient biochar remediation for PFAS-contaminated systems is outlined below.

3.1. pH

The pH of the liquid phase, in both soil and water, critically influences the electrical charge on the biochar surface and the formation of PFAS complexes. Solution pH impacts the biochar surface charge of functional groups, the ionization of solutes, and the generation of other substances (Gao et al., 2017; Zhang et al., 2021). The pH at the point of zero charge (pH_{pzc}) is particularly significant, as it determines the net charge of the biochar surface. Above the pH_{pzc}, the surface tends to bear a net negative charge, whereas below it, a net positive charge is observed (Fabregat-Palau et al., 2022). At pH values below the point of pH_{pzc}, the functional groups on the biochar surface, including carboxyl, aldehyde, and hydroxyl groups, are readily protonated, resulting in a positive charge. This protonation process facilitates the removal of PFOS through ion exchange reactions and electrostatic interactions (Hassan et al., 2020). In their experimental investigation on the adsorption of PFOA and PFBA by biochar, Liu et al. (2023b) observed a pH in the solution ranging from 3 to 11. They observed systematic deprotonation of functional groups on the surface of the biochar with increasing pH. This chemical transformation resulted in a notable weakening of electrostatic interactions. Furthermore, as the pH continued to rise, it induced electrostatic repulsion of anionic PFOA and PFBA by the biochar, consequently, a discernible decrease in the adsorption was observed (Liu et al., 2023b). Kundu et al. (2021) investigated the adsorption of PFAS by biochar derived from biosolids, finding that the biochar sorption efficiency of PFAS was significantly greater at a solution pH of 4.3 compared to a solution pH of 7.85. Lower pH values intensified electrostatic adsorption due to the positively charged surface of the biochar at a lower pH, enhancing the interaction with the negatively charged PFAS.

3.2. Ionic strength

The presence of salts or other ions in solution, commonly known as ionic strength, can influence the adsorption of PFAS onto biochar through competition for adsorption sites, electrostatic interactions, and pH buffering (Rodrigo et al., 2022). Saeidi et al. (2020) found that elevated sulfate concentrations significantly decreased the adsorption affinity of activated carbon for PFOA and PFOS. This finding suggests that biochars may exhibit a similar response, given their structural similarities to activated carbon. Sulfate ions and chloride ions can also compete with PFOS anions for adsorption sites. A salting-out effect may occur with high inorganic ion concentrations, leading to PFOA precipitation (Wu et al., 2022). It is also important to note that pH variation influences the surface charge of PFOS and PFOA, altering electrostatic attraction. PFOS exhibits greater pH sensitivity, likely due to changes in ionic strength (Cheng et al., 2009; Deng et al., 2015). Conversely, as an increase in pH could alter the biochar surface charge to negative and hence electrostatic attraction to repulsion, the presence of cations can increase biochar PFAS sorption through electrical double-layer compression (Du et al., 2014).

Marzeddu et al. (2022) investigated the influence of calcium and magnesium ions on the adsorption of PFOS by waste coffee biochar, observing a 24 % increase in the adsorption rate. This enhancement can

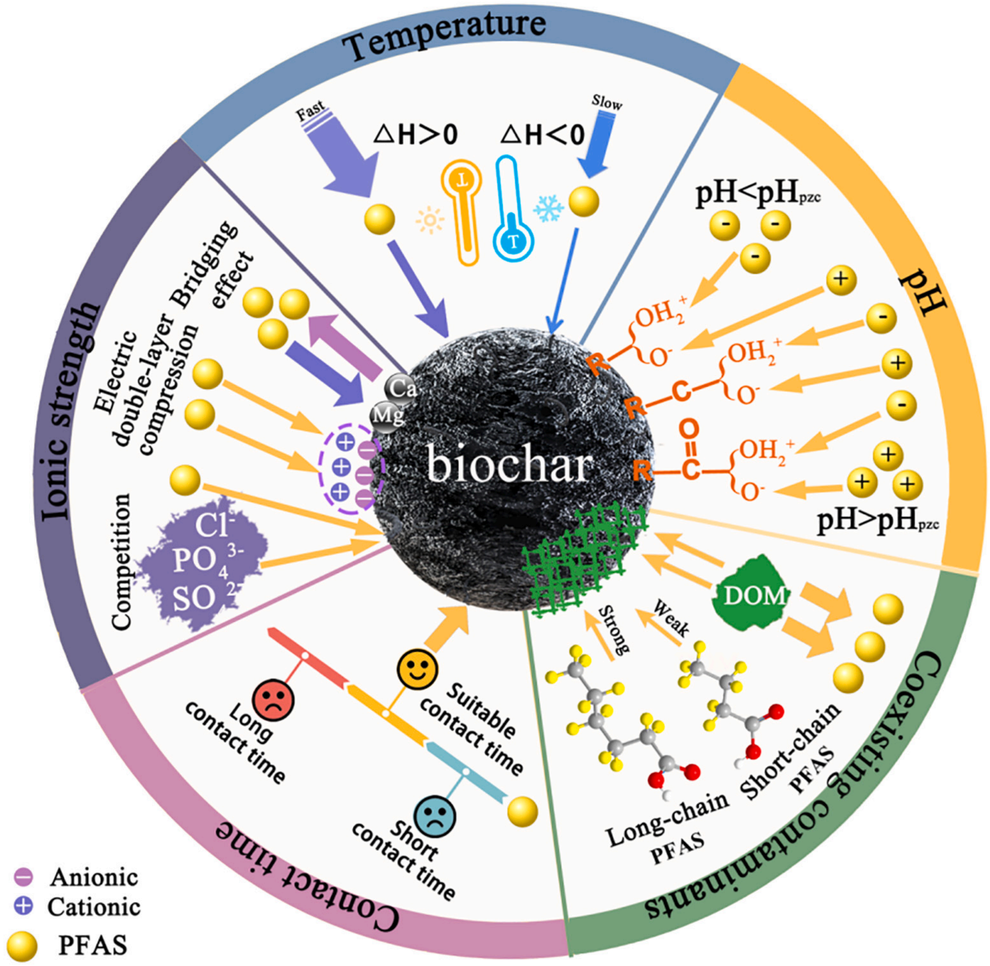

Fig. 3. Factors influencing the adsorption efficiency of biochar for PFAS.

be attributed to the cation bridging effect, wherein the positively charged calcium and magnesium ions interact with the negatively charged surface of the adsorbent and the anionic headgroup of PFOS, thereby enhancing the overall removal efficiency (Steigerwald and Ray, 2021). Wang et al. (2023b) demonstrated that the presence of phosphate ions influences the adsorption behavior of perfluorobutanesulfonate (PFBS) and PFPeA on biochar, possibly through the preferential ion exchange between phosphate ions and biochar or their competitive adsorption with PFBS and PFPeA (Wang et al., 2020).

3.3. *Coexisting contaminants*

The coexistence of other contaminants within the soil or water matrix can compete with PFAS for biochar adsorption sites (Krahn et al., 2023; Zhang et al., 2021). Understanding the interactions between these co-existing contaminants and PFAS for sorption onto biochars is essential for accurately predicting and optimizing the efficacy of biochar-based remediation strategies. Comparing single solution and mixed PFAS experiments reveals a reduction in PFAS removal ranging from 32.8 % to 57.9 % in a mixed solution compared to a single solution scenario (Zhang et al., 2021). This decline in PFAS removal is attributed to the competitive adsorption of PFAS with coexisting pollutants, vying for available adsorption sites on biochar surfaces (Krahn et al., 2023). A reduction in PFAS sorption may also be attributed to pore clogging and thus a reduction in diffusion processes (Inyang and Dickenson, 2017; Zhang et al., 2021).

In the presence of coexisting pollutants, long-chain PFAS tend to exhibit a preferential adsorption tendency on the biochar surface compared to short-chain PFAS, owing to the greater hydrophobicity of long-chain PFAS (Du et al., 2015; Murray et al., 2019; Sörengård et al., 2020). The presence of dissolved organic matter (DOM) may hinder the removal of PFAS by obstructing adsorption sites or interfering with the adsorption mechanism; short-chain PFAS, however, appeared to be less affected by DOM as compared to long-chain PFAS (Liu et al., 2021; Sørmo et al., 2021). According to Inyang and Dickenson (2017), the presence of dissolved organic carbon (DOC) and humic substances in wastewater can lead to the occupation of high-energy biochar pore sites by organic matter. This occupation results in the blockage of adsorption sites essential for PFOA adsorption onto biochar, thereby reducing overall adsorption efficiency (Militao et al., 2021; Qi et al., 2022). Moreover, certain organic compounds such as humic acid, 1-naphthol, benzoic acid, and phenol have been found to diminish the adsorption of PFOA by 17 % to 34 %. These organic compounds likely impede PFOA adsorption processes through mechanisms involving electrostatic repulsion and pore blockage (Gagliano et al., 2020; Nguyen et al., 2023).

3.4. *Contact time*

The temporal interaction between biochar and PFAS-contaminated media plays a pivotal role in governing adsorption kinetics and equilibrium capacity. While prolonged contact times facilitate heightened adsorption surpassing an optimal contact duration may lead to diminishing returns (Liu et al., 2021; Park et al., 2020). This phenomenon arises from the potential emergence and exacerbation of competitive adsorption effects among solutes, coupled with the risk of desorption (Militao et al., 2023). Furthermore, the adsorption of PFAS substances onto biochar initiates a phase of rapid adsorption, driven by the initial abundance of PFAS molecules, resulting in elevated adsorption efficiencies. Rapid adsorption typically involves the transfer of molecules from the liquid phase to the adsorbent surface. Subsequently, a phase of slow kinetics ensues, where the time required to attain equilibrium is intricately linked to the microporous properties of the adsorbent (Militao et al., 2023; Zhang et al., 2019). In practical terms, manipulating the duration of adsorption contact time in experiments, such as through its reduction, curtails the diffusion of PFAA into the interior or sub-pores of the adsorbent and consequently diminishes adsorption efficiency (Liu et al., 2021). Understanding the distinct phases of fast, slow, and equilibrium adsorption times during PFAS adsorption by biochar requires scrutinizing the adsorption kinetics of biochar and identifying the optimal adsorption contact time.

3.5. Temperature

The adsorption capacity of PFAS is influenced by temperature variations, a critical factor governing the interaction between PFAS substances and the adsorbent (Zhang et al., 2019). Owing to the spontaneous nature of adsorption, a temperature rise generally leads to a reduction in adsorption (Fontecha-Cámara et al., 2006). However, exceptions exist, such as in the adsorption of PFOS by corn stover biochar, where a reported spontaneous heat absorption process led to an increased adsorption capacity with rising temperature (Guo et al., 2017). This phenomenon was likely attributed to the comprehensive influence of interactions in solution, encompassing adsorbent-adsorbate, solvent-adsorbent, and solvent-adsorbate interactions (Fontecha-Cámara et al., 2006; Zhang et al., 2019). In an experiment conducted by Rodrigo et al. (2022), the adsorption capacity of biochar for PFOA and PFOS was found to be higher at 10 °C compared to that at 25 °C. This observation may be attributed to the impact of temperature on PFAS aggregation, which tends to be more pronounced at lower temperatures, facilitating increased partitioning or adsorption on the biochar surface. Conversely, reduced aggregation occurs at higher temperatures.

4. Case studies and field applications

Multiple case studies have demonstrated the successful implementation of biochar for remediating PFAS contamination across various soil and water matrices. The studies outlined below underscore the efficacy of biochar-based systems for reducing PFAS concentrations and highlight their adaptability in diverse contaminated environments.

4.1. Soil remediation

In soil environments, pollutants migrate through mechanisms such as dissolution, desorption, and complexation reactions. Biochar has emerged as a promising and sustainable adsorbent capable of immobilizing PFAS substances through sorption, thus mitigating their leaching in soil and uptake by plants. Notably, widespread soil contamination is caused by large amounts of PFAS compounds in conventional aqueous film-forming foam formulations, with end products such as PFOA and PFHxA converted from precursors widely remaining in the soil environment (Bolan et al., 2021; Sørmo et al., 2021). As depicted in Table 1, the addition of biochar has proven effective in immobilizing PFAS in soil.

For instance, Askeland et al. (2020) investigated the long-term treatment of soil contaminated with PFAS substances using pine biochar. They found that the desorption of PFOS, PFOA, and PFHxA in biochar-amended soil was significantly lower compared to untreated soil. Moreover, the sorption quantity of PFOS in a sandy clay loam was greater than in a loam (Askeland et al., 2020). These findings suggest that the adsorption efficiency of PFOS in different soils may be influenced by the physicochemical properties of the soil and its homologues. This effect could be attributed to various factors, such as hydrophobic interactions, electrostatic interactions, and changes in mobility. Therefore, the efficacy of biochar as a soil amendment is likely closely intertwined with the inherent characteristics of the soil (Milinovic et al., 2015; Oliver et al., 2019).

The impact of varying total organic carbon (TOC) contents in soil on the immobilization of PFAS compounds using biochar was investigated by Sørmo et al. (2021). The authors found that the PFAS immobilization efficacy of biochar, at an application rate of 1 % (*w*/w), was significantly greater in soils with low TOC content (1.6 %) compared to those with high TOC content (34.2 %). This suggests that the presence of high organic matter concentrations in soil may increase competition for biochar adsorption sites and pore walls, thereby impeding the immobilization process (Sørmo et al., 2021). The sorption strength of the soil itself is higher in high TOC soils. Less PFAS are released from the soil and can partition into biochar compared to soils with low TOC. Moreover, increasing the biochar dosage by up to 5 % resulted in a complete reduction (up to 100 %) of soil PFAS leaching (Sørmo et al., 2021). However, while higher biochar application rates can effectively eliminate PFAS leaching, it is important to consider the practical economic implications associated with such application rates.

Zhang and Liang (2022b) examined whether biochar aging would influence the desorption of PFAS compounds. Their results revealed that after a 52-day aging period, the leaching rates of PFOS, PFOA, PFHxS, and PFHxA were significantly lower compared to untreated samples (24.5 %, 42.8 %, 43.5 %, and 64.6 %, respectively). Moreover, biochar aging did not result in any additional release of PFAS compounds. Furthermore, extending the immobilization period (Day 21 to Day 105) can enhance the adsorption efficiency of short-chain PFAS.

Sørmo et al. (2024) investigated the effects of waste-based biochars

Table 1
A summary of cases on PFAS immobilization by biochar.

Types of biochar	Soil	TOC content (%)	Add scale (%w/w)	PFAS leaching loss reduction (%)				References
				PFOS	PFOA	PFHxS	PFHxA	
Pine biochar	Loamy sand soil	–	5	20.1	41.6	28.3	19.3	(Askeland et al., 2020)
	Sandy clay loam	–	5	42.7	58.9	26.8	45.4	
Waste timber biochar	Moraine soil	1.6	1	93	72	81	61	(Sørmo et al., 2021)
		1.6	5	100	100	100	100	
		34.2	1	59	21	17	22	
		34.2	5	78	51	59	38	
Shredded timber waste biochar	Eluvial and illuvial mineral horizons	1.6	20	86	70	72	31	(Silvani et al., 2019)
Forest wood waste biochar	Sandy loam soil	–	2	9.8	22.1	32.5	50.9	(Zhang and Liang, 2022a)
Forest wood waste biochar	Sandy loam texture	1.6	2	24.5	42.8	43.5	64.6	(Zhang and Liang, 2022b)
Sludge biochars	Sandy soil	0.57	1	92–99	80–85	75–79	35–40	(Sørmo et al., 2024)

on the leaching of PFAS from sandy soil (TOC of 0.57 %) in up-flow column percolation tests (15 days, 16 pore volumes replaced). Amendment with 1 % biochar retained PFOS by up to 99.9 % for an activated waste timber biochar, followed by three sludge-based chars (92–99 % reduction). Non-activated wood-based biochars, on the other hand, reduced leaching by <43 %. This was explained by the dominance of pores <1.5 nm in the latter chars; these pores are too narrow to accommodate most PFAS molecules. Effects were less strong for short-chain PFAS, with e.g., PFOA leaching (95 %) being reduced by 95 % vs. 67 % for PFHxA.

4.2. *Water treatment*

Biochars can also be used for the removal of PFAS from contaminated water. Dalahmeh et al. (2019) demonstrated that biochar-based filtration systems involving filter cartridges effectively reduced PFAS concentrations in water. Four different cartridges were compared: 1) biochar without biofilm (BC-no biofilm); 2) biochar with active biofilm (BC-active biofilm); 3) biochar with inactive biofilm (BC-inactive biofilm); and 4) sand with active biofilm (sand-active biofilm). Over 22 weeks of continuous monitoring, simulated field loading rates were employed to assess the concentrations of 13 PFAS substances removed by the cartridges. Results showed that all three types of biochar cartridges (BC-no biofilm, BC-active biofilm, and BC-inactive biofilm) exhibited significant PFAS removal capabilities. Interestingly, the removal efficiencies of PFAS by BC-active biofilm showed no significant differences compared to those of BC-no biofilm. BC-no biofilm demonstrated high removal efficiency (90–99 %) for C_7-C_{11} PFCA, C_6 and C_8 PFSA, and FOSA (C_8). However, it exhibited relatively lower removal efficiency (20–60 %) for short-chain PFCAs (C_3-C_6) and PFSA (C_4). In contrast, sand-active biofilm demonstrated low removal efficiency (0–70 %) for all PFAS compounds. This study underscores the promising potential of biochar for treating and removing certain PFAS compounds from water sources.

Liu et al. (2021) evaluated the performance of a reed straw biochar filter for removing PFAS compounds from groundwater. To simulate real-world conditions, four different groundwater samples were used as background solutions to encompass variations in flow rate and the presence of other substances alongside PFAS compounds. The investigation focused on six representative PFCAs and PFSAs, considering various chain lengths and functional groups, to assess their removal efficiencies in biochar microfilters. The results indicated that the reed straw biochar filter exhibited average removal efficiencies of 56 % for PFBA, 61 % for PFBS, 63 % for PFHxA, 73 % for PFHxS, 73 % for PFOA, and 83 % for PFOS. Furthermore, the study examined the impact of varying concentrations of DOC under simulated conditions. Groundwater samples with high DOC concentrations exhibited an average removal efficiency reduction of 29 % for PFBA, 19 % for PFBS, and 26 % for PFHxA, particularly for short-chain PFAA. However, the impact was comparatively minimal for long-chain PFAA, and PFOS remained largely unaffected by changes in DOC concentration (Liu et al., 2021). For further details on the adsorption kinetics and capacities of biochar adsorbents within aqueous systems, please refer to Table S4.

4.3. *Sediment remediation*

Biochar has shown efficacy in remediating PFAS-contaminated sediments. Guo et al. (2019) found that corn stover biochar at 2 % and 5 % (*w*/w) concentrations reduced free PFAS by 1.7–3.5 times compared to untreated sediments. Biochar also tripled the sediment's water partition coefficient, enhancing PFOS affinity and reducing its mobility in the water-sediment system. Guo et al. (2017) confirmed biochar's ability to reduce PFAS concentrations in sediments. Sørmo et al. (2021) reported similar reductions in PFAS leaching from contaminated soil treated with activated biochar. Krahn et al. (2023) further validated biochar's effectiveness, particularly sewage sludge-derived biochar, in sorbing PFAS from water.

However, research on using biochar for sediment remediation is limited, necessitating further investigation. Future studies should explore biochar's efficacy across diverse aquatic environments, considering the influence of ionic strength and pH on PFAS sorption. Mahinroosta and Senevirathna (2020) support this need, identifying carbonaceous sorbents like biochar as promising for PFAS-contaminated soil remediation.

5. Challenges and future directions

When scaling up biochar-based remediation techniques, numerous challenges emerge, such as devising effective regeneration strategies and addressing potential long-term impacts. These challenges underscore the urgency for further research, particularly in biochar modification, refining production methods, and conducting thorough evaluations of biochar efficacy at field scale to ensure success.

5.1. *Costs and availability*

Table S5 compares the adsorption capacities of various materials, including biochar, and highlights their cost-effectiveness in removing PFAS substances. Notably, the cost of anion exchange resin is three times higher than that of activated carbon, making biochar a potentially more economically viable option for PFAS remediation (Yadav et al., 2022). Biochar is priced at US$246 per ton, significantly lower than commercial activated carbon, which is approximately six times more expensive than biochar (Premarathna et al., 2019). Biochar's economic advantage makes it a potential alternative to activated carbon in sorption applications (Alhashimi and Aktas, 2017; O'Connor et al., 2022). However, large-scale biochar production can entail significant costs, depending on the availability of local biomass resources. According to Homagain et al. (2016), the pyrolysis process constitutes approximately 36 % of the total production costs, while land use, feedstock collection, and transportation account for 14 %, 12 %, and 9 %, respectively. Efficient and optimized pyrolysis is therefore crucial for cost reduction, highlighting the significance of identifying cost-effective production methods and diversifying feedstock sources for wider biochar utilization. In addition, biochar remediation is more sustainable than conventional activated carbon from a life cycle assessment perspective, as demonstrated by the sediment remediation of polychlorinated dibenzo-p-dioxins and furans (Sparrevik et al., 2011).

5.2. *Biochar modification*

Most past studies have shown that activated carbon seems to be more effective than biochar for PFAS (Kabiri et al., 2023; Zhang et al., 2019), but the adsorption efficiency of biochar is greatly affected by different biomass species, and its performance can be greatly improved by modification. For example, Liu et al. (2021) found that the adsorption efficiency of reed straw biochar for PFBA at 900 °C was higher than that of GAC. With further research on biochar in recent years, the effect of biochar on PFAS was gradually seen (refer to Tables S2 and S3). For example, Rodrigo et al. (2022) modified Douglas fir biochar with magnetic Fe_3O_4, and the maximum adsorption capacity of PFOA increased from 9 mg g^{-1} to an astonishing 652 mg g^{-1} after the modification compared with the original biochar. In addition, Zhou et al. (2021) modified microporous biochar with liquid-alkali treatment, and the adsorption capacity of PFOA in an aqueous solution could be as astonishingly high as 1269 mg g^{-1}. The plasticity of biochar demonstrates the great development potential of biochar for PFAS remediation.

Biochar modification techniques encompass physical, chemical, and biological approaches, with chemical modification being widely regarded as the primary choice and future direction for biochar modification (Chen et al., 2022; Lu et al., 2022). Modifying biochar enhances its functionality (Table 2). Modified biochar alginate beads exhibit

Table 2
Cases on the adsorption of PFAS by modified biochars.

Modified biochar	PFAS compounds	Observations	Environmental media	References
Biochar-alginate composite beads	PFOS	99 % removal was achieved within <16 h, starting from an initial PFOS concentration of 100 μg L^{-1}.	Aqueous solution	(Militao et al., 2023)
Carbon nanomaterial-coated biochar	PFOS, PFOA, PFHxS	Nanomaterial-coated biochar exhibited a 79 % removal rate for PFAS substances, significantly surpassing the removal rate achieved with the original biochar treatment.	Wastewater	(Patel et al., 2023)
Thermally modified hydrophobic biochars, metallic oxide modified biochars	PFOS	A higher adsorption capacity for PFOS was observed at pH 3.1, reaching 178.1 mg g^{-1} for thermally modified biochar and 194.6 mg g^{-1} for metallic oxide-modified biochar.	Aqueous solution	(Hassan et al., 2020)
Magnetic biochar	PFOS	The maximum adsorption capacity of PFOS was determined to be approximately 120.44 ± 12.37 mg g^{-1}.	Aqueous solution	(Hassan et al., 2022)
Biochar activated with steam/CO_2	PFOS, PFOA, PFHxS, PFHxA	Activated biochar (63–95 %) exhibited a significantly greater reduction in leaching compared to activated biochar (23–78 %).	Soil	(Sørmo et al., 2021)
$FeCl_3$ and carbon nanotube-modified biochar	PFOA	Anionic PFOA exhibited a higher likelihood of adhering to surfaces and forming ion bonds, thereby leading to an increased adsorption capacity.	Simulated wastewater	(Wu et al., 2022)
Clay-biochar composites	PFOAB	The removal of zwitterionic PFAS in water demonstrated significant sorption efficacy.	Aqueous solution	(Mukhopadhyay et al., 2021)

consistent efficacy in PFOS removal, remaining largely unaffected by factors such as natural organic matter, pH, and ionic strength, typically found in natural water bodies (Militao et al., 2023). The incorporation of carbon nanotubes and $FeCl_3$ into biochar has significantly enhanced adsorption efficiency, by increasing the specific surface area, porosity, and pore volume of the biochar (Wu et al., 2022). Modifying the physical properties (SSA and PV) of biochars through activation with steam or CO_2 has also been documented to improve biochar PFAS sorption in soil. Activation expands the volume and surface area of mesopores (>1.5 nm), providing the biochars with better capacities for entrapping and sorbing PFAS, and making biochars less prone to clogging and competitive sorption from DOM (Sørmo et al., 2021). Furthermore, physical activation increases the amount of ConAC in the biochars, which results in a higher affinity for binding sorbates through hydrophobic interactions, i.e., long-chain PFAS (Goranov et al., 2024). Nevertheless, it is worth noting that the application of biochar modification is mostly confined to laboratory research, necessitating additional investments in upscaling to reduce process costs and production time. Additional research should delineate how the modification of biochar properties can enhance its adsorption capacity and selectivity for various PFAS compounds.

5.3. Regeneration strategies

Over time, biochar may undergo saturation with PFAS, necessitating regeneration, treatment to restore its adsorption capacity, or removal and incineration to ensure the PFAS compounds are fully destroyed and not released in the off-gas fraction. However, the existing regeneration strategy is only effective for the biochar that has been used for water or waste gas treatment. In soil and sediment remediation, one will not be able to remove the biochar after application. If the applied biochar becomes saturated, one needs to apply more biochar. The benefit of this approach is the biochar carbon storage effect in the soil/sediment (Lehmann et al., 2021).

Typically, the regeneration process of biochar involves removing PFAS substances from the adsorbent, using methanol to strip PFAS from biochar, followed by repeating the regeneration process by drying cycles in an oven (Liu et al., 2023b; Rodrigo et al., 2022). Associated studies showed that after regeneration, the ability of biochar to sorb PFAS fluctuated. For example, Liu et al. (2023b) found that the sorption capacity of biochar for hexafluoropropyleneoxide dimeric acid (HFPODA, also known as GenX) decreased by 10.1 % after one regeneration cycle. Additionally, a marginal loss in the weight of the adsorbent was noted (Rodrigo et al., 2022). However, it is commonly practiced that the chemical regeneration of saturated adsorbents is performed in situ during full-scale processing to address concerns regarding transportation and the utilization of consumables in the treatment process (Gagliano et al., 2020). During thermal regeneration, several factors, including the complete decomposition of PFAS compounds at elevated temperatures, the formation of by-products such as volatile organic fluorine (VOF) or short-chain compounds, and the alteration of adsorbent performance, need to be considered (Watanabe et al., 2018, 2016). Spent activated carbon has been efficiently regenerated on a lab-scale system, and a wide range of VOF compounds were detected in the flue gas (Xiao et al., 2020). However, biochar regeneration faces significant challenges as this simply has not been attempted frequently enough in the past to draw definitive conclusions on efficacy. Therefore, developing effective regeneration strategies is crucial to ensuring the long-term efficiency and sustainability of biochar-based systems.

5.4. Site-scale performance and long-term impacts

Although laboratory studies have shown promising results, further research is needed to assess the performance of biochar in real-world, site-scale locations with diverse conditions and contaminants. During the treatment of PFAA substances at pilot-scale sites, it has been observed that prolonged flushing and backwashing of biochar media can generate fine particulate matter due to physical abrasion. This particulate matter, in turn, has an impact on the backwashing and filtration processes, necessitating an evaluation of the biochar's service life to determine the appropriate timing for replacement (Inyang and Dickenson, 2017). Biochar granules and biochar filter cartridges can be used to overcome the issues resulting from the breakdown of biochar (Li et al., 2016). Biochar filters can be employed for the treatment of PFAS-contaminated wastewater at a site where the surface adsorption capacity of the biochar becomes depleted over time and desorption takes place due to prolonged exposure to the contaminants (Dalahmeh et al., 2019). The long-term fate and potential release of adsorbed PFAS into the environment require meticulous consideration.

Following adsorption onto biochar, PFAS compounds can undergo various transformation pathways (Zhi and Liu, 2018). They may persist as physically adsorbed species on the biochar surface, exhibiting reduced mobility and bioavailability (Zhi and Liu, 2018). However, under specific conditions, desorption or re-solubilization of certain PFAS compounds may occur, potentially leading to their release back into the environment. Research indicates that biochar undergoes aging processes in soil, including physical fragmentation and ash dissolution (Bolan et al., 2023; Wang et al., 2022), which can weaken electrostatic interactions and induce alterations in biochar's functional groups (Bolan et al., 2023; Mia et al., 2017). Additionally, there is a tendency for preferential microbial metabolism and the decomposition of select unstable carbons within the biochar matrix (Bolan et al., 2023).

Collectively, these transformations may influence the efficacy of PFAS substances' immobilization on biochar, potentially leading to their re-release into the environment. Further investigations are essential to comprehend the stability of PFAS adsorption on biochar under diverse environmental conditions and to evaluate any potential leaching or desorption over time. Conducting field-scale demonstrations is imperative to assess factors such as sorption attenuation, longevity, site-specific interactions, and potential impacts on the surrounding ecosystem.

6. Conclusions and outlook

This review provides a comprehensive overview of the adsorption mechanisms by which biochar interacts with PFAS, the various factors that influence sorption efficacy, and the application of biochar for the remediation of contaminated sites and aquatic environments. Moving forward, the sorption capacity of biochar for anionic PFAS can be optimized by tailoring the pore size of the biochar, enhancing the presence of positively charged functional groups on biochar surfaces, and augmenting biochar's hydrophobic characteristics. In practical remediation efforts, it is crucial to account for the influence of ionic strength and DOM across different media. Furthermore, when employing biochar for soil remediation, factors such as soil texture, TOC content, and the optimal dosage of biochar must be meticulously considered to ensure effective immobilization and remediation outcomes. The potential for biochar aging in soil and the associated microbial activities that could lead to the desorption of PFAS immobilized by biochar are also considerations that warrant attention.

The traits of certain plants that take up short-chain PFAS may enable the eventual remediation of contaminated soils. These challenging-to-remove PFAS are first accumulated through phytoremediation and subsequently transformed into biochar via pyrolysis of the contaminated plant biomass. This biochar can then be deployed for the immobilization of long-chain PFAS. Analogously, biosolids biochar, derived from the pyrolysis of PFAS-laden biosolids, can be repurposed within the same biosolids treatment process to treat contaminated wastewater, thus enhancing the circular utility of biochar applications.

Given the current state of knowledge regarding the use of biochar for remediating PFAS-contaminated soils and waters, we propose the following future research priorities:

- The adsorption rate of short-chain PFAS may be comparatively lower than that of long-chain PFAS due to the weaker hydrophobic interaction and limited presence of positively charged surface functional groups. Consequently, the removal of short-chain PFAS poses greater challenges in practical applications, necessitating the development of modified and/or compound biochars.
- Although modified biochar presents a promising avenue for future development, current research is predominantly centered around laboratory-based studies. To assess its practical applicability, conducting field experiments with modified biochar is essential.
- Further field applications are required to validate the effectiveness of multiple biochars derived from diverse feedstock materials in actual soil, sediment, water, and wastewater treatment scenarios.
- Environmental field assessments are essential to investigating potential leaching following remediation, assessing soil bioavailability and potential alterations of microbial communities, and monitoring plant growth and toxicity. These investigations are crucial for determining the efficacy of biochar for on-site PFAS remediation.
- Developing innovative strategies for regenerating biochar once it has reached its adsorption capacity. Technologies like microwave radiation show promise in this context, offering advantages over traditional thermal regeneration methods.
- It is crucial to develop technologies for sustainable management of PFAS-saturated spent biochar and the recovery of residual PFAS from this spent biochar.

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Declaration of competing interest

The authors have no conflicts of interest to disclose, financial or otherwise.

Availability of data and materials

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.174962.

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