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Biochar

REVIEW

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Environmental behavior of per- and polyfluoroalkyl substances (PFASs) and the potential role of biochar for its remediation: a review

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Abstract

Per- and polyfluoroalkyl substances (PFASs), commonly known as "forever chemicals", are persistent organic pollutants that are widely distributed in the environment. Due to their toxicity and resistance to degradation, PFASs are classified as emerging contaminants, and increasing attention is being paid to their remediation. Biochar, an environmentally friendly and cost-effective adsorbent, shows potential for remediating PFASs contamination. The application of biochar for PFASs remediation has garnered growing interest. Compared to other adsorbents, biochar is more economical and the raw materials for its preparation are more readily available. However, there is currently no comprehensive review summarizing the effects of biochar on the environmental behavior of PFASs. This review aims to fill that gap by providing an in-depth discussion and synthesis of the existing literature in this area. It focuses on the environmental behavior of PFASs, specifically addressing the adsorption mechanisms and factors influencing the effectiveness of biochar in PFASs remediation. A proposed mechanism by which biochar photodegrades PFASs through the generation of free radicals, in addition to conventional adsorption mechanisms (such as pore filling, hydrogen bonding, hydrophobic interactions, and electrostatic interactions), is explored. Furthermore, this review discusses the ability of biochar to reduce the likelihood of PFASs entering the food chain through water and soil and evaluates the feasibility and limitations of using biochar for PFASs removal. Finally, we identify future research directions to support the safe and effective use of biochar for PFASs remediation, so as to promote the advancement of green remediation technologies.

Highlights

- Migration in the environment and toxicity to organisms of PFASs have been elucidated.
- Possible mechanisms for the degradation of PFASs by biochar were elaborated.
- Pathways of biochar to reduce PFASs into the food chain through water and soil were summarized.
- Feasibility and limitations of biochar for PFASs removal were delineated.

Keywords Emerging pollutants, Environmental behavior, Environmental risk, Biosensor, Adsorption mechanisms

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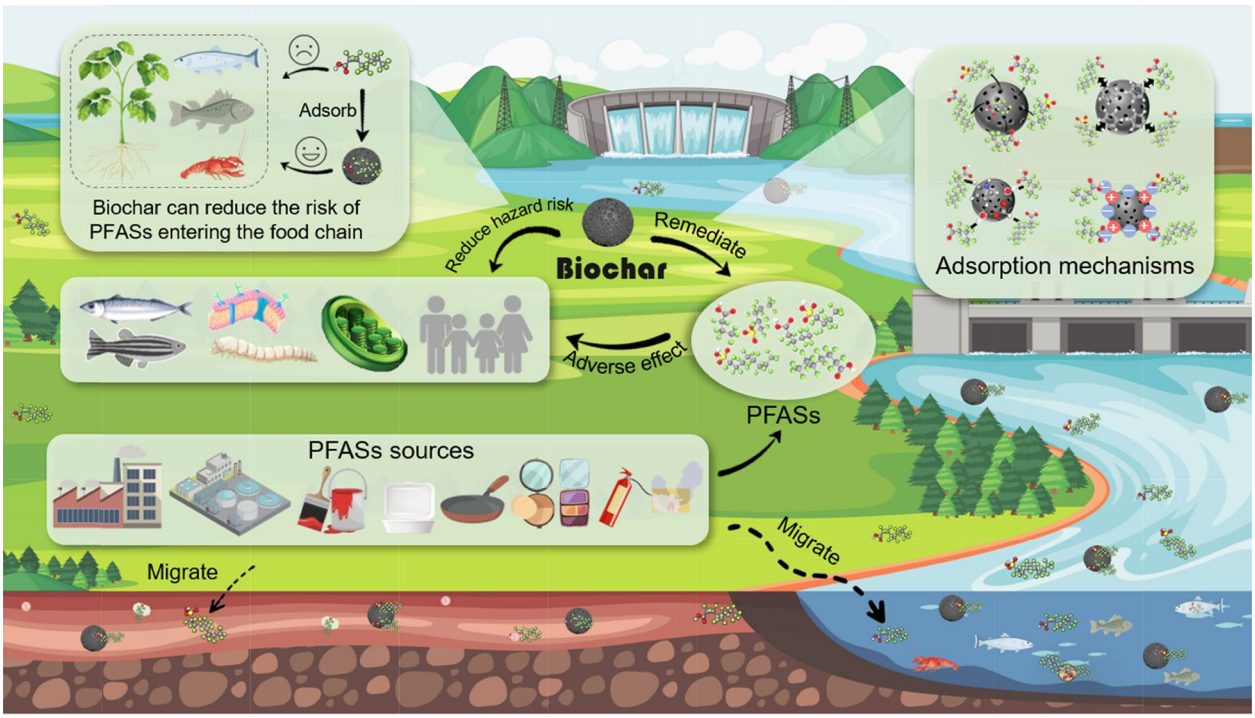
Graphic Abstract

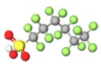
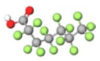
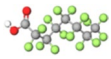
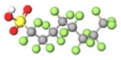
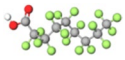
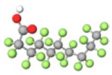


1 Introduction

Since the 1940s, per- and polyfluoroalkyl substances (PFASs) have been widely manufactured and used in numerous industrial and commercial items like paints, furniture, textiles, packaging, cosmetics, and firefighting supplies (Gobelius et al. 2023; ITRC 2020). These compounds have also been discovered in dairy products and even in infant formula (Schwartz-Narbonne et al. 2023). PFASs are categorized into long-chain ($\geq$8 carbon atoms) and short-chain ($\leq$7 carbon atoms) compounds based on their carbon chain length (USEPA 2009). Depending on the functional groups, these compounds can be divided into anionic, cationic or zwitterionic PFASs (Backe et al. 2013). Notably, most newly identified PFASs are zwitterionic or cationic surfactants, which contain functional groups such as sulfonyl, thioether, amine, quaternary ammonium, carboxylate, sulfonate, amine oxide, and betaine (Place and Field 2012; Backe et al. 2013). Perfluoroalkyl carboxylic acids (PFCAs, containing a carboxylic acid group) and perfluoroalkyl sulfonic acids (PFSAs, containing a sulfonic acid group) are the most prevalent PFASs. Table 1 provides an overview of various PFASs (Post 2021). Common examples include perfluorobutanoic acid (PFBA), perfluorobutane sulfonate (PFBS), perfluoropentanoic acid (PFPeA), perfluoropentane sulfonate (PFPeS), perfluorohexanoic acid (PFHxA), and perfluorohexane sulfonate (PFHxS). These compounds are classified as persistent organic pollutants due to the replacement of hydrogen atoms by fluorine atoms in the carbon chain, creating a strong carbon–fluorine (C-F) bond that resists degradation (Xu et al. 2022).

With both hydrophobic C-F bonds (bond energy approximately 485.5 kJ mol^{-1}) and hydrophilic functional groups such as carboxylates and sulfonates, PFASs exhibit low surface tension due to weak intermolecular forces within their structure, thereby reducing the surface tension of the target solution (Arvaniti and Stasinakis 2015). This property has contributed to their widespread use. Eight PFASs (PFBA, PFPeA, PFHxA, Perfluoroheptanoic acid (PFHpA), Perfluorooctanoic acid (PFOA), Perfluorononanoic acid (PFNA), PFBS, Perfluorooctane sulfonate (PFOS)) have been detected globally, with the highest prevalence in Europe and Asia (Fig. 1). This widespread detection has led to increased regulation and research in these regions. For instance, PFOS has been regulated by Canada, the United States,

Table 1 Basic information of common Per- and polyfluoroalkyl substances (PFASs)

Full Name in English	Abbreviation	CAS#	Molecular formula	Structure
Perfluorobutanoic acid	PFBA	375-22-4	$C_4HF_7O_2$	
Perfluorobutane sulfonate	PFBS	375-73-5	$C_4HF_9O_3S$	
Perfluoropentanoic acid	PFPeA	2706-90-3	$C_5HF_9O_2$	
Perfluoropentane sulfonate	PFPeS	2706-91-4	$C_5HF_{11}O_3S$	
Perfluorohexanoic acid	PFHxA	307-24-4	$C_6HF_{11}O_2$	
Perfluorohexane sulfonate	PFHxS	355-46-4	$C_6HF_{13}O_3S$	
Perfluoroheptanoic acid	PFHpA	375-85-9	$C_7HF_{13}O_2$	
Perfluoroheptane sulfonate	PFHpS	375-92-8	$C_7HF_{15}O_3S$	
Perfluorooctanoic acid	PFOA	335-67-1	$C_8HF_{15}O_2$	
Perfluorooctane sulfonate	PFOS	1763-23-1	$C_8HF_{17}O_3S$	
Perfluorononanoic acid	PFNA	375-95-1	$C_9HF_{17}O_2$	
Perfluorodecanoic acid	PFDA	335-76-2	$C_{10}HF_{19}O_2$	

Note: Gray represents carbon atoms, green represents fluorine atoms, red represents oxygen atoms, yellow represents sulfur atoms, and white represents hydrogen atoms. Refer to Post (Post 2021) for tabular information

and the European Union since 2005 (Ghisi et al. 2019; Mudumbi et al. 2017). In March 2014, China's Ministry of Environmental Protection, along with 12 other ministries and commissions, issued Announcement No. 21, prohibiting the production, circulation, use, import, and export of PFOS and perfluorooctane sulfonyl fluoride (PFOSF), with certain specific exemptions. The toxicity of PFASs to plants, animals, and humans has been widely reported, leading to growing concern (Sheng et al. 2018). In 2016, the U.S. Environmental Protection Agency (EPA) established a lifetime health advisory level (HAL) of 70 ng L^{-1} for both PFOA and PFOS in drinking water (USEPA 2016). In June 2022, the U.S. EPA further tightened the HAL for PFOS and PFOA to 0.004 ng L^{-1} and 0.02 ng L^{-1}, respectively (USEPA 2022).

Given the widespread dispersion of PFASs in the environment and their contribution to ongoing pollution, managing PFASs contamination has garnered increasing attention. Current technologies for PFASs remediation include adsorption, ion exchange, membrane filtration, advanced oxidation, biotransformation, and novel functional materials (Zhang et al. 2024a). Among these, adsorption is a frequently employed method for removing PFASs pollution (Lei et al. 2023). Biochar, a carbon-rich material produced by the incomplete combustion of biomass under low-oxygen or oxygen-free conditions at high temperatures (Tomczyk et al. 2020; Sun et al. 2024), has emerged as a promising adsorbent. Biochar is cost-effective and promotes environmental sustainability, as it can be produced from organic waste or agricultural and forestry residues (Li et al. 2024; Pradhan et al. 2024). Additionally, its use can reduce greenhouse gas emissions, contributing to efforts toward "carbon neutrality" (Zhou et al. 2024a, 2024b; Xie et al. 2024). Biochar has demonstrated effectiveness in remediating environmental pollution caused by both heavy metals and organic contaminants (Bogusz et al. 2017; He et al. 2018). Recent studies have shown promising results in using biochar to remediate PFASs contamination (Zhang et al. 2023b; Hassan et al. 2020, 2022; Yea et al. 2022). As a result, biochar has gained increasing attention as an eco-friendly

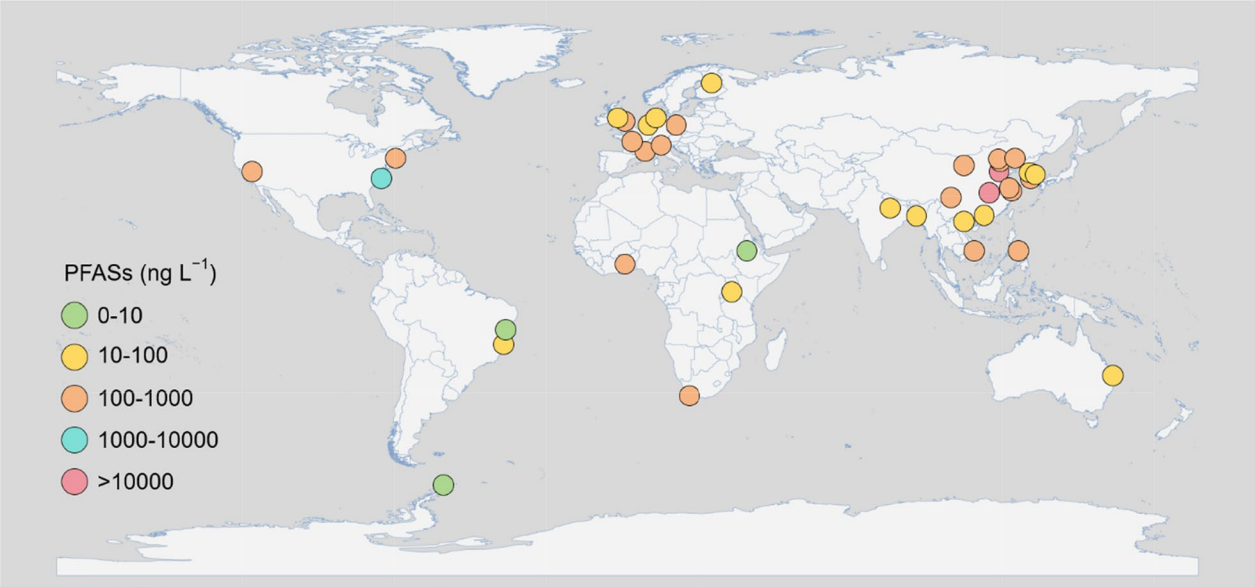


Fig. 1 Global occurrences of PFASs in surface water systems from 2011 to 2020. Each point represents data from a study of a particular area. The concentration range at each point is the sum of the eight PFASs, including Perfluorobutanoic acid, Perfluoropentanoic acid, Perfluorohexanoic acid, Perfluoroheptanoic acid, Perfluorooctanoic acid, Perfluorononanoic acid, Perfluorobutane sulfonate, and Perfluorooctane sulfonate. Data were generated from (Podder et al. 2021)

adsorbent for PFASs remediation (Inyang and Dickenson 2017; Nguyen et al. 2023).

As the use of biochar for PFASs remediation is a relatively new research direction, there are currently no articles that systematically evaluate the environmental behavior of PFASs or the effects, mechanisms, and influencing factors of biochar in PFASs remediation. The primary objective of this review is to focus on anionic PFASs and to provide a comprehensive overview of (1) the migration of PFASs in the environment and their toxic effects on organisms, (2) the metrological studies, adsorption mechanisms, and factors influencing the use of biochar for PFAS remediation, and (3) the pathways through which biochar can reduce the entry of PFASs into the food chain. This review aims to offer a theoretical foundation for utilizing biochar to remediate PFASs contamination.

2 Environmental behavior of PFASs

2.1 Migration of PFASs in the environment

PFASs can enter the soil through point sources (e.g., manufacturing and processing sites, use of aqueous film-forming foams, wastewater treatment plants, landfills) or diffusion sources (e.g., atmospheric deposition, runoff, use of flonicamid) (Kim et al. 2014), as shown in Fig. 2. The products containing PFASs, including E-waste and factory-produced waste, can result in the introduction of PFASs into the environment, especially aqueous film-forming foams, which can contaminate soil and groundwater on an ongoing basis (Baduel et al. 2017; Lesmeister et al. 2021). PFASs can migrate among soil, water, and air. It has been reported that volatilization, diffusion, leaching, and runoff are the main processes for PFASs in soil to move into the atmosphere, surface water, and groundwater (Armitage et al. 2009a; Xiao et al. 2015). PFASs can be found in both gas (Armitage et al. 2009b; Thackray et al. 2020) and particle phases (Johansson et al. 2019; MacInnis et al. 2019) in the atmosphere, resulting in its depositing in isolated locations distant from any local point sources (Faust 2023), such as the Antarctic (Garnett et al. 2022), the Arctic (MacInnis et al. 2019) and the Tibetan Plateau (Chen et al. 2023). Casas et al. (2020) simultaneously measured PFASs in large quantities of seawater, sea surface microlayers, sea mist aerosols at the site, and found that the concentration of PFASs in wave spray aerosols was 522 to 4690 times higher than in seawater. A study has also shown that aquatic organisms directly ingest PFASs in water and enter the food chain cycle (Zhu et al. 2021). An important route of exposure to contaminants for individuals and ecosystems is their dietary intake, which encompasses consuming polluted drinking water and contaminated food items like seafood and other products (Lesmeister et al. 2021; Post et al. 2017; Sunderland et al. 2019). In this paper, we focus on the remediation of PFASs in water and soil. An in-depth understanding of the environmental behavior of PFASs is important for effective management strategies.

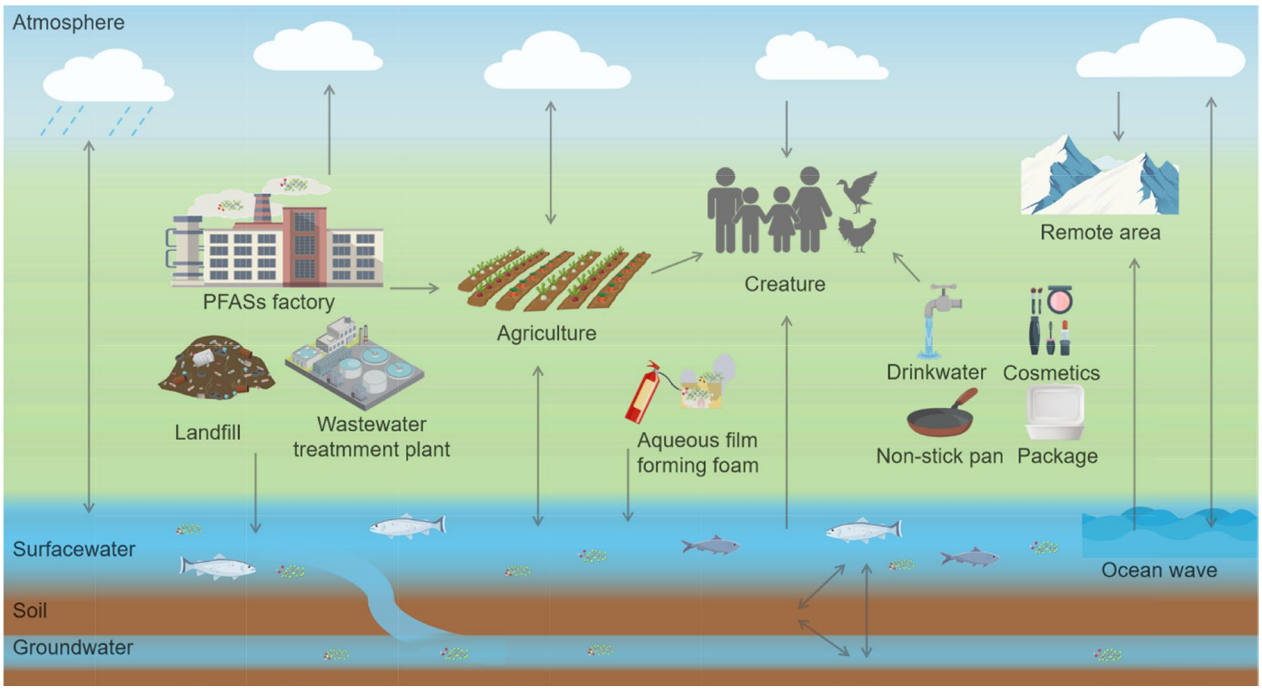


Fig. 2 Migration of PFASs in different environmental medias (Designed by Freepik)

2.2 The toxic effect of PFASs

2.2.1 Toxicity of single PFASs to organisms

PFASs have various toxic effects on humans when they reach a certain threshold (Pasecnaja et al. 2022), including possible carcinogenic, reproductive, endocrine, neurotoxic, dyslipidemia, and immunotoxic effects (Bonato et al. 2020; Fenton et al. 2021; Fig. 3a). For example, PFOA can corrode the skin even at low concentrations because of its strong acid (Mousavi et al. 2021), and it could also hinder the organisms' resistance to external poisons and the adaptive immune system (Pecquet et al. 2020). The exposure of PFOS and PFOA can also lead to splenic

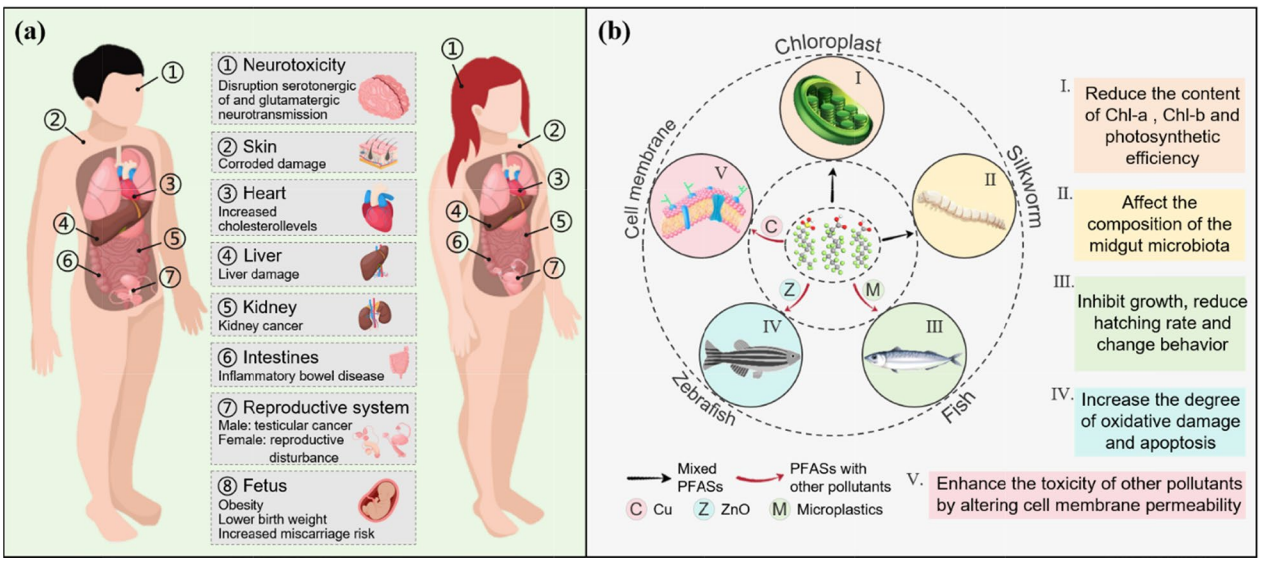


Fig. 3 Effects of exposure to PFASs on organisms (Designed by Freepik). **a** Exposure to single PFAS, and **b** Exposure to multiple PFASs or the coexistence of PFASs with other contaminants

atrophy (Wang et al. 2014, 2011). PFASs, with their strong protein-binding capabilities, allow them to accumulate in the liver and muscle, which are rich in protein and fat. Compared with long-chain PFASs such as PFOA and PFOS, short-chain PFASs like PFBS and PFHpA have higher placental transfer efficiency (Cai et al. 2020), and they can promote disturbances in gonadal hormone and free androgen levels, and have reproductive toxicity (Nian et al. 2020). Moreover, PFOA and PFOS can bind to estrogen and increase the secretion of proteins by liver cells. PFOA induces oocyte development in the testes of freshwater rare minnow (*Gobiocypris rarus*) males and degeneration of the ovaries in females (Wei et al. 2007), resulting in smaller body size, reduced egg production, and lower embryo survival in females (Jantzen et al. 2017). PFOS caused a significant reduction in blood steroid hormones and increased time to first spawning in the black-headed dace (*Pimephales promelas*) (Oakes et al. 2004). In addition to this, PFASs in pregnant women can be passed to the fetus via the bloodstream across the placental barrier during pregnancy, as well as to the infant via breast milk during breastfeeding (Hu and Dai 2013), which would increase children's exposure to PFASs as the duration of breastfeeding increases (Gyllenhammar et al. 2018; VanNoy et al. 2018). PFASs adversely affect the growth of plants (Adu et al. 2023). These compounds can damage the cell walls of plants, altering their ability to cope with harsh environments. In addition, they can cause damage to mitochondria and affect the photosynthetic efficiency of plants (Adu et al. 2023).

2.2.2 Toxicity of multiple PFASs to organisms

In the natural environment, PFASs tend to be two or more co-existent, and may also be in combination with other contaminants. The potential hazards of PFASs to living organisms are shown in Fig. 3b; it may be magnified when PFASs are co-existent in the natural environment, resulting in additive, synergistic (Liu et al. 2022), and antagonistic effects (Zhu et al. 2021). The properties and amounts of PFASs may be responsible for these consequences. Liu et al. (2022) found that compared with the single PFASs exposure at the same concentration, the contents of chlorophyll a and b in algae (*Chlorella pyrenoidosa*) were significantly reduced after 12 days of mixed PFASs exposure, thereby reducing the photosynthetic efficiency. The combined toxic effects of PFOA and PFNA have been reported to have an additive effect on the growth of *Dunaliella salina* but a synergistic effect on *Phaeodactylum triconutum* (Zhou et al. 2016). Besides, it has been found that fish transport and fatty acid biosynthesis-related genes were negatively expressed in response to PFASs (Wei et al. 2009). Liu et al. (2024) found that exposure to mixed PFASs affected microbiota composition, transcription profile, metabolic pathways and biological processes related to the digestive system in the midgut of silkworms, ultimately hindering the normal growth of the silkworms.

2.2.3 Toxicity of PFASs in combination with other contaminants to organisms

When PFASs coexist with other pollutants in the environment, they can also have a combined toxic effect on organisms, as shown in Fig. 3b. The combined toxicity of PFCAs and Cu manifests itself as a synergistic effect, enhancing the toxic effects of other toxic substances by altering cell membrane permeability (Sun 2011). Zebrafish embryos exposed to PFOS and Nano-ZnO showed significantly more oxidative damage and apoptosis than individual exposures (Du et al. 2015a). Studies have also demonstrated that PFASs' coexistence with microplastics can adversely affect fish (Dai et al. 2022; Parashar et al. 2023). These toxic effects lead to a high environmental risk for PFASs. As a result, the process of removing PFASs from the environment has received more attention. As mentioned above, biochar is considered an environmentally beneficial material for the remediation of PFASs pollution in the environment, and the progress of this research will be discussed in detail below.

3 Using biochar for the treatment of PFASs pollution

Extensive research has been conducted on using biochar to remove organic pollutants and heavy metals from the environment. The number of research papers in this field has continued to rise in recent years. As an emerging pollutant, studies on using biochar to clean up PFASs pollution are still in their infancy.

3.1 Bibliometrics of biochar and PFASs

The rational use of bibliometrics can review the research process and reflect the research hotspots and research directions in specific fields (Zheng et al. 2022). Data presented in this review were generated from Web of Science. To acquire accurate records, specific parameters were set for the search query: the TS (Topic, which consists of titles, abstracts, and keywords) = ("PFASs*" OR "Perfluorinated compounds*" OR "Per- and polyfluoroalkyl substance*"). Additionally, "Biochar*" was added in the TS to analyze the research direction between PFASs and biochar.

By limiting the time frame to 2014–2023 and the article type (here we only focus on data from articles), a total of 20,586 keywords were retrieved from 7610 literature. A network map was constructed for 252 keywords with a frequency of 50 times or more. As shown in Fig. 4a, research on PFASs has focused mainly on

its environmental and organismal hazards and remediation, with PFOS and PFOA receiving the most attention. The remediation strategies of these compounds are mainly divided into adsorption and degradation, with the former method mostly using carbonaceous materials. Further, we counted the number of publications and citations on PFASs removal in the past decade, as shown in Fig. 4b. From 2014 to 2023, the number of publications and citations of PFASs has shown an increasing trend, and the number of papers published in 2023 (470) is nearly ten times of that in 2014 (51). Especially in the past five years, more scholars have paid attention to the removal of PFASs in the environment. Despite this, there is a scarcity of articles that explore the combination of PFASs with biochar. From 2014 to 2023, 79 articles were identified that explored the relationship between biochar and PFASs. As shown in Fig. 4c, the main research focuses on water and soil, especially water. The biomass source, biochar adsorption mechanism on PFASs, and adsorption effect are the hot spots of research, and more studies focus on enhancing adsorption capacity. This review counts the number of articles published on "Biochar + Pollutants" and "Biochar + PFASs" in the past 10 years, demonstrating a rising trend in both areas (Fig. 4d). However, the number of papers published on "Biochar + PFASs" is limited compared to those on "Biochar + Pollutions", indicating that this area has not received sufficient attention. With research in this domain commencing around 2016, it is evident that this emerging field requires additional investigation.

3.2 Mechanisms of biochar for remediation of PFASs pollution

3.2.1 Adsorption mechanisms

As shown in Fig. 5, the removal of PFASs by biochar is mainly through adsorption. The adsorption process is barely affected by van der Waals interactions and π-π bonds since PFASs lack benzene ring structure and have

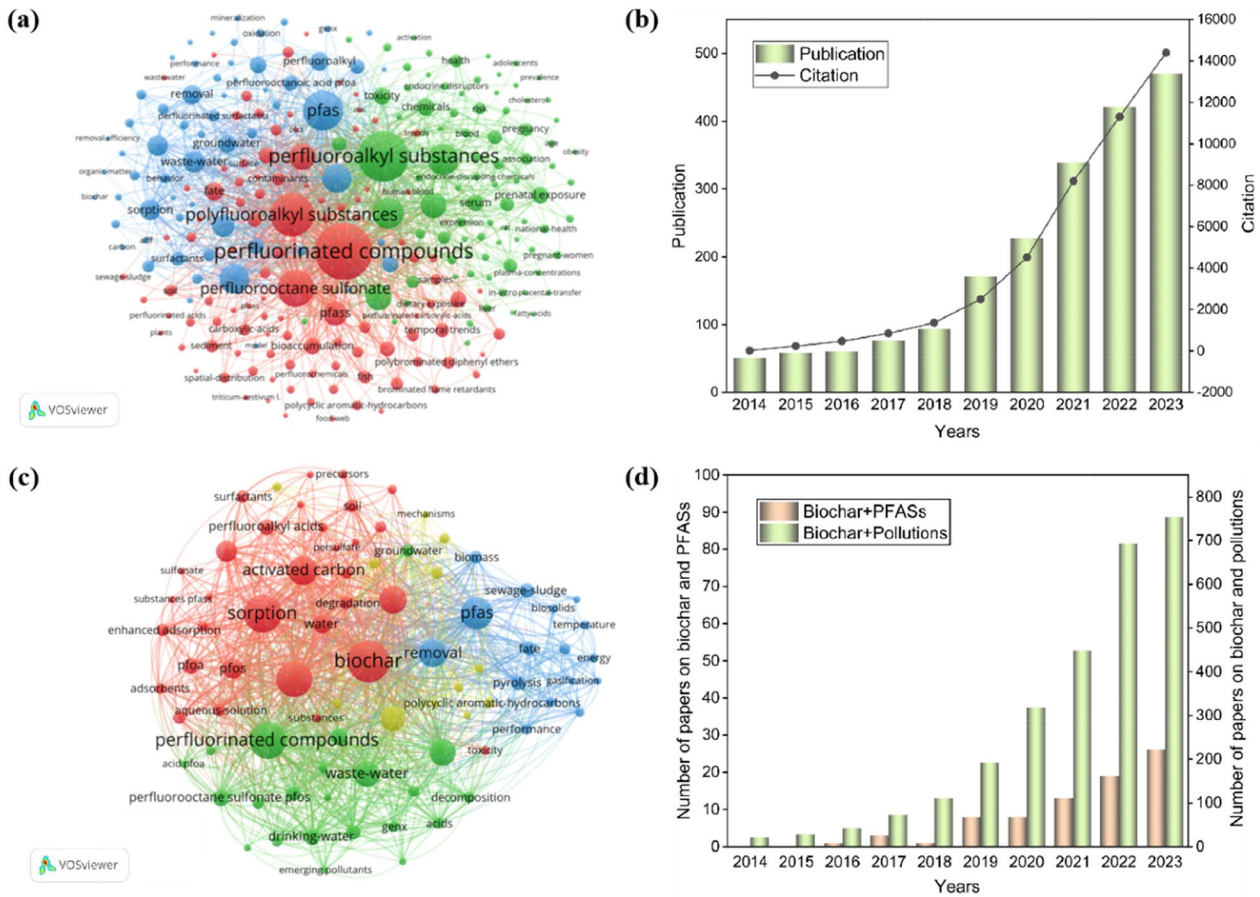


Fig. 4 A graphical representation of the bibliometric visualization using biochar and PFASs as keywords. **a** PFASs, **b** the number of published articles and citations of PFASs, **c** Biochar and PFASs, and **d** the number of papers published on "Biochar + Pollutants" and "Biochar + PFASs" in the past 10 years

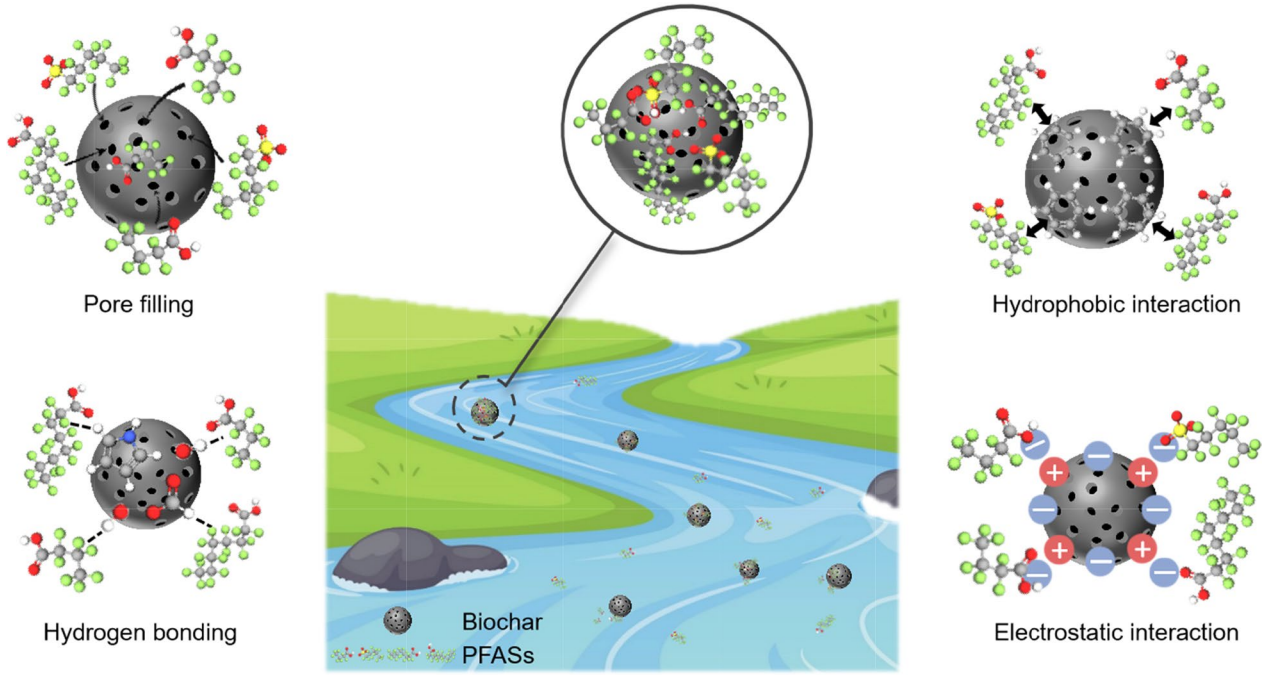


Fig. 5 Adsorption mechanisms of PFASs by biochar. The background of this figure is designed by Freepik

poor polarizability (Zhou et al. 2021). In general, combining several adsorption mechanisms leads to the adsorption process (Chen et al. 2008; Inyang and Dickenson 2015), and hydrophobic and electrostatic interactions are the most critical adsorption mechanisms for biochar to remove PFASs (Wu et al. 2022). PFOS molecules are much smaller than the mesopores of biochar; therefore, pore filling is one of the adsorption mechanisms for biochar to remediate PFOS contamination (Liu et al. 2023). Krebsbach et al. (2023) proposed that a pore size range of ~ 7.5–11 nm is ideal for biochar to adsorb PFOS in water, which can effectively adsorb PFOS through the "trapping" mechanism and can protect the adsorbed PFOS molecules from water turbulence and desorption. With the increase of biochar pore volume, this "trapping" adsorption effect will be enhanced, providing more space for PFOS molecules to be adsorbed within the pore structure (the ideal pore/pore volume ratio is ~ 50–150 nm cm^{-3} g^{-1}).

The functional groups of biochar can interact, and some functional groups can also form hydrogen bonds with PFASs (Vijay et al. 2008), making them have strong bond energy and difficult to separate (Cheng et al. 2021). Oxygen-containing functional groups (OFGs), such as carboxyl and hydroxyl groups, are present on the adsorbent surface, and PFASs can form hydrogen bonds with OFGs on biochar (Lyu et al. 2022). Therefore, biochar with a large number of OFGs on the surface, such as hydroxyl, carbonyl, and carboxyl groups (Chen et al. 2019) can bound PFOS through the formation of hydrogen bonds, subsequently reducing its environmental risk. In addition, if pyrrole N is present in biochar, it can form weak hydrogen bonds with PFASs (Cheng et al. 2022). Zhang et al. (2023b) showed that the increase of pyrrole N content enhanced the hydrogen bonding of hydrochloric acid-modified sludge (H-SL) biochar to PFASs during the adsorption of PFOS and PFOA from water, thereby promoting the adsorption of PFASs by biochar.

Hydrophobic interaction is the repulsive force between water molecules and non-polar groups (like C–H) (Xie et al. 2020). Hydrophobic interaction is often prominent in biochar obtained from high-temperature pyrolysis due to the high aromaticity and low polarity of the resultant biochar (Hassan et al. 2022). With the increase in temperature, elements such as N, O, and H in biomass are consumed, and amorphous C is gradually converted into aromatic C, causing the polarity to decrease gradually and the aromaticity to grow gradually (Min et al. 2021). The hydrophobic interaction is an important mechanism in the adsorption of PFASs by biochar, with varying effects under different conditions. Hassan et al. (2020) showed that both hydrophobic and electrostatic interactions controlled the adsorption of PFOS by red mud-modified sawdust biochar in wastewater, the former of which plays a major role. This is because the abundant protonation metal functional groups in red

mud and the catalytic degradation and conversion of cellulose and hemicellulose make biochar have a more graphitic C structure. In contrast, the aromatic structure can enhance the adsorption of PFOS through non-ionic interactions. Hydrophobic interaction has been demonstrated to play a key role in the adsorption of PFASs by adsorbents at higher ion concentrations (Park et al. 2020a, b). Liu et al. (2021) synthesized reed straw-derived biochar to study the removal effect of short-chain perfluoroalkyl acids (PFAAs) at environmentally relevant concentrations (e.g., 1 μg L^{-1}), and found that the highly hydrophobic surface of biochar was associated with its rapid adsorption of short-chain PFAAs.

Electrostatic interaction is an important factor in controlling the adsorption and transport of PFASs in environmental media (Zhang et al. 2023b). Hassan et al. (2022) used magnetic biochar (MBC) synthesized from hematite nanoparticles modified bagasse to adsorb PFOS from water. They found that the distribution of fluorine was closely related to the C, O, calcium, aluminum, and silicon content in MBC. Due to the lack of hydrophobic interaction, they concluded that PFOS is mainly adsorbed by electrostatic interaction with magnetically modified biochar (Hassan et al. 2022). It has been clarified that low-temperature pyrolytic biochar adsorbs PFOS through electrostatic interaction, while high-temperature pyrolytic biochar, graphene, and C nanotubes primarily rely on hydrophobic interaction for adsorption (Deng et al. 2015). This may be due to the increase in aromatic functional groups on the biochar surface with the increase in pyrolysis temperature, which enhances the hydrophobic interaction of biochar adsorbed PFASs (Calisto et al. 2014).

3.2.2 Degradation mechanisms

Notably, the remediation of PFASs pollution by biochar is not just through adsorption. Although PFASs are very difficult to degrade due to the high stability of C-F bonds (Xu et al. 2022), Zhang et al. (2023a) produced iron-rich sludge biochar from iron-rich dewatered sludge at 800℃ and effectively biodegraded PFOA in contaminated soil and groundwater by integrating the biochar and vitamin B_{12} into microbial systems, as shown in Fig. 6a. Vitamin B_{12} greatly contributes to the evolution of *Spromusa* (Stupperich and Eisinger 1989), which can be dehalogenated through co-metabolic reduction to break C−F bonds, and biochar promotes the biodegradation of PFOA by providing reaction sites and mediating electron transfer between species (Im et al. 2019).

Many OFGs exist on biochar surfaces, such as quinone, hydroquinone, and redox-active groups with condensed aromatic structures, which can promote electron migration and catalysis (Klüpfel et al. 2014). Biochar can generate free radicals such as $HO\cdot$,$\cdot O_2^-$ under UV conditions, which facilitates the degradation of pollutants (Fang et al. 2017). Under UV conditions, pine needles

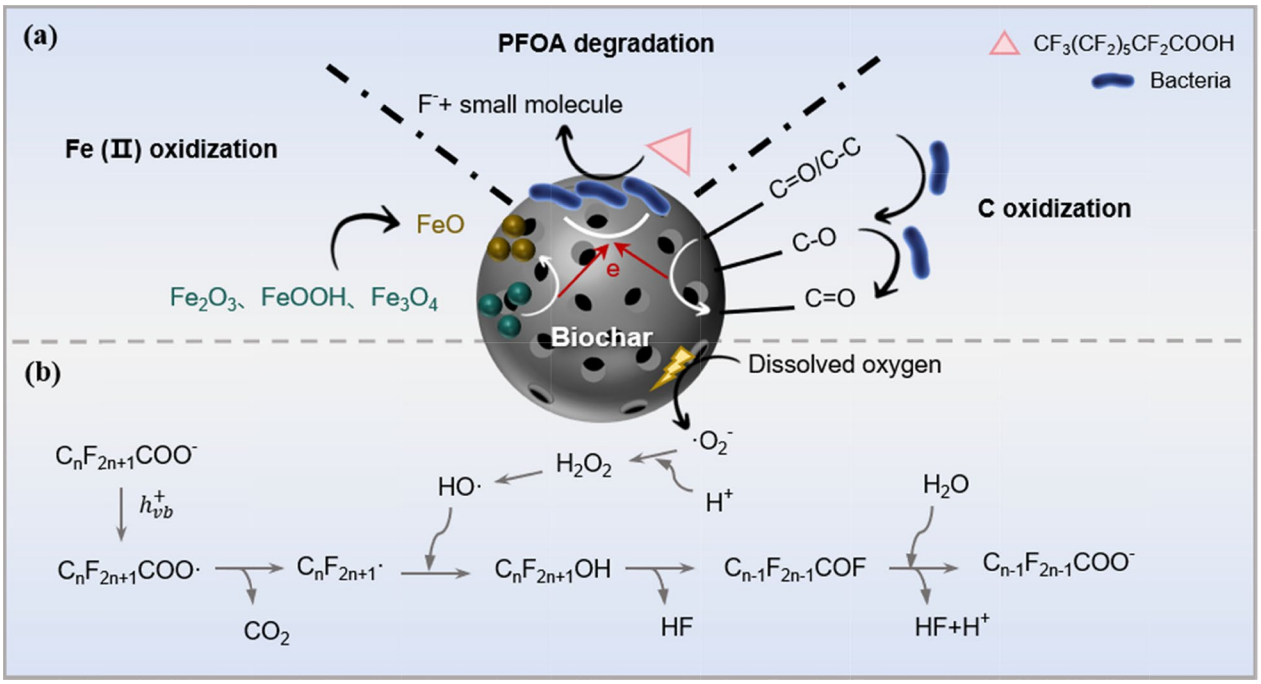


Fig. 6 Possible degradation mechanisms of PFASs by biochar. **a** Integrated system degrade PFOA (Zhang et al. 2023a), and **b** Biochar generates free radicals to degrade PFCAs (Duan et al. 2020; Fang et al. 2017)

and wheat-derived biochar produce H^+ HO and $\cdot O_2^-$ that are involved in the degradation of diethyl phthalate (DEP) (Fang et al. 2017). Under light conditions, OFGs enriched in biochar can transfer electrons to dissolved oxygen to form superoxide radicals ($\cdot O_2^-$), and $\cdot O_2^-$ reacts with H^+ to form hydrogen peroxide (H_2O_2), which is further converted to HO·. In the case of PFCAs, the general degradation mechanism can be described by Eqs. 1–5 (Duan et al. 2020; Fig. 6b). PFCAs first generate unstable $C_nF_{2n+1}COO\cdot$ radicals in the presence of photo-induced holes (h_{vb}^+) (Eq. 1) which are then decarboxylated to generate perfluoroalkyl radical $C_nF_{2n+1}\cdot$(Eq. 2). In the liquid-phase photocatalytic process, HO· is produced by water splitting under UV or visible light irradiation, which reacts with $C_nF_{2n+1}\cdot$ to produce $C_nF_{2n+1}OH$ (Eq. 3) (Liu et al. 2020a). Elimination of HF from $C_nF_{2n+1}OH$ produces $C_{n-1}F_{2n-1}COF$ (Eq. 4) which undergoes hydrolysis to give short-chain PFCA (e.g., $C_{n-1}F_{2n-1}COOH$) (Eq. 5).

The degradation of $C_{n-1}F_{2n-1}COOH$ can be continued in the same way. The role of h_{vb}^+ is important in the degradation process, which can be generated by the addition of the semiconductor catalyst TiO_2 under UV irradiation (Li et al. 2012). Kim and Kan (2016) achieved sulfamethoxazole (SMX) degradation with TiO_2/BC-based catalyst and the semiconductor catalyst TiO_2 under UV irradiation produces photo-induced holes. HO· can also be produced by biochar. Therefore, we believe that, theoretically, biochar degraded PFASs in the catalytic system, but further studies are needed to determine whether it can work in practice.

$$C_nF_{2n+1}COO^- + h_{vb}^+ \rightarrow C_nF_{2n+1}COO\cdot \quad (1)$$

$$C_nF_{2n+1}COO\cdot \rightarrow C_nF_{2n+1}\cdot + CO_2 \quad (2)$$

$$C_nF_{2n+1}\cdot + HO\cdot \rightarrow C_nF_{2n+1}OH \quad (3)$$

$$C_nF_{2n+1}OH \rightarrow C_{n-1}F_{2n-1}COF + HF \quad (4)$$

$$C_{n-1}F_{2n-1}COF + H_2O \rightarrow C_{n-1}F_{2n-1}COO^- + HF + H^+ \quad (5)$$

3.3 Factors affect the adsorption of PFASs by biochar

3.3.1 Biochar properties

Biochar is derived from carbonized biomass, and the varying properties of the biomass lead to variations in the adsorption capacity of the biochar (Wu et al. 2021). Different raw materials have considerably different elemental compositions (C, H, O, N, and S) and structural compositions (cellulose, hemicellulose, and lignin) (Weber and Quicker 2018). For example, the N content of sludge biochar is high, and the atoms in biochar combine with heterocycles to form pyrrole N, which can form weak hydrogen bonds with compounds and enhance the adsorption capacity of biochar for PFASs (Zhang et al. 2023b). Generally, the O content of C-based adsorbents can be considered as an indicator of their hydrophobicity, which can affect their hydrophobic interaction (Thue et al. 2021).

Additionally, the adsorption of PFASs by biochar influences their pore size, volume, and functional groups (Saeidi et al. 2020). The volatilization of volatile substances from biomass makes biochar have a porous structure (Weber and Quicker 2018), which in turn affects the adsorption of biochar on pollutants (Wu et al. 2021). Calisto et al. (2014) found that biochar pyrolyzed at high temperatures exhibited an increased aromatic structure, lower apparent density, higher specific surface area, larger total pore volume, and more micropores, potentially enhancing PFASs adsorption through pore filling. As the pyrolysis temperature rises, the contents of C–O bonds, C–H bonds, O–H bonds, and acidic groups such as hydroxyl and carboxyl groups in biochar decreased, while the basic groups increased (Zhang et al. 2022b). This shift is attributed to the increase in the content of minerals and carbonates and the decrease in acidic volatile products as the biomass is being cracked (Parthasarathy et al. 2022). Consequently, this reduces the polarity and hydrophilicity of biochar, enhances its aromatization, stabilizes its structure, and ultimately improves its effectiveness in adsorbing and removing PFASs (Zhao et al. 2020).

3.3.2 Environmental factors

Studies have shown that environmental pH changes the behavior of functional groups on the surface of biochar and therefore affects the efficiency of biochar in adsorbing pollutants (Abbas et al. 2018; Chen et al. 2022). As shown in Fig. 7, when the pH of the solution < pH_{pzc} (zero charge point), the surface functional groups of biochar are protonated by H^+ and subsequently converted into positively charged functional groups ($COOH^{2+}$/COH^{2+}/OH^{2+}/M-OH^{2+}), facilitating the adsorption of PFOS by biochar through electrostatic interaction and ion exchange reactions (Hassan et al. 2020). Conversely, when the pH of the solution > pH_{pzc}, the surface functional groups are deprotonated and subsequently converted to negatively charged functional groups (COO–/CHO–/OH–/M–O–), enhancing the electrostatic repulsion between the biochar surface and the negatively charged PFOS (Hassan et al. 2020). Significantly, protonation and deprotonation depend not only on the pH_{pzc} of biochar but also on the individual pKa values of

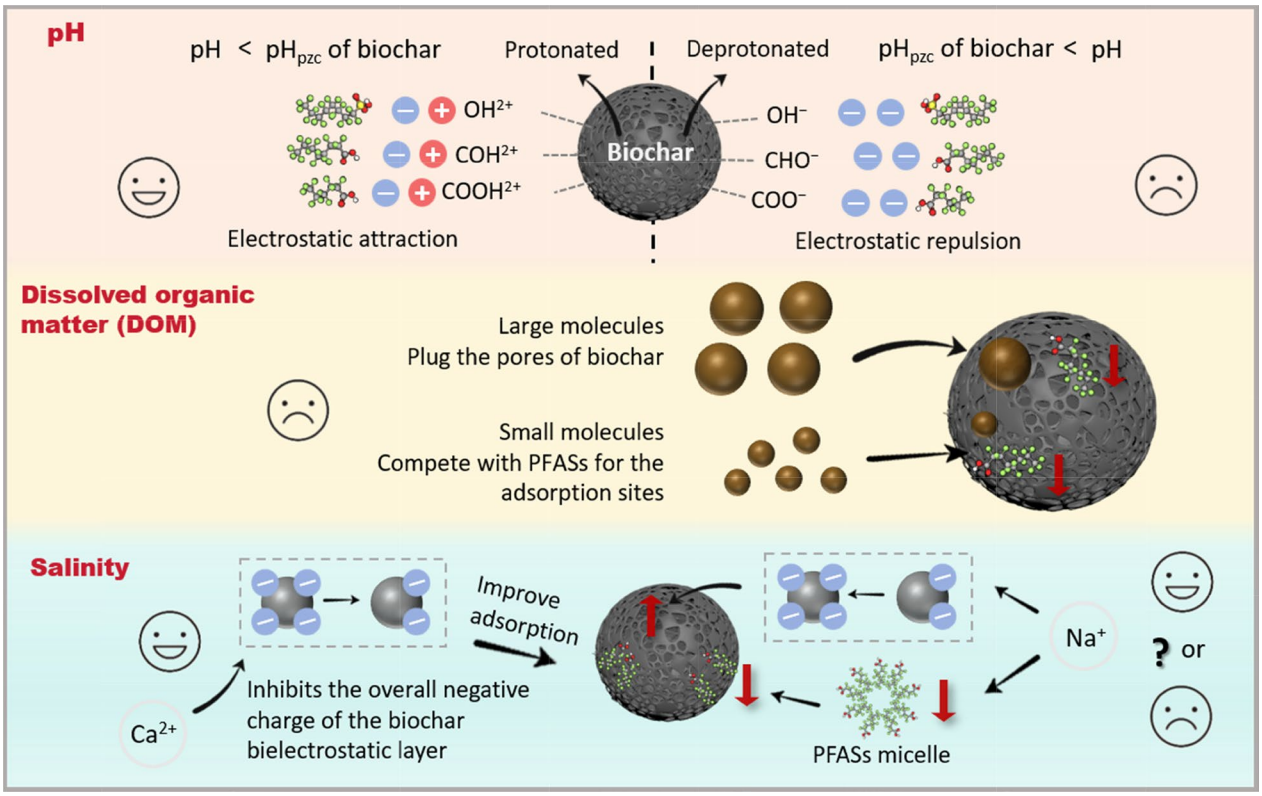


Fig. 7 Effects of environmental conditions on the remediation of PFASs by biochar (Designed by Freepik)

the functional groups on the biochar. PFOS molecules adsorbed on adsorbents through hydrophobic interaction are usually difficult to desorb, and the adsorption effect is not significantly affected by pH. In contrast, the electrostatic interaction between biochar and PFOS molecules is highly dependent on pH (Hassan et al. 2020), which significantly impacts the effectiveness of adsorption of PFAS by biochar.

Dissolved organic matter (DOM) can more significantly impact the adsorption of PFASs by biochar compared to pH (Vo et al. 2022). Research indicates that DOM might prevent PFASs from being adsorbed by biochar (Yu et al. 2012). According to Fig. 7, the pores of biochar are anticipated to be blocked by the massive and intricate supramolecular structure of organic matter, which also occupies some fraction of surface area, thereby reducing the efficiency of biochar adsorption of PFASs (Vo et al. 2022). Smaller humus molecules can compete with PFASs for surface adsorption sites, reducing the adsorption capacity of biochar (Du et al. 2014). Aromatic DOMs have a hydrophobic backbone similar to PFASs, allowing them to compete with adsorption sites. Humic acid (HA) may be negatively charged through deprotonation, enhancing the electrostatic repulsion between the short-chain PFASs and the adsorbent, thereby reducing their removal efficiency (Vo et al. 2022).

The complex effects of salinity on PFOA removal have been reported in different studies, and the results have been inconsistent (Wu et al. 2022). Inorganic ions can enhance or hinder the adsorption of PFASs by biochar through competition, electric double-layer compression, or salting-out effects (Du et al. 2014). For instance, Ca^{2+} promotes the adsorption of PFOA and PFOS through biochar (Tang et al. 2010). It may be attributed to the fact that Ca^{2+} has a charge-shielding effect on biochar and inhibits the overall negative charge of the biochar bielectrostatic layer (Rahman et al. 2022; Taylor et al. 2021). This process weakens the electrostatic repulsion between negatively charged biochar and anionic PFASs, increasing biochar adsorption ability (Chen et al. 2020). The bridging effect of Ca^{2+} between biochar and anionic PFASs (such as PFOA and PFBA) also increases their adsorption (Du et al. 2015b). However, the adsorption appears to be attenuated by the presence of other PFASs, suggesting that adsorption attenuation is more the result of competition for binding sites amongst comparable chemicals, instead of pore clogging and competition for binding sites for soil dissolved organic carbon molecules (Krahn et al. 2023). In terms of Na^{+}, it will promote the

adsorption of PFOS by biochar because the overall zeta potential of biochar adsorbed PFOS is significantly more negative (Krebsbach et al. 2023). Nevertheless, Na^+ decreased the adsorption capacity of PFOA and PFBA due to the restriction of PFASs micelle formation and the inability to support PFASs hydrophobic partitioning on biochars (Liu et al. 2023).

3.3.3 PFASs structure

The C chain length of PFASs significantly influences their adsorption by biochar because it determines the hydrophobic interactiom (Kabiri et al. 2023; Hong et al. 2021). The longer the C chain of PFASs with the same end group, the more significant the hydrophobic interaction during adsorption (Zhang et al. 2021). This phenomenon may be due to the dissociation constant (K_d), which tends to increase with the length of the perfluoroalkyl chain. Specifically, adding one $-CF_2$ group increased the K_d values of PFCAs and PFSAs by 0.5 and 0.8 log units, respectively (Park et al. 2020b). Many studies have shown that medium and long-chain PFASs are more easily absorbed by biochar than short-chains (Zhang et al. 2013; Zhu et al. 2020).

The functional groups of PFASs, like the carboxyl group of PFCAs and the sulfonic acid group of PFSAs (Vo et al. 2022), mainly affect the hydrophobic interaction and hydrogen bonding between PFASs and adsorbents. The smaller size of the carboxyl functional group of PFCAs may make them less hydrophobic than the sulfonic acid functional group (Oliver et al. 2020), which makes PFSAs have a higher adsorption affinity to absorbents than PFCAs (Wang et al. 2019a). In addition, PFSAs contain two more C–F bonds than their counterparts such as PFOA with the same number of carbon atoms in their structure, contributing to stronger hydrophobicity and enhanced adsorption (Merino et al. 2016). Moreover, the hydrogen bonds formed between the hydroxyl groups (H donors) on biochar and the electronegative O atoms (H acceptors) in the carboxyl groups (2O, 2H acceptors) and sulfonic acid groups (3O, 3H acceptors) of PFCAs and PFSAs may also contribute to the adsorption of target PFASs to biochar (Liu et al. 2015). The hydrogen bond between PFOS and biochar may be stronger than that between PFOA and biochar due to the presence of one more H receptor in PFOS than in PFOA (Liu et al. 2020b).

4 Impact of biochar on reducing the risk of PFASs from entering the food chain

Plants can take PFASs from the soil and transport them into the food chain, where they can biomagnify and pose a potential health risk to humans. Long-chain PFASs are more difficult to transport due to their high lipophilicity and relative molecular weight, while PFASs with low lipophilicity and molecular weight are more likely to be absorbed by plant roots and moved to shoots (Collins et al. 2006; Zhao et al. 2012). Therefore, some short-chain PFASs are absorbed and accumulated by crops after entering the soil. For instance, PFCAs and PFBS with shorter C chains are easily transported upward through

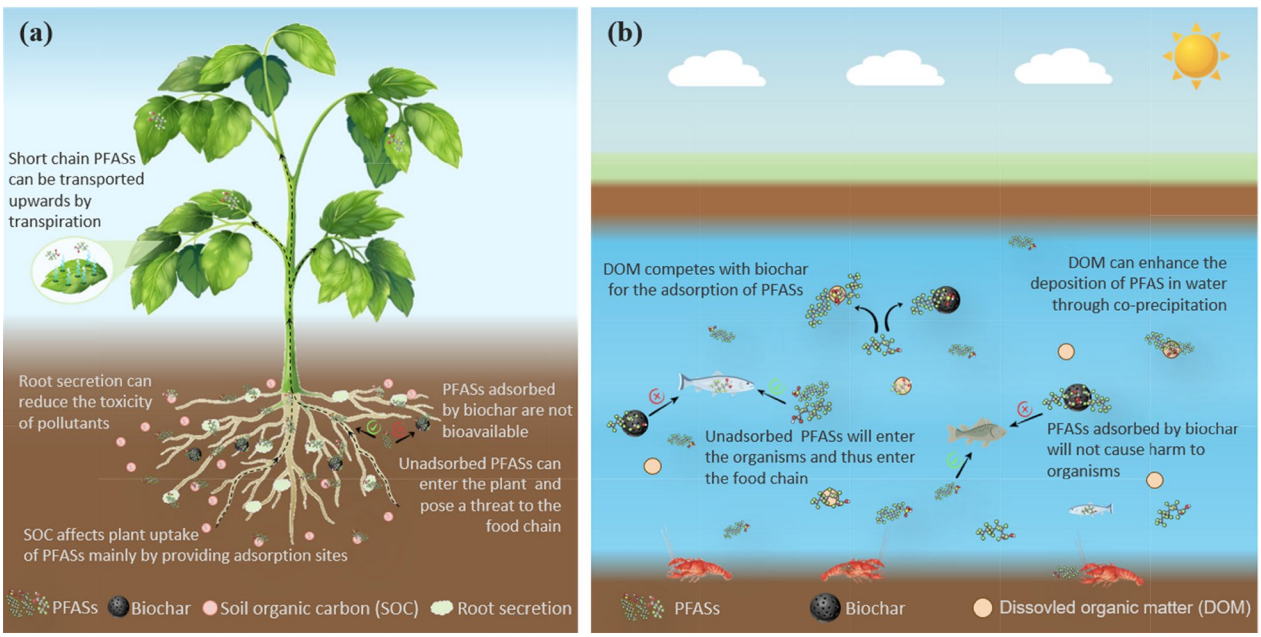


Fig. 8 Possible pathways that biochar reduces PFASs to enter the food chain in **a** soil and **b** water (Designed by Freepik)

plant transpiration, while other PFCAs with longer C chains tend to remain in the roots and are largely adsorbed by the soil (McLachlan et al. 2019). As shown in Fig. 8a, the accumulation of PFASs in plants is mainly dominated by root uptake, and uptake in above-ground parts plays a secondary role in PFASs accumulation (Wang et al. 2020a, 2020b). Biochar in the soil immobilizes PFASs through adsorption (Sørmo et al. 2024). The bioavailability of PFASs adsorbed by biochar in the soil is reduced, thus reducing their entry into the plant and reducing the harm to the food chain. Besides, root secretions have shown the ability to mitigate pollution toxicity, contribute directly or indirectly to the degradation of organic pollutants, and exhibit both additive and synergistic effects (Xu et al. 2017). Biochar can potentially affect the composition of root secretions, thereby altering the behavior of PFASs in the rhizosphere. However, no studies have yet investigated whether root secretions can degrade PFASs. In addition, soil organic matter (SOM) affects plant uptake of PFASs mainly by altering the adsorption capacity of PFASs in soil, including hydrophobic interaction, electrostatic interactions, and hydrogen bonding (Vierke et al. 2013; Wei et al. 2017). This mechanism exhibits a resemblance to the adsorption of PFASs by biochar. SOM can also block the pores of biochar and affect its adsorption capacity. Whether this process reduces or increases the adsorption capacity of biochar for pollutants has not been uniformly concluded, and this needs to be further studied. Moreover, adding biochar to soil can significantly improve the soil microbial community, thereby accelerating microbial degradation of organic pollutants (Kong et al. 2018; Mukherjee et al. 2022; Zhang et al. 2024a, b, c). For PFASs, biochar may also increase the degradation of PFASs by enhancing soil microbial activity. Given the complexity of soil systems, the underlying mechanisms of biochar addition for remediating PFASs pollution warrant further study.

PFASs in water systems may be transported through the food chain and accumulate in organisms. DOM in water has a great influence on the bioavailability of organic pollutants. As shown in Fig. 8b, through co-precipitation, DOM can increase the deposition of PFASs in water, slowing down their movement and lowering contamination levels in the process (Yu et al. 2021). DOM adversely affects the adsorption of PFOA on activated charcoal through direct site competition and pore blockage effects (Yu et al. 2012), aligning with the mechanism by which DOM inhibits PFASs adsorption on biochar as described in Sect. 3.3.2. The effect of DOM on the adsorption capacity of biochar for PFASs is influenced by its composition and molecular structure. The properties of DOM in different water systems are quite different, and its influence on the adsorption of PFASs by biochar is also different. The specific influence mechanism needs to be further studied. In summary, biochar in soil and water systems can reduce the harmful effects of PFASs on plants and aquatic organisms. However, these effects vary depending on environmental conditions, PFASs species, biological species, and biochar properties, and more research is needed to gain insights into the mechanisms and effects.

5 Feasibility and limitations of PFASs remediation by biochar

Overall, most of the PFASs studied in biochar remediation are anionic PFASs, and there are few studies on zwitterionic and cationic PFASs. Mukhopadhyay et al. (2021) found that clay-biochar composites have a good adsorption effect on zwitterionic PFASs (perfluorooctane amido betaine) in water, and it is worthwhile to study the zwitterionic and cationic PFASs in biochar remediation in the future. Other methods, such as membrane separation (Boo et al. 2018), photochemistry (Li et al. 2020) and electrochemistry (Fang et al. 2019), can remove more than 90% of PFOA and PFOS, but their material preparation is complex and costly. Adsorption is widely recognized as an effective technique for PFASs remediation (Lei et al. 2023). In contrast to alternative adsorbents like carbon nanotubes and activated carbon, the removal efficiency of pristine biochar for remediation of PFASs pollution, especially short-chain PFASs, is not high, with most studies reporting less than 40% removal (Dalahmeh et al. 2019). Biochar can be modified in several ways to increase the removal capacity of PFASs, such as by functionalizing particular functional groups, altering minerals and nanoparticles, or subjecting them to acid, alkali, or redox treatment (Zhang et al. 2023b). These modifications can potentially alter not only the specific surface area and surface functional groups of biochar, but also the pore size distribution and structure (Cheng et al. 2021). The adsorption capacities of both unmodified and modified biochar on PFASs are summarized in Table 2. Zhang et al (2023b) found that the theoretical maximum adsorption capacities for PFOS and PFOA were 72.17 and 45.88 mg g^{-1} of acid-modified sludge biochar, respectively. The adsorption capacity of PFOA was increased from 23.4 to 42.2 mg g^{-1} by loading $FeCl_3$ on the biochar derived from oak leaves compared with pristine biochar (Wu et al. 2022). The red mud-modified sawdust biochar enhanced the adsorption efficiency of PFOS in aqueous solution from 178.6 to 194.6 mg g^{-1} compared to unmodified sawdust biochar (Hassan et al. 2020). Even though activated carbon usually has a much higher adsorption capacity than

Table 2 Adsorption of PFASs by original and modified biochar

Raw material	PFAS	Modification method	Pyrolysis temperature (℃)	Adsorption capacity (mg g^{-1})	Removal rate (%)	References
Sludge	PFOA PFOS	Hydrochloric acid	300	45.88 72.17	–	Zhang et al. 2023b
Sludge containing iron	PFOA	EDTA-citric acid leaching/pyrolysis	900	–	99.6	Fu et al. 2022
Sugarcane bagasse	PFOS	Hematite nanoparticles	200	120.44 ± 12.37	–	Hassan et al. 2022
Sawdust	PFOS	Raw red mud (Fe_3O_4)	600	194.6	–	Hassan et al. 2020
Douglas fir	PFOA PFOS	$FeCl_3$/Fe_3O_4	900–1000	652 16.6	–	Rodrigo et al. 2022
Oak	PFHpA PFOA PFBS PFHxS PFHpS PFOS	Zero-valent iron	700	17 60 20 30–40 60–70 94	–	Liu et al. 2020b
Corn straw	PFOA	Zero-valent iron	900	–	99	Yang et al. 2022
Coconut shells	PFOA	Molten alkali (KOH)	900	1269	–	Zhou et al. 2021
Corn straw	PFBA PFOA	Wet ball-milling with $FeCl_3$ solution and high-temperature carbonization	900	10.1 39.1	–	Liu et al. 2023
Bamboo	PFOA PFHxS PFOS	Polyaniline	500	264.6 327.6 349.5	–	Yea et al. 2022
Biosolid	PFOA PFOS PFHxS	Chemical vapor deposition	700	–	71 95 72	Patel et al. 2023
Reed straw	PFBA PFBS PFHxA	–	900	6.88 11.11 13.52	92 ± 1 93 ± 3 92 ± 2	Liu et al. 2021
Hardwood	PFBA	–	900	–	87	Inyang and Dickenson 2017
Pinewood	PFBA	–	700	–	18	

biochar, its cost (\$ 1500 t^{-1}) is much more expensive than the latter (\$ 246 t^{-1}) (Du et al. 2014). Another study also showed that commercial biochar (Oregon Biochar Solutions) is more cost-effective than activated carbon (Zhang et al. 2023b). Therefore, from an economical, practical, and feasibility perspective, biochar or chemically modified biochar can be used as an effective adsorbent for the remediation of PFASs contamination (Hassan et al. 2022).

However, the widespread application of biochar has potential environmental risks (Fig. 9). The low bulk density, large surface area, and variable particle size distribution of biochar can lead to its release into the atmosphere through natural or mechanical disturbances (Gelardi et al. 2019), potentially increasing PM_{10} emissions (Li et al. 2018). Some biomass sources of biochar may contain PFASs, which may be retained in the biochar after pyrolysis. Kim et al. (2015) found that the total residual concentration of PFOA and PFOS in sludge biochar was 15.8 ~ 16.9 ng g^{-1}, with no significant decrease after pyrolysis. As pyrolysis temperature rises, the acidic functional groups in biochar decrease, altering its pH (Wang et al. 2019b). This alteration may further limit plant nutrient supply and affect plant growth (Zhang et al. 2019).

Biochar also has an impact on the survival of soil fauna. For instance, earthworms can consume biochar, and the contaminants in biochar enter the earthworms and may cause serious harm to earthworms (Huang et al. 2020; Wang and Zhou 2013). In particular, biochar derived from poultry manure is significantly toxic to earthworms due to the high ammonium concentration in poultry manure (Liesch et al. 2010). Smith et al. (2013) studied the toxicity of water-soluble organic compounds in biochar on cyanobacteria and eukaryotic green algae in aquatic environments. They found that the water-soluble organic compounds from pine biochar inhibited the growth of these organisms. It is likely due to "some type of 500-dalton (or smaller) organic chemical species that contains at least one carboxyl group", but the detailed mechanism is unclear.

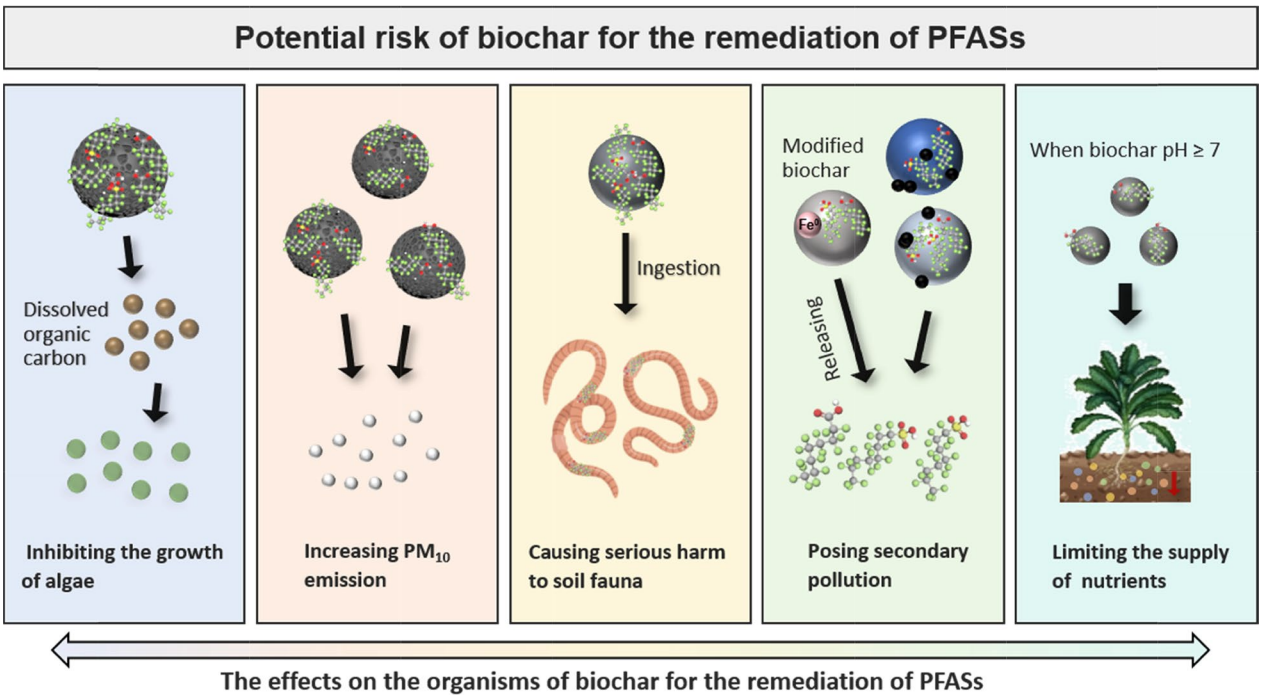


Fig. 9 Potential risk of biochar for the remediation of PFASs (Designed by Freepik)

Chemical modified biochar may pose a potential risk of environmental secondary pollution due to its susceptibility to pH changes, turbulence, and aging (Zhang et al. 2022a). The long-term stability of engineered biochar used to immobilize pollutants is uncertain (Xiang et al. 2021; Wang et al. 2021). There is no conclusive evidence that large-scale application of biochar in soil is environmentally friendly and cost-effective in the long term (Tan and Yu 2023). In addition, biochar had a better removal efficiency for long-chain PFASs than short-chain PFASs (Zhang et al. 2023b). With the gradual banning of long-chain PFASs, short-chain PFASs began to be widely used, with detection frequencies almost tripling between 1996 and 2019 (Zheng et al. 2021). Short-chain PFAAs are frequently detected in tap water fields in the United States (88–100%) (Boone et al. 2019), and recent studies have found the presence of ultra-short and short-chain PFAAs in indoor and outdoor dust (Wang et al. 2022). The harm of short-chain PFASs cannot be ignored (Nian et al. 2020), but they have received less attention compered to long-chain PFASs (Fang et al. 2024). Research on biochar remediation of short-chain PFASs is insufficient and deserves further attention.

More research is required to determine how biochar interacts with different environmental media, like the atmosphere, water, and soil, as well as how biochar generally has a negative impact on the environment, and the technology to reduce the risk of biochar is worthy further research. The biochar used to remediate PFASs pollution should meet the standards for the safe use of micropollutants in biochar set by the International Biochar Initiative and the European Biochar Certificate. Novel approaches need to be developed to mitigate or address the potential environmental risks of biochar. There is uncertainty regarding the bioavailability of PFASs adsorbed by biochar and the impact of biochar aging post-PFASs adsorption on PFASs desorption in the environment. It is suggested that models or whole-cell biosensors be used to conduct environmental risk assessments of raw biochar or biochar adsorbed with PFASs (Zhang et al. 2024b). Raw materials and production conditions are the primary causes of the toxicity of biochar, so it can be pyrolyzed slowly, and the selection of feedstocks should be made with minimal levels of dangerous compounds (Xiang et al. 2021).

6 Conclusions and prospects

As persistent organic pollutants, PFASs can adversely affect living organisms, alone or in combination with other pollutants, representing a severe risk to ecosystem and human health. Biochar has been extensively utilized for the adsorption and removal of pollutants and has a strong ability to adsorb various contaminants. It mainly adsorbs PFASs through electrostatic interaction, hydrophobic interaction, hydrogen bonding, and pore filling, and the adsorption effect is affected by the properties of

biochar itself, environmental factors, and PFASs structure. In addition, biochar can degrade PFASs by producing free radicals. Biochar can prevent PFASs from entering the food chain and reduce environmental risk. Although research on biochar and PFASs is increasing year by year, the studies on using biochar for the remediation of PFASs pollution are not enough. Through a literature review, we found that biochar offers good promise for remediating PFASs pollution. Based on the literature review, to better efficient and safe remediation of PFASs using biochar, the following suggestions and perspectives are proposed for future research directions:

- Since the adsorption efficiency of the initial biochar is not optimal, modifying the biochar is better. The existing modification methods are mainly to load inorganic or organic matter on biochar, and the microbial immobilization technology for the remediation of pollutants has developed into a novel research direction. Biochar technology can combine the adsorption of biochar with the degradation of microorganisms to realize the degradation of PFASs. Biochar-immobilized cells have been used to adsorb and synergistically biodegrade heavy metals and organic pollutants such as mercury, manganese, cadmium, copper, lead, paraquat, and other pollutants. The reversible electron transfer process of iron can completely degrade various organic pollutants, and whether it is possible to load bacteria on the surface of biochar and remediate PFASs in the presence of iron, to achieve their degradation. The key is to find a more appropriate microorganism that can efficiently degrade PFASs, and more research is needed to explore its feasibility.
- Environmental risk assessment on the adsorption of PFASs by biochar should be investigated. If biochar made from raw biomass containing pollutants is used for the remediation of PFASs pollution, whether it will affect the adsorption capacity of PFASs or combine with PFASs to form more serious pollutants is still unknown. Whether the absorbed PFASs are bioavailable when inhaled by the human body, and thus adversely affecting the human body is still unknown. Therefore, an environmental risk assessment should be carried out on the whole process of using biochar to remediate pollutants, from the preparation of biochar to the ecological risk after the remediation of pollutants.
- Biochar can be reduced to the size of the nanoscale, and compared to macro biochar, nanobiochar has a unique nanostructure, higher stability, and larger specific surface area, showing better potential for removing new pollutants in laboratory-scale studies. At present, there is no research on the use of nanobiochar for the remediation of PFASs pollution, and whether it has a better adsorption effect on PFASs than conventional biochar needs to be explored.

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Author contributions
Haiyan Wang: conceptualization, data curation, investigation, visualization, writing—original draft. Haiyan Zhang: writing—review and editing. Lizhi He: writing—review and editing. Jie Wang: writing—review and editing. Shuo Wang: writing—review and editing. Xiaokai Zhang: conceptualization, supervision, writing—review and editing. Hailong Wang: writing—review and editing. Feng He: writing—review and editing.

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Availability of data and materials
The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests
Hailong Wang is an Executive Editor of the journal Biochar, and he was not involved in the peer-review or handling of the manuscript. The authors have no other competing interests to disclose.

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