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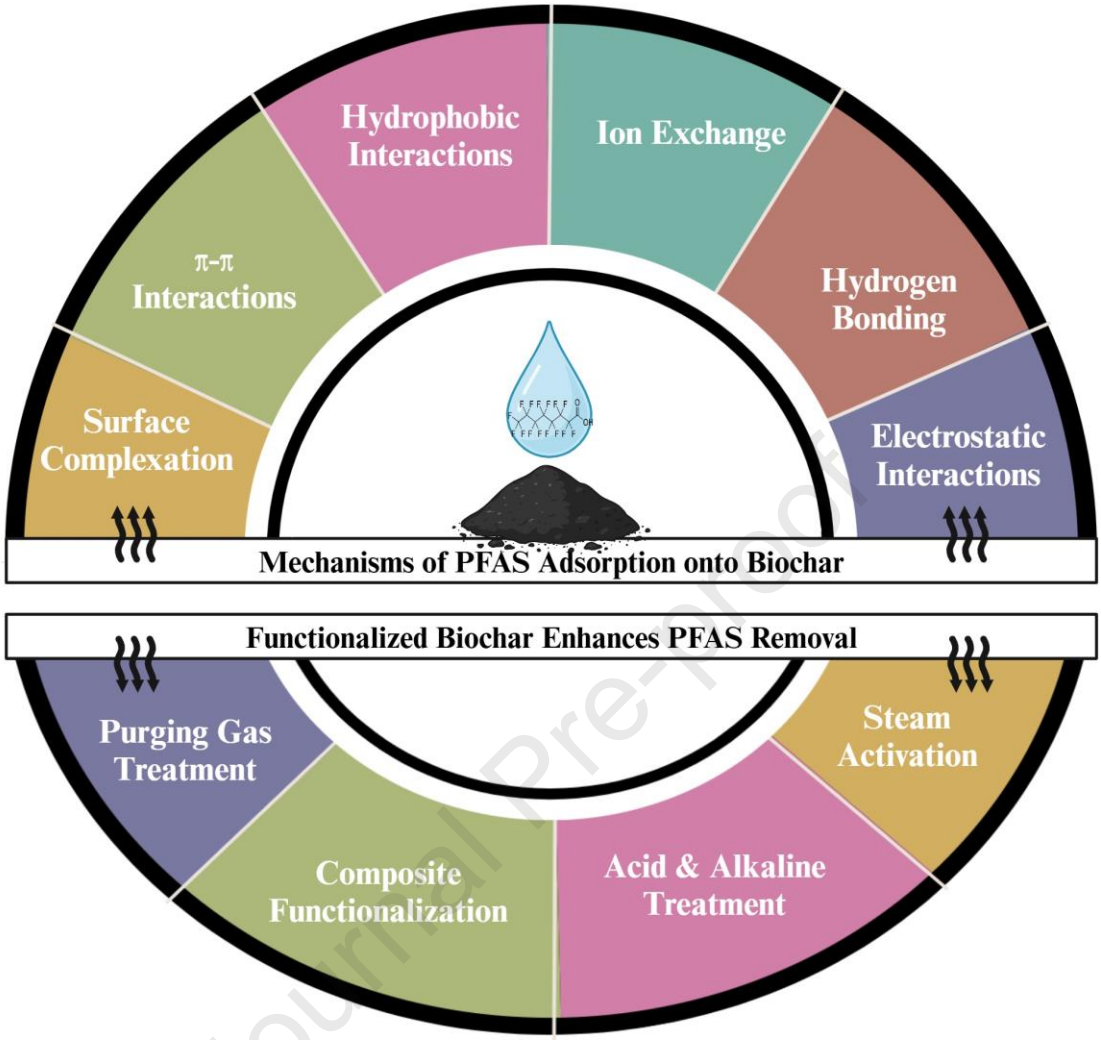

Functionalized Biochar for the Removal of Poly- and Perfluoroalkyl Substances in Aqueous Media

Sepideh Nasrollahpour[1], Rama Pulicharla[1], Satinder Kaur Brar[1,*]

[1]Department of Civil Engineering, Lassonde School of Engineering, York University, Toronto, Canada.
[*]Corresponding author: satinderbrar@lassonde.yorku.ca

Abstract

Biochar has gained attention as a promising adsorbent for removing various environmental pollutants due to its availability, cost-effectiveness, eco-friendly nature, and high adsorption capacity. This review focuses on using biochar to remove poly- and perfluoroalkyl substances (PFAS), emerging contaminants that pose significant environmental and health risks due to their toxicity, persistence, and bioaccumulation potential. The classification of biochar and using pristine and functionalized biochar for pollutant removal are addressed, along with an overview of the various functionalization techniques employed to enhance biochar's adsorption capacity. Different factors influencing the removal of poly- and perfluoroalkyl substances (PFAS), such as pH, the molecular chain length of PFAS, and biochar characteristics like pyrolysis temperature, particle size, and dosage, are investigated. Long-chain PFAS, such as perfluoro octane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), are more effectively adsorbed than short-chain PFAS, with competitive sorption effects observed in mixed-solution environments. A decrease in pH, smaller biochar particle sizes, and optimized pyrolysis temperatures have been found to enhance biochar's sorption capacity. Furthermore, biochar demonstrates higher efficiency in single-solution systems compared to mixed solutions when removing PFAS.

Keywords: Biochar, Poly- and Perfluoroalkyl Substances (PFAS), Functionalization, Removal.

Introduction

Biochar is a carbon-rich material produced through the pyrolysis of biomass in the absence of oxygen. Its unique physicochemical properties, such as high surface area, porosity, and chemical stability, make it an appealing material for a wide range of applications, including agriculture, energy production, and environmental remediation. Derived from organic waste materials such as agricultural residues, wood chips, and sewage sludge, biochar contributes to sustainable waste management and carbon sequestration. Its low cost and high availability make it an attractive alternative to conventional adsorbents like activated carbon in water and soil treatment [1].

In wastewater treatment, biochar has demonstrated considerable potential through mechanisms such as adsorption, catalysis, and ion exchange. However, the adsorption capacity of pristine biochar is often limited by its low surface area and susceptibility to abiotic and biotic degradation. To overcome these limitations, researchers have focused on the functionalization of biochar. Functionalization processes, such as impregnation with metal oxides, steam activation, and acid-base treatments, are designed to enhance biochar surface area, introduce more active sites, and improve its mechanical properties. Functionalized biochar, with its increased adsorption capacity,

has shown great promise in efficiently removing organic and inorganic pollutants from aqueous solutions [2].

One of the latest environmental challenges is the removal of perfluoroalkyl and polyfluoroalkyl substances (PFAS) from contaminated water. PFAS are synthetic chemicals used in various industries, including firefighting foams, textiles, and food packaging. Due to their strong carbon-fluorine (C-F) bonds, PFAS are chemically stable and resistant to environmental degradation, leading to their accumulation in water, soil, and living organisms. Long-chain PFAS compounds, such as perfluorooctanoic acid (PFOA) and perfluoro octane sulfonate (PFOS), are particularly harmful, having been linked to health issues such as elevated cholesterol, cancer, and developmental effects in children [3,4].

The persistence and bioaccumulative nature of PFAS make them difficult to remove from the environment, posing a significant risk to human health. In the United States alone, As of May 2024, 6189 sites have been identified as PFAS-contaminated, affecting public and private water supplies. In Canada, more than 100 federal sites are confirmed or suspected to be contaminated with PFAS. These sites are spread across all provinces and territories, with the majority linked to the past or ongoing use of aqueous film-forming foam (AFFF) at airports and military facilities. The hydrophobic nature and high Log K_{OW} values of PFAS, especially the long-chain compounds, make them poorly soluble in water and prone to accumulate in natural water bodies. Regulatory agencies, such as the U.S. Environmental Protection Agency (EPA), have set a 70 ppt limit for PFOA and PFOS in drinking water, but achieving these limits through traditional remediation methods is challenging [5,6,7].

Various techniques, including ion exchange, advanced oxidation, coagulation, graphene and membrane filtration, have been explored for PFAS remediation. However, these methods often suffer from drawbacks such as high costs, low efficiency, and the production of secondary pollutants[8,9]Among the solutions, biochar, particularly functionalized biochar, has shown great promise for PFAS removal due to its low cost, wide availability, and environmentally friendly nature. The functionalization of biochar enhances its ability to adsorb PFAS through mechanisms such as hydrophobic interactions, electrostatic attraction, and, in certain cases, π-π bonding when aromatic systems are present [10,11,12,13,14]. Recent advancements in functionalization techniques have significantly improved biochar performance in PFAS removal by increasing its surface area and functional group density[15,16].

This review explores the potential of biochar, especially functionalized biochar, as a sustainable material for PFAS removal from aqueous environments. It offers a detailed synthesis of biochar characterization methodologies (physical and chemical), pollutant removal mechanisms, and limitations of conventional PFAS treatments. By examining the role of pristine and functionalized biochars, functionalization techniques, and key variables affecting PFAS removal (e.g., pH, PFAS chain length, pyrolysis conditions, and particle size), this review identifies pathways to optimize biochar performance. This review focuses on integrating these insights to bridge gaps in knowledge and advance biochar-based PFAS remediation.

Biochar characterization methodologies

Recent research highlights the importance of comprehensive characterization techniques for biochar to identify its agricultural and environmental benefits and differentiate it from other organic materials with similar properties. The diverse characteristics of biochar, include its stability, specific surface area, functional groups on its surface, structure, and elemental composition, make it difficult to select the most appropriate characterization methods. The characteristics of biochar can be categorized into four main groups, including chemical, physical, structural, and thermal stability properties. Various techniques are reported in literature, including Cation Exchange Capacity (CEC), Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX or EDS), X-Ray Diffraction (XRD), Zeta potential, Fourier Transform Infrared Spectrometer (FTIR), X-Ray photoelectron spectrometry (XPS), Brunauer Emmett Teller (BET), Differential scanning calorimetry (DSC), Ash and moisture, Thermo Gravimetric Analysis (TGA), and Raman spectroscopy [17,18,19].

The frequency of using various techniques for biochar characterization in PFAS elimination investigations is displayed in **Figure 1**. The most used techniques in biochar literature are FTIR, SEM/TEM, and BET, respectively.

Physical characteristics

The physical attributes of biochar, such as particle size distribution, bulk density, pore size and volume distribution, and specific surface area (SSA), are influenced by factors such as pyrolysis conditions (temperature, residence time) and the presence of oxygen-containing media like air, CO_2, or steam. These properties are key in determining biochar adsorption capacity. Characterization techniques, particularly the BET method, are critical for assessing SSA and how pyrolysis conditions modify biochar's structural features. Studies have demonstrated that higher pyrolysis temperatures can increase both SSA and total pore volume. Moreover, post-treatment processes like acid treatments enhance SSA by introducing inorganic materials on the biochar surface, modifying the pore structure. Additionally, reduced pore sizes are observed alongside increases in total pore volume, revealing a complex relationship between these factors [20,21,22].

Chemical characteristics

The chemical properties of biochar, including its surface functional groups, oxygen-to-carbon (O/C) ratio, and CEC, are crucial in determining its effectiveness for PFAS removal. The O/C ratio, often analyzed through EDX/EDS, directly correlates with the extent of carbonization. Lower O/C ratios indicate higher aromaticity, which can enhance hydrophobic interactions with PFAS, reducing surface polarity and improving adsorption capacity. CEC, representing the biochar's ability to exchange cations, enhances PFAS adsorption by providing ionic exchange sites. Higher CEC biochars are more effective, particularly for cationic or zwitterionic PFAS, due to increased electrostatic interactions. Environmental factors like competing ions and pH further influence this property [23].

Surface functional groups, such as carboxyl and hydroxyl groups, identified via XPS and FTIR, are one of the most critical properties for PFAS removal. These groups facilitate key interactions—

such as electrostatic attractions and hydrogen bonding—with PFAS molecules. FTIR analysis can detect changes in these functional groups before and after adsorption, providing insights into the mechanisms at play during the removal process [24].

The point of zero charge (PZC) of biochar is another critical factor, as it dictates the surface charge under different pH conditions. When the PZC is lower than the solution pH, the biochar surface becomes negatively charged, promoting the adsorption of cationic PFAS or PFAS molecules in acidic environments [25].

Surface morphology

Surface morphology analysis via SEM/TEM offers critical insights into the pore structure and surface defects of biochar, both pre- and post-treatment. High-resolution imaging can reveal porosity alterations associated with PFAS adsorption, providing essential data on biochar reactive sites. Raman spectroscopy is pivotal for assessing structural defects (D band) and graphitization (G band), with the ID/IG ratio serving as a key metric for disorder. A higher ID/IG ratio signifies more defective sites, enhancing PFAS adsorption. Additionally, XRD can identify crystalline versus amorphous phases, offering insights into the stability of functionalized biochar, particularly in metal oxide-modified composites critical for PFAS removal efficiency [26].

Stability characteristic of biochar

TGA is crucial for evaluating biochar's thermal stability, revealing degradation profiles tied to its structural composition. TGA differentiates distinct thermal decomposition stages: dehydration (below 300°C), breakdown of labile components (300-400°C), and the gradual degradation of recalcitrant carbon fractions at higher temperatures. For instance, a study on maple leaf-derived biochar reported a 10% weight loss due to moisture evaporation and volatile release below 300°C, followed by a 45% loss between 300-400°C, attributed to cellulose and hemicellulose degradation, with minor weight loss above 400°C, corresponding to lignin and stable carbon forms. The steep weight reduction between 300-400°C highlights biochar's susceptibility to thermal degradation in this temperature range, providing insights into its recalcitrance and potential long-term environmental stability [27].

Biochar's function in removal of pollutants

Biochar removes pollutants through a combination of adsorption, ion exchange, complexation, and precipitation mechanisms. These processes are governed by the physicochemical properties of biochar, which depend on its feedstock and pyrolysis conditions.

Adsorption

The high surface area and porous structure of biochar enable it to physically adsorb a wide range of contaminants. Organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs) and pesticides, are trapped within its micropores through van der Waals forces. Chemisorption, involving covalent or hydrogen bonding, occurs when pollutant molecules interact with functional groups such as hydroxyl (-OH), carboxyl (-COOH), and amine ($-NH_2$) on the biochar surface. These groups enhance the binding of inorganic pollutants, including heavy metals like lead (Pb) and cadmium (Cd). Adsorption efficiency is influenced by pH, ionic strength, temperature, and the presence of competing contaminants. For instance, acidic conditions promote the adsorption of

cationic heavy metals by increasing electrostatic attraction to negatively charged biochar surfaces [28].

Ion Exchange

Ion exchange processes allow biochar to replace its surface ions (e.g., H^+, Na^+, K^+) with pollutant ions. This mechanism is particularly effective for the removal of cationic species such as ammonium (NH^{4+}), zinc (Zn^{2+}), and copper (Cu^{2+}). Biochar derived from nutrient-rich feedstocks, such as animal manure, exhibits a higher cation exchange capacity (CEC) due to its abundance of negatively charged functional groups and mineral constituents. The effectiveness of ion exchange depends on environmental factors such as competing ions and solution pH, which influence the surface charge and exchangeable ion availability of biochar [29].

Complexation

Functional groups on the surface of biochar interact with pollutants, forming stable complexes that immobilize contaminants. For example, carboxyl and phenolic groups bind with metals like chromium (Cr) and mercury (Hg) to form chelated structures, reducing their solubility and mobility. This mechanism is particularly relevant in water treatment and soil remediation, where the immobilization of toxic elements is essential for environmental and public health [30].

Precipitation

Mineral components within biochar, such as calcium (Ca) and magnesium (Mg), promote the precipitation of certain pollutants into insoluble compounds. For instance, phosphate ions in wastewater can react with calcium to form hydroxyapatite, effectively removing phosphates through mineral precipitation. Similarly, fluoride ions interact with magnesium to form stable precipitates, mitigating their environmental impact [31].

Additionally, pollutant removal is not restricted to just one mechanism but can entail several methods. This multi-functionality is an advantage of biochar, but it complicates identifying which mechanisms are most effective under specific conditions. Future research should clarify these mechanisms to better tailor biochar applications for different pollutants.

A summary of PFAS treatment

The persistence of PFAS in aquatic ecosystems, including surface and groundwater, is due to their resistance to conventional treatment processes. Industrial waste, wastewater discharge, and biosolid applications lead to the accumulation of PFAS in tap water because of their strong carbon-fluorine (C–F) bonds, which make them difficult to remove [32].

Current strategies for PFAS removal include destructive techniques (e.g., thermal and electrochemical treatments) and separation methods (e.g., adsorption and membrane filtration). Destructive methods often result in incomplete degradation and harmful byproducts due to the stability of PFAS, which limits their real-world applicability as the production of secondary pollutants complicates the remediation process. Moreover, these methods frequently fail to achieve complete mineralization of PFAS, leaving behind harmful intermediates that reduce their effectiveness for large-scale water treatment applications. Separation methods, such as reverse osmosis and nanofiltration, are effective but costly, energy-intensive, and generate concentrated PFAS waste streams. Coagulation-flocculation serves as a pretreatment, but alone it is insufficient for PFAS removal [33].

Granular activated carbon (GAC) is widely used, but its efficiency drops significantly in the presence of natural organic matter (NOM) and with short-chain PFAS. Studies report that GAC cannot be effective in removing short-chain PFAS like PFBS in complex wastewater. Ion-exchange resins, while effective, have high costs and may produce carcinogenic byproducts, such as nitrosamines, during water treatment [34]. This raises health and safety concerns, particularly when these byproducts are not sufficiently addressed during treatment processes.

Biochar, particularly when functionalized with substances like iron oxides or through other chemical processes, offers a promising alternative, achieving over 80% removal of long-chain PFAS. Unlike GAC, biochar is renewable, making it a sustainable option for large-scale applications. While challenges remain for short-chain PFAS, biochar's potential as a low-cost, environmentally friendly solution continues to grow [35].

Different pristine biochar for PFAS treatment

Some studies have used biochar for PFAS removal due to its unique features, as illustrated in **figure 2** by the abundance of PFAS contaminants removed by biochar and the number of publications in the field of PFAS removal using biochar. Guo et al. found that corn straw biochar could remove PFOS through hydrophobic and electrostatic interactions, with a maximum adsorption capacity of 0.34 mmol/g in eight hours. Increasing the pyrolysis temperature above 400°C improved the biochar's ability to remove PFOS by increasing hydrophobicity, fine-pore structures, and surface area. However, the PFOS adsorption capability of biochar decreased as the pH of the solution rose. PFOS adsorption on biochar was identified as an endothermic and spontaneous process, suggesting the feasibility of biochar for treating wastewater under varying conditions [36].

Inyang and Dickenson investigated biochar derived from pinewood and hardwood for PFOA removal. Their study identified hydrophobic interactions as the primary mechanism for adsorption, with a maximum adsorption capacity of 0.099 mmol/g. However, the presence of dissolved organic carbon (DOC) in wastewater led to competitive sorption, filling the biochar pores and limiting PFOA uptake. This underscores the challenge posed by co-contaminants in real-world wastewater matrices. Notably, biochar was less effective at removing shorter-chain PFAAs compared to longer-chain counterparts like PFOS, consistent with the enhanced sorption potential for more hydrophobic PFAS molecules [37]. Waste wood from the timber industry was also used to make biochar for the remediation of PFOA, PFBS, PFBA, and PFOS, and similar adsorption capabilities were identified. Electrostatic attraction as well as hydrophobic interaction were implicated in the adsorption process for PFAS. The study found that competitive sorption of PFASs happened during the adsorption mechanism, decreasing the removal efficiency of PFASs and adding four compounds to a solution decreased the effectiveness of PFOS removal by 32.8% to 57.9% compared to a solution which contains a single PFAS substance. This dramatic decrease in efficiency raises concerns about biochar's reliability in environments where multiple contaminants coexist, which is typical in most real-world water treatment scenarios. Such findings suggest that biochar practical application may require additional pre-treatment steps or post-treatment methods to ensure the effective removal of all contaminants. Surface examination using FTIR revealed the existence of diverse functional groups on the adsorbents, with some alterations in FTIR responses revealing electronic interactions throughout sorption. The outcomes show that the adsorption

method is a promising strategy for controlling PFAS pollution in wastewater, and biochar has been shown to be an efficient PFAS adsorbent [38].

Chen et al. investigated biochar produced from maize straw and willow sawdust and found that hydrophobic interactions were the primary mechanism for PFOS removal. Despite the negatively charged surfaces of these biochars, which posed a challenge for PFOS adsorption, the study reported maximum sorption capacities of 0.18 mmol/g and 0.33 mmol/g for willow sawdust and maize straw biochar, respectively. The larger surface area of maize straw biochar (11.63 m^2/g) compared to willow sawdust biochar (7.21 m^2/g) have contributed to its higher adsorption capacity. However, other factors, such as pore size distribution and the presence of competing chemicals in the water, also influence the effectiveness of PFAS removal [39].

Overall, pristine biochar has proven to be efficient adsorbents for PFAS, particularly through hydrophobic and electrostatic interactions. However, the variability in raw materials and the influence of external factors such as pH, DOC, and competing contaminants limit their widespread application without further optimization. The development of functionalization techniques could enhance their adsorption capacity for PFAS. The word cloud in **Figure 3** illustrates the keywords commonly used in articles discussing PFAS removal using biochar.

Functionalized biochar for PFAS removal

Functionalization of biochar can enhance its removal capabilities for PFASs by modifying its surface chemistry, increasing its surface area, and introducing new functional groups. These changes improve the biochar's affinity for PFAS through enhanced adsorption mechanisms, such as electrostatic interactions, hydrophobic interactions, and improved sorption capacity. **Figure 4** illustrates the functionalization approaches applied to biochar for PFAS remediation, where nearly half of the studies involved pristine biochar, and the most commonly used functionalization agents were KOH and ZVI. Additionally, Table S1 summarizes the experimental conditions and results from these studies.

Biochar functionalization by composites for PFAS removal

In recent years, incorporating foreign components into biochar has become a technique for producing hybrid composite materials with multiple functions. These composites offer novel physicochemical features unavailable in the feedstock or pyrolyzed biomass. Tan et al. (2016) classified biochar-based nanocomposites into groups: magnetized biochar, functional nanoparticle-impregnated biochar composites, and nanometal oxide/hydroxide-biochar composites [40].

Magnetic biochar

Magnetization of biochar involves incorporating magnetic materials, typically iron oxides (such as Fe_3O_4), through methods like pyrolysis or co-precipitation. This enhancement allows for easy separation of the biochar from water using magnets, reducing the need for additional filtration

processes. Magnetic biochar has gained significant attention for wastewater treatment due to its high efficiency in adsorbing contaminants and its reusability [41].

Magnetic biochar has shown notable efficacy in the adsorption of PFAS. Hassan et al. demonstrated that sugarcane bagasse, functionalized with Fe_2O_3 and subjected to low-temperature pyrolysis, retained hydrophilic oxygen-containing groups, enhancing its PFOS adsorption capacity to 120.44 mg/g. Electrostatic interactions and chemisorption played a significant role in binding PFOS to the biochar surface [42].

In another study, Calotropis gigantea fibres were pyrolyzed and magnetized with Fe_3O_4 nanoparticles. The resulting composite exhibited adsorption capacities of 204.7 mg/g for PFOA and 195.5 mg/g for PFOS. These values were higher compared to non-magnetic biochar, showcasing the enhanced affinity for PFAS removal [43].

Magnetic biochar presents notable benefits, such as improved separation efficiency; however, its practical application is not without challenges. The process of magnetic functionalization can significantly raise production costs, potentially hindering its scalability for widespread use. Additionally, the durability of magnetic biochar's adsorption efficiency in real-world conditions, particularly in complex water systems with competing ions and contaminants, is still poorly studied. Long-term research is needed to evaluate whether magnetic biochar can sustain its high adsorption performance over repeated treatment cycles.

Functional nanoparticle-impregnated biochar

Functional nanoparticle-impregnated biochar composites have demonstrated efficiency in removing PFAS. Nanoparticles such as nanoscale zero-valent iron (nZVI), graphene, carbon nanotubes, and metal oxides like ZnS and Fe3O4, are incorporated into biochar to enhance its adsorption and reactivity properties. For instance, nZVI-modified biochar can induce redox reactions, helping to break down PFAS molecules while increasing the adsorption capacity. The high surface area and reactivity of nanoparticles can compensate for the potential pore-blocking effect during functionalization, allowing superior pollutant removal efficiency [44].

Studies reveal that biochar impregnated with nZVI has shown enhanced performance for removing perfluorooctanoic acid (PFOA). In one study, a composite biochar created using nZVI via carbothermal reduction demonstrated a remarkable 99.9% PFOA removal rate at high temperatures within six hours. Furthermore, a defluorination rate of 63.2% was achieved after prolonged treatment. This was largely attributed to the prevention of nZVI particle agglomeration during the carbothermal process, thus increasing the exposure of reactive sites for PFAS degradation. Such composites also exhibit electron transfer capabilities, contributing to the breakdown of PFAS via mechanisms like Kolbe decarboxylation, which results in shorter-chain, less toxic perfluorinated compounds.

Additionally, studies on other nanoparticles, such as graphene oxide and chitosan-modified biochar, show that these materials can enhance PFAS removal through mechanisms like electrostatic interactions and hydrophobic adsorption. The versatility of biochar composites means that their modification with nanoparticles can be tailored to target specific PFAS compounds or mixtures [45].

Despite the promising results, nanoparticle-impregnated biochar may introduce environmental and operational concerns. The release of nanoparticles into treated water can pose additional environmental risks, and the potential health impacts of such nanoparticles are not well studied. Moreover, the synthesis of these composite materials often requires complex and costly procedures, which may not be sustainable for widespread implementation.

Composites of nanometal oxide/hydroxide and biochar

Nanometal oxide-biochar composites have significant potential for PFAS removal due to their synergistic physicochemical properties. The integration of nanometal oxides, such as MnO_2, Fe_3O_4, and Al_2O_3, with biochar enhances adsorption by providing additional active sites and promoting mechanisms such as surface complexation, electrostatic interactions, and hydrophobic attraction. Biochar's porous structure facilitates the adsorption of hydrophobic PFAS chains, while the nanometal oxides contribute positively charged functional groups that attract the negatively charged PFAS molecules [46].

In one study, researchers produced Nano-MnO_2-biochar composites (NMBCs) by reducing potassium permanganate in a biochar suspension with ethanol. The maximum Cu(II) sorption capacity of NMBCs reached 142.02 mg/g, significantly higher than that of biochar (26.88 mg/g) and nano-MnO_2 alone (93.91 mg/g) [47]. Such enhancements indicate that nanometal oxide-biochar composites have strong potential for PFAS removal, though direct studies specifically targeting PFAS are still limited. Further research should prioritize exploring their effectiveness in PFAS remediation.

Biochar Functionalization by Steam

Steam activation is a process that enhances the physical properties of biochar, such as its surface area, pore volume, and polarity, thereby improving its capacity to adsorb pollutants from water. Following the first pyrolysis stage, steam is introduced to the reactor for 0.5 to 3 hours, which expands inner pores and removes trapped volatile compounds like aldehydes and acids. This results in a higher micropore volume and increased oxygen-containing functional groups, making steam-activated biochar more effective in removing contaminants [48].

In a study, Seven different biochars were evaluated for their ability to remove perfluoroalkyl acids (PFAA) from field waters. Steam-activated pinewood biochar, produced at 700°C, showed significantly higher adsorption of PFOA with a K_d value of 49 L/g, compared to other biochars. This enhanced performance is due to its greater pore volume and carbon content. Moreover, steam-activated biochar have faster sorption kinetics for PFAS like PFOA and PFBA, indicating that the activation process may be optimizing the biochar for PFAS-specific sorption mechanisms [37]. Despite these promising results, it is important to note that the high energy requirements for steam activation could be a limiting factor for large-scale applications, making it less cost-effective compared to other functionalization methods.

Functionalization by purging gas

This technique is employed during biomass pyrolysis or biochar activation, where specific gases are introduced to modify the biochar's properties. This process can enhance the microporous

structure, increase the surface area, and alter the pore morphology and chemical composition of biochar, thereby improving its effectiveness in various applications [49].

Gases such as carbon dioxide (CO_2) and ammonia (NH_3) have been utilized at varying temperatures for biochar activation and modification. The choice of gas and its flow rate can significantly influence the characteristics of the biochar. For instance, CO_2-assisted activation can increase the biochar's surface area and develop a microporous structure, making it particularly beneficial for applications such as water and wastewater treatment. Additionally, the incorporation of alkali metals during this process can enhance cation exchange capacity, further improving biochar's functionality [50].

While gas purging methods have been explored for the removal of heavy metals—such as the use of nitrogen or CO_2 to remove lead (II), cadmium (II), copper (II), and nickel (II)—their application in PFAS removal has been less explored and requires further investigation [51].

Acid and Alkaline treatment

These treatments influence the biochar surface area, pore structure, and chemical functionality, improving both physical adsorption and chemical interaction with pollutants. Acid treatments, using agents like hydrochloric, nitric, citric, or phosphoric acid, are commonly applied to remove inorganic ash, increase surface oxygenated functional groups, and improve porosity. This enhances biochar's capacity for adsorbing organic compounds and metals from contaminated media [52]. Alkaline treatments, typically involving sodium hydroxide (NaOH) or potassium hydroxide (KOH), create significant structural changes by increasing surface area, pore volume, and hydrophobicity. This modification is particularly effective for hydrophobic contaminants like PFAS, as it enhances the biochar affinity for these compounds [53].

For instance, coconut shell-derived biochar treated with molten KOH at 900°C produced a series of hierarchically microporous biochars (HMBs), with surface areas ranging from 462 to 1322 m^2/g. The biochar's hydrophobicity also increased, making it more effective at adsorbing PFOA. The most efficient biochar (HMB900-2.4) showed a remarkable PFOA adsorption capacity of 423 mg/g within 30 minutes and a maximum Langmuir adsorption capacity of 1269 mg/g, due to its increased surface area and hydrophobic nature [54].

While both acid and alkaline treatments show promise in improving biochar adsorption efficiency, they also come with certain drawbacks. Acid treatments, for instance, can cause severe corrosion of equipment, raising concerns about operational costs and safety. Furthermore, while alkaline treatments increase hydrophobicity, they may also introduce structural weaknesses that could reduce the biochar's durability in long-term applications. There is also limited data on how these treatments affect biochar reusability and potential for secondary pollution, which could limit their sustainability. Hence, further research is needed to optimize these treatments to balance performance, cost, and environmental safety.

Additional functionalization techniques

In addition to what has been stated thus far, biochar can be functionalized using several other methods such as employing peroxides and organic solvents. For instance, functionalizing with

hydrogen peroxide can enhance the amount of carboxyl groups found on the biochar surface, thus offering more sites for metal ion adsorption. Methanol can also be used to functionalize biochar by increasing the number of O-containing groups, thereby enhancing tetracycline removal. Furthermore, N-functional groups can be added to the surface of biochar by using N-containing chemicals like urea and melamine. Several treatments, including 3-aminopropyltrimethoxysilane, aniline, and melamine, were employed effectively to boost the N concentration of coffee-ground biochar. Similarly, the addition of methyl diethanolamine increased the N concentration of biochar generated from corncobs. Prior to functionalizing a material for a certain purpose, it is essential to assess the proposed functionalization procedure thoroughly [55].

However, these methods come with some challenges. For example, while methanol effectively increases oxygen-containing groups, it also increases the risk of organic solvent leaching into treated water, which poses additional environmental challenges. Additionally, the use of N-containing chemicals raises concerns about nutrient leaching and the long-term environmental effects of nitrogen enrichment in water systems. This underscores the need for a more sustainable and eco-friendly approach to biochar functionalization, which has been largely overlooked in the current literature.

Variables affecting PFAS removal

Effect of pH

The pH of the solution plays a pivotal role in the adsorption of PFAS onto biochar, as it directly influences electrostatic forces, hydrophobic effects, and ion exchange mechanisms. **Figure 5** depicts the pH ranges used in various studies on PFAS adsorption using biochar, highlighting the variability in adsorption performance based on the selected pH conditions.

At lower pH levels, biochar surfaces tend to have more protonated functional groups, resulting in a positively charged surface. This enhances electrostatic attraction between the negatively charged PFAS molecules, such as PFOS and PFOA, and the biochar, leading to greater adsorption efficiency. For instance, in a study using corn straw biochar with a point of zero charge (pH_{PZC}) of 10.3, the sorption capacity of PFOS decreased from 63 to 55 mg/g as the pH increased from 3 to 10. This indicates that at lower pH, the positively charged biochar surface creates stronger electrostatic interactions with the negatively charged PFAS molecules, enhancing adsorption [56] .

A similar trend was observed with biochar derived from sawdust and red mud, where PFOS adsorption values were 178.1 mg/g and 194.6 mg/g at a pH of 3.1, respectively, but dropped to 124 mg/g and 132 mg/g at a pH of 10.2. This reduction in adsorption capacity is attributed to the diminished positive charge on the biochar surface at higher pH levels, which weakens the electrostatic interactions. However, this suggests a potential limitation when applying biochar in natural environments where pH varies, such as in industrial wastewater. Nevertheless, hydrophobic interactions between the PFOS molecules' fluorinated carbon chains and the biochar surface remained significant, especially at higher pH values, where electrostatic repulsion is more pronounced [57].

Conversely, at higher pH levels, biochar surfaces become negatively charged due to the deprotonation of functional groups, leading to electrostatic repulsion between the negatively charged PFAS molecules and the biochar surface. This generally reduces adsorption efficiency. However, hydrophobic interactions between the PFAS molecules and the biochar surface continue to play a substantial role, especially for long-chain PFAS. These interactions remain effective even at basic pH levels, compensating to some extent for the reduced electrostatic attraction. This was seen in the study involving sawdust and red mud-derived biochar, where adsorption capacities diminished with rising pH but persisted due to hydrophobic effects [57,58].

Thus, optimizing the pH during PFAS treatment using biochar is critical. Acidic conditions tend to favor electrostatic interactions, while neutral to basic conditions rely more on hydrophobic interactions. However, the practical challenges of maintaining optimal pH in diverse environmental settings cannot be ignored. A careful balance between these factors can maximize the efficacy of biochar in removing both short- and long-chain PFAS.

Effect of chain length

According to previous research, the adsorption distribution coefficient (Kd) of PFAS increases with the length of the perfluorinated carbon chain. This is due to stronger hydrophobic interactions associated with longer chains. The perfluorinated tail, with a larger surface area, requires more free energy for cavity formation in water, leading to stronger adsorption behavior. Long-chain PFAS compounds demonstrate a higher affinity for biochar adsorption compared to shorter-chain compounds. For example, biochar derived from biosolids was able to capture over 80% of long-chain PFAS but only 19-27% of short-chain PFAS. This is attributed to the higher hydrophobicity and stronger interactions of long-chain PFAS with biochar surfaces [59].

Du et al. (2014) highlighted those hydrophobic interactions, including van der Waals forces, play a key role in the sorption of long-chain PFAS (>C_6) onto biochar [60]. In contrast, shorter-chain PFAS are influenced more by electrostatic interactions, which tend to result in weaker sorption. Supporting this, Higgins and Luthy (2006) found that long-chain PFAS exhibit stronger sorption to sediments compared to shorter chains. Vo et al. (2022) noted that log K_d values for long-chain PFAS ranged between 0.77 and 4.63, whereas for short-chain PFAS, the log K_d remained below 0.68 [61] .

The hydrophobicity of PFAS is an important factor in their adsorption, and this property increases with the length of the carbon chain. This is quantified by the octanol-water partition coefficient (log K_{OW}), which measures the compound's tendency to partition between water and organic phases. Fabregat-Palau et al. (2022) reported a linear increase in hydrophobicity with each additional CF_2 unit, corresponding to an increase of 0.5 log K_{OW} per CF_2 for perfluoro carboxylic acids (PFCAs) and 0.8 log K_{OW} per CF_2 for perfluoro sulfonic acids (PFSAs) [62, 63].

Effect of pyrolysis temperature

Figure 6 depicts the pyrolysis temperature selected for biochar in the PFAS adsorption literature published to date. Corn straw TG-DTG curves were utilized by Guo et al. (2017) to examine the

non-condensable gases and biochar residue during biochar production [51]. The biochar preparation temperatures used in their study (250, 400, 550, and 700°C) aligned with different stages of hemicellulose and cellulose decomposition. At lower temperatures (250°C), hemicellulose partially decomposed, while at 400°C, hemicellulose was fully decomposed, and cellulose began decomposing. Temperatures at 550°C and 700°C resulted in complete decomposition of both hemicellulose and cellulose, producing highly carbonized biochar. Biochar produced at 700°C (BC700) displayed a cleaner surface compared to that produced at lower temperatures, as confirmed by studies using straw and pine wood biochar. At lower pyrolysis temperatures, incomplete decomposition results in residual organic matter coating the biochar surface. These residues can obstruct pore structures and create a less-defined surface morphology. Conversely, at higher temperatures, such as 700°C, the thermal energy is sufficient to drive off these residues, leaving a cleaner, more developed pore structure [64].

Guo et al. also found that increasing the pyrolysis temperature from 250°C to 700°C decreased the biochar yield but increased the ash content. The proportion of organic carbon increased, and the H/C ratio decreased, leading to higher aromaticity and lower polarity. The specific surface area (SSA) of the biochar also increased with temperature, indicating a higher degree of pore formation. This is critical because PFAS adsorption is strongly influenced by both the availability of micropores and surface hydrophobicity. The adsorption of PFOS was reported to be hydrophobic in nature, and this was enhanced at higher pyrolytic temperatures [53]. Among the biochars, BC700 exhibited the highest PFOS adsorption capacity (169.30 mg/g), attributed to its higher abundance of aromatic and non-polar groups. Furthermore, elevated temperatures led to an increase in aromatic ring C=O and C-H groups, which reduced the number of polar groups on the biochar surface, further enhancing its hydrophobicity and making it more favorable for PFOS adsorption [65].

Wang et al. (2023) expanded on these findings by examining biochar produced at pyrolysis temperatures of 300°C, 400°C, 500°C, and 600°C for PFAS remediation. They observed that as the pyrolysis temperature increased, the O/C ratio of the biochar decreased from 0.250 to 0.0553, while the H/C ratio dropped from 0.785 to 0.251. This indicates that the biochar became more aromatic and less polar as temperature increased. The specific surface area (SSA), measured using CO_2 adsorption, increased significantly from 219 to 698 m^2/g as the pyrolysis temperature rose. This increase in surface area, coupled with a more condensed aromatic structure, boosted the biochar adsorption capacity, as reflected in the higher K_D values observed for biochar pyrolyzed at 600°C [66].

Overall, these findings show that higher pyrolysis temperatures lead to more carbonized biochar with increased surface area, porosity, and hydrophobicity, which generally enhance PFAS removal performance. However, excessively high pyrolysis conditions may lead to diminishing returns in certain environmental contexts. For instance, very high pyrolysis temperatures (above ~700°C) can sometimes reduce micropore volume through sintering, which could negatively affect the adsorption of short-chain PFAS. Short-chain PFAS typically rely more on electrostatic and weaker hydrophobic interactions, which may be less effective with highly carbonized biochar. Therefore, optimizing pyrolysis temperature based on the specific application, biochar feedstock, and PFAS

chain length is crucial. Moreover, the high energy costs associated with extreme pyrolysis temperatures may limit the scalability of this approach for large-scale environmental applications, creating a trade-off between biochar effectiveness and economic feasibility, which has not been adequately addressed in much of the current literature.

Effect of particle size

Particle size of biochar is a critical parameter influencing PFAS sorption capacity in biochar. **Figure 7** presents the biochar particle sizes reported in the literature for PFAS adsorption. Smaller particles generally exhibit higher adsorption capacities due to increased surface area and exposure of more active sites. Hassan et al. (2020) demonstrated that biochar with smaller particle sizes (0.5 mm) showed significantly enhanced PFOS adsorption compared to larger particles (up to 2 mm). This increase in adsorption is attributed to the greater surface area and more accessible sorption sites [67].

Similarly, Xiao et al. (2017) found that PFOS and PFOA removal improved with finer particles, indicating that smaller particles reduce intraparticle diffusion limitations, thus enhancing sorption efficiency. However, larger particles may suffer from slower adsorption kinetics due to diffusion constraints. Despite these advantages, smaller particles may pose operational challenges in large-scale systems, including difficulties in separation, regeneration, and the risk of clogging in filtration setups. Therefore, an optimal particle size needs to be selected to balance sorption performance and practical feasibility in real-world applications [68].

Effect of competitive sorption

In order to examine how co-existing compounds affect PFASs sorption, Zhang et all (2019) studied the removal of PFOA, PFBS, PFOS, and PFBA in both single and mixed solutions using biochar [69]. Biochar was more effective at removing PFASs in Single-solution rather than mixed-solution, according to the results. PFAS removal efficiencies decreased by 32.8% to 57.9% in mixed-solutions, indicating competitive PFAS sorption throughout the sorption procedure. As previously reported [37], this competition between co-existing compounds and PFASs on the adsorbent surface could contribute to slow kinetics for PFASs adsorption, like pore block and diffusion-controlled transport into the pores of the adsorbent. As mentioned previously, in the presence of co-existing compounds, long-chain PFASs were preferentially adsorbed onto the sorbents due to their greater hydrophobic interaction than short chains [69].

While previous studies provided valuable insights, it is important to note that real-world scenarios, particularly in wastewater treatment, often involve complex mixtures of contaminants. For instance, real wastewater matrices contain natural organic matter (NOM), which could further interfere with PFAS sorption efficiency. This highlights a gap in the study where the potential impacts of NOM or other ubiquitous contaminants were not considered.

Effect of biochar dosage

The dosage of biochar is a key factor influencing PFAS adsorption, as numerous studies demonstrate a strong correlation between sorbent dosage and removal efficiency. However, there

is an optimal dosage beyond which additional biochar does not significantly improve removal. Once this point is exceeded, the availability of active sites diminishes due to particle aggregation or diffusion limitations, reducing the overall sorption capacity [7019].

At lower concentrations, smaller dosages can achieve effective removal, while higher concentrations require more biochar to ensure sufficient active site coverage. Additionally, higher dosages may initially accelerate adsorption, as observed in studies where increasing the biochar dosage significantly improved adsorption rates. However, excessive amounts can lead to diminishing returns, with reduced overall efficiency due to the saturation of available sites and physical limitations [7172].

Challenges in Scaling Functionalized Biochar for PFAS Remediation

The large-scale implementation of functionalized biochar for the remediation PFAS presents multifaceted challenges spanning technical, environmental, economic, and regulatory domains.

Technical Challenges

The efficacy of biochar in adsorbing PFAS is influenced by the chain length of the compounds. Studies demonstrate that biochar exhibits reduced removal efficiency for short-chain PFAS compared to long-chain counterparts, necessitating the development of tailored functionalization strategies to enhance adsorption across diverse PFAS structures [73].

The physicochemical properties of biochar, including pore structure and functional groups, are highly dependent on the feedstock and pyrolysis conditions. This variability can lead to inconsistent performance, underscoring the need for standardized production protocols to ensure uniform efficacy in PFAS remediation.

Developing efficient and cost-effective regeneration techniques for spent biochar remains an active area of research. Current methods, such as thermal treatment and solvent extraction, are often energy-intensive or environmentally taxing, making them impractical for large-scale real-world applications [74].

Environmental Challenges

The environmental sustainability of biochar production is influenced by the carbon footprint associated with pyrolysis processes, which vary based on biomass type and energy inputs. Mitigation strategies, including the use of renewable energy sources and optimization of pyrolysis parameters, are essential to minimize greenhouse gas emissions and enhance the overall environmental benefits of biochar application [75].

The improper disposal of PFAS-laden biochar poses a risk of secondary contamination to soil and water systems. Ensuring the safe handling, stabilization, and disposal of spent biochar is critical to prevent the re-release of adsorbed PFAS into the environment.

Economic Challenges

Although biochar is generally affordable, the functionalization processes required for PFAS remediation significantly increase costs. Scaling up these processes also incurs additional expenses for transportation, storage, and specialized application equipment.

The transition from laboratory-scale studies to full-scale applications introduces challenges in maintaining cost-effectiveness and operational efficiency. Addressing scalability concerns requires comprehensive pilot studies and the development of standardized protocols to ensure consistent performance across varying operational contexts [76].

Regulatory Challenges

The use of certain functionalization agents, such as nanoparticles, may pose environmental or health risks. Comprehensive risk assessments and the development of safer functionalization methods are necessary to meet regulatory standards [12].

Addressing these challenges requires a multidisciplinary approach, integrating advancements in material science, environmental engineering, economics, and policy development to realize the potential of functionalized biochar for PFAS remediation at scale.

Conclusions, gaps, and future perspectives

Numerous studies on environmental remediation are now concentrating on biochars and functiona lized biochars. Their extensive availability, cost-effectiveness, environmental acceptability, and significant sorption capacity make them appropriate for the sorption of numerous pollutant species. Based on the pollutant type and the technique used for generating the biochar, however, their adsorption capability varies significantly. Therefore, selecting the proper biochar for the appropriate pollutants is essential. In addition, a single type of biochar is probably insufficient to remove all categories of pollutants. Porosity, surface charge, pH, surface area, functional groups, and mineral content are physicochemical properties that affect the adsorption capacity of biochar. Therefore, the features of biochar must be comprehended and accounted for.

This paper reports a comprehensive analysis of the utilization of biochar to eliminate contaminants. The manuscript encompasses diverse parts, including the classification of biochar, the utilization of pristine and functionalized biochar for the removal of pollutants, and the eradication of PFASs and related techniques. In addition to highlighting the limitations and high costs of traditional contaminant removal methods, this article presents biochar as a promising alternative. This paper summarizes previous research on the application of pristine and functionalized biochar for PFAS removal and identifies key variables that influence the efficacy of this technique. Given that the utilization of biochar for PFAS removals a relatively new discipline, the paper suggests that additional research is necessary for the cases listed below.

- There are several types of functionalization strategies for improving the sorption capacity of biochar. Nevertheless, few studies have been conducted in this field, and the majority of research has employed unmodified biochar for removing PFAS contaminants. Therefore, additional research on the functionalization of biochar is required prior to its implementation for removal goals.

- Few investigations have been devoted to short-chain PFAS, and the available research shows that their removal efficacy is declining. Future research should prioritize the increased removal of short-chain PFAS compounds and expand its reach to include a wider variety of PFAS species in order to address this problem. This is especially crucial given that short-chain PFASs are anticipated to become more common in the environment as long-chain PFAS are replaced by them.

- To enhance the removal efficiency of short-chain PFAS, future research should explore the synergistic use of biochar with other treatment methods. For instance, coupling biochar adsorption with degradation techniques, such as advanced oxidation processes, photocatalysis, or enzymatic treatments, can improve the overall efficiency of PFAS remediation. Developing a framework that combines multiple treatment strategies will allow for the simultaneous capture and breakdown of PFAS, addressing both the persistence and mobility of these contaminants. This approach could offer a more comprehensive solution, particularly in real-world applications where PFAS co-exist with other pollutants in complex matrices.
- Machine learning, artificial intelligence, and data analytics are relatively new fields. The vast amount of data generated by biochar studies related to remediation necessitates the development of decision-making tools based on data-driven modelling, deep learning, and artificial intelligence. This will aid in the design, scalability, and development of biochar utilization for PFASs remediation. To accomplish this, a framework for incorporating AI and machine learning into the use of biochar has been proposed.
- To ascertain the sorption capacity of biochar, additional research is required. While some research has been conducted in this area, comparison is difficult because adsorption capacities have been measured in a variety of methods, including batch experiments and column modes. In addition, the preparation conditions for biochar adsorbents, such as temperature, time, and atmosphere, vary greatly, which further complicates efforts to compare them.
- Utilizing economical and eco-friendly modifiers, like industrial solid residues, could provide a viable future development path for reducing costs and promoting environmental sustainability. These pollutants include phosphogypsum, tailings, red mud, coal gangue, fly ash, and etc. By combining the pyrolysis of these industrial solid wastes with biochar raw materials, it is possible to reduce their toxicity while achieving stabilization and resource utilization, thereby reducing their negative environmental impact.
- Most studies on functionalized biochars have been conducted under controlled laboratory conditions, limiting their applicability to real wastewater systems. Future research should emphasize pilot-scale studies and field trials to evaluate the performance of biochar in the presence of co-contaminants and varying water chemistries. Addressing these operational challenges will help bridge the gap between laboratory findings and practical implementation in large-scale wastewater treatment systems.

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Declaration of interests

The authors declare no competing interests.

Figure Titles

Figure 1. Frequency of biochar characterization techniques in PFAS removal studies

Figure 2. a) The number of publications in the field of PFAS removal using biochar, b) The quantity of various PFAS contaminants eliminated by biochar

Figure 3. Word cloud of the keywords used in articles about PFAS removal utilizing biochar.

Figure 4. The techniques employed so far to functionalize biochar for removing PFASs.

Figure 5. The pH range of studies investigating biochar's capacity for PFAS removal.

Figure 6. The pyrolysis temperature selected for biochar in the currently available literature for PFAS sorption.

Figure 7. Biochar particle sizes reported in the literature for PFAS adsorption.

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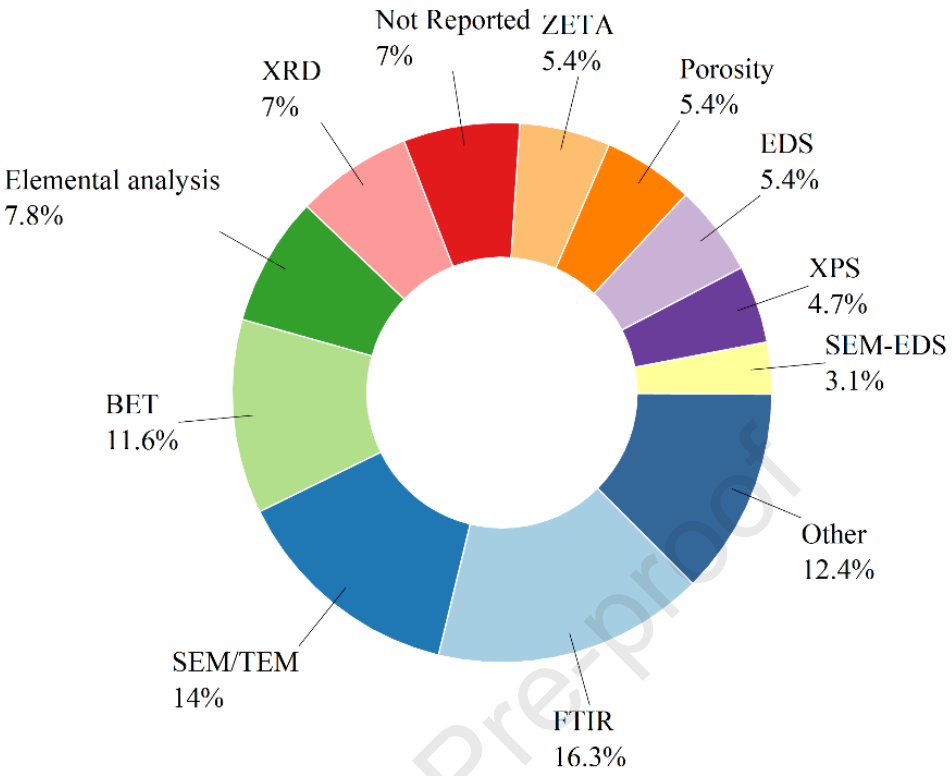

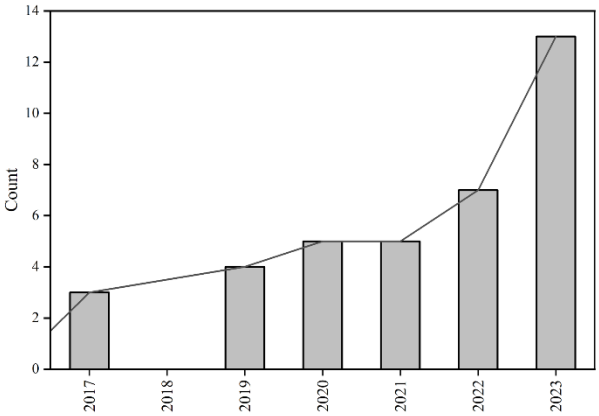

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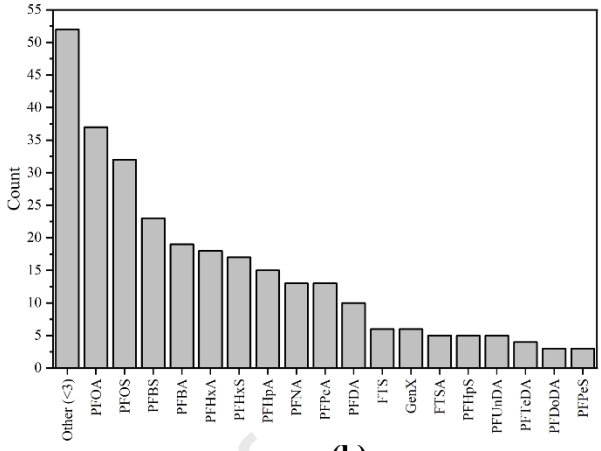

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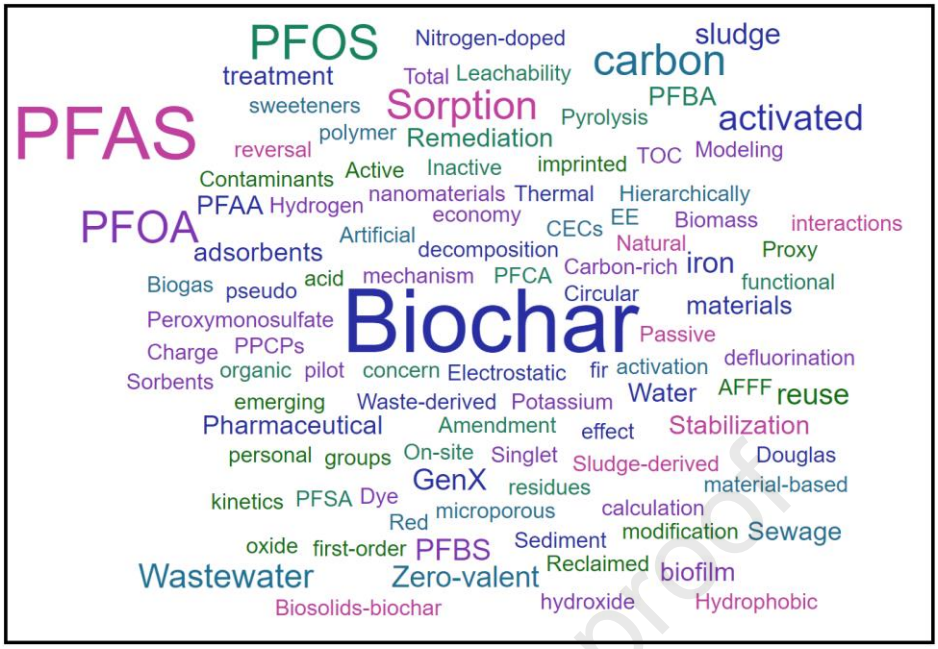

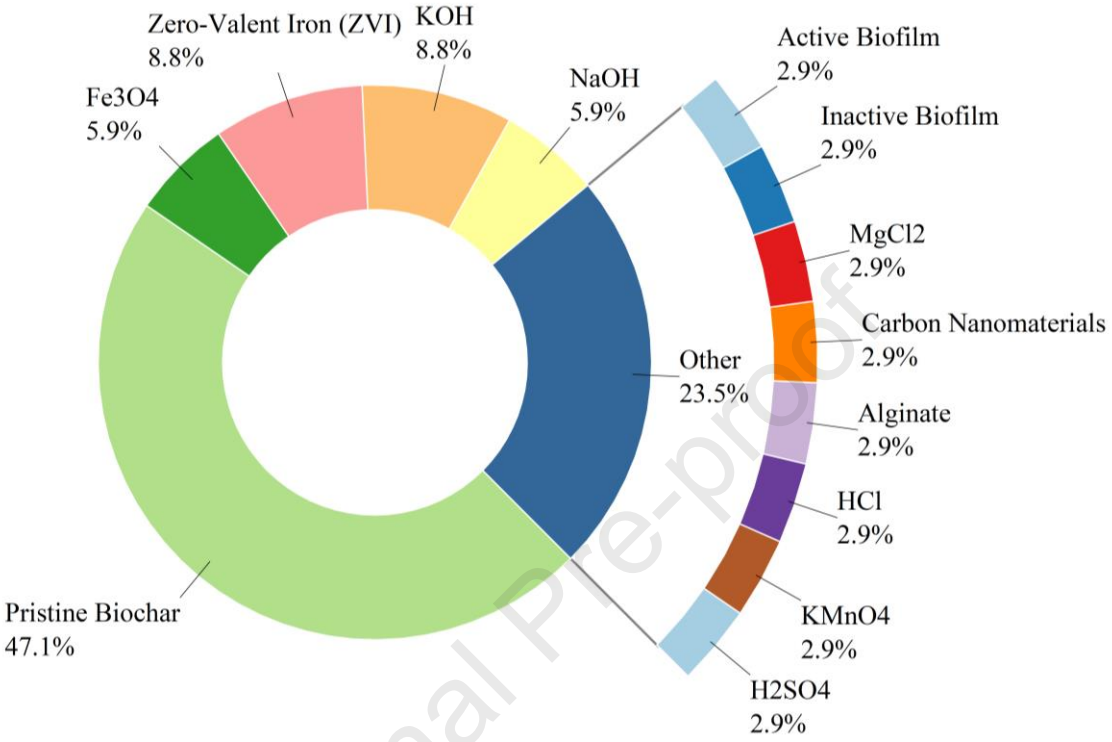

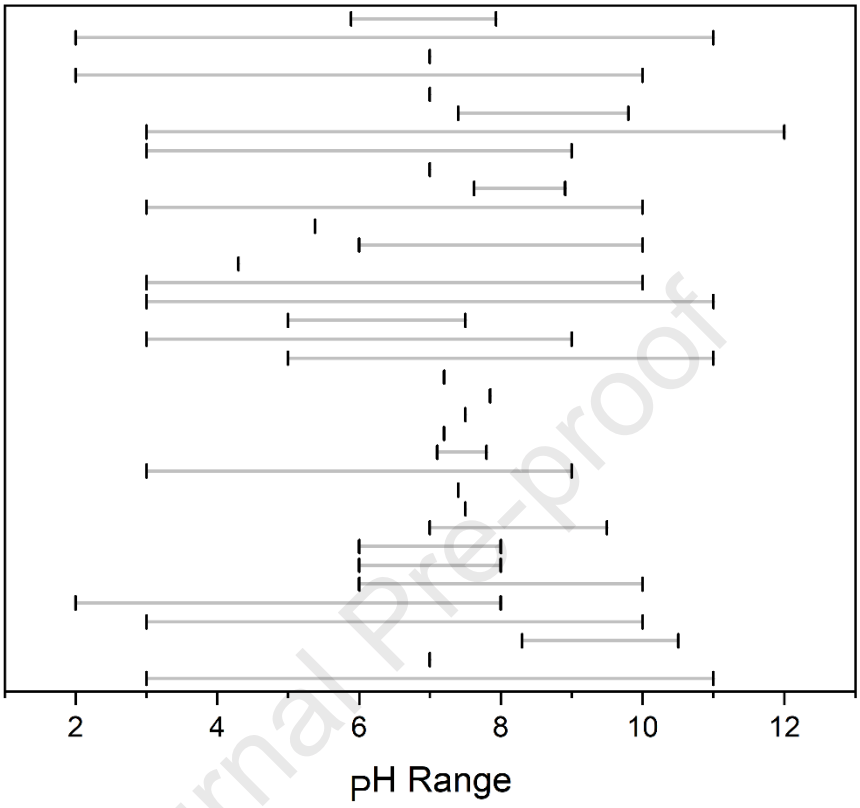

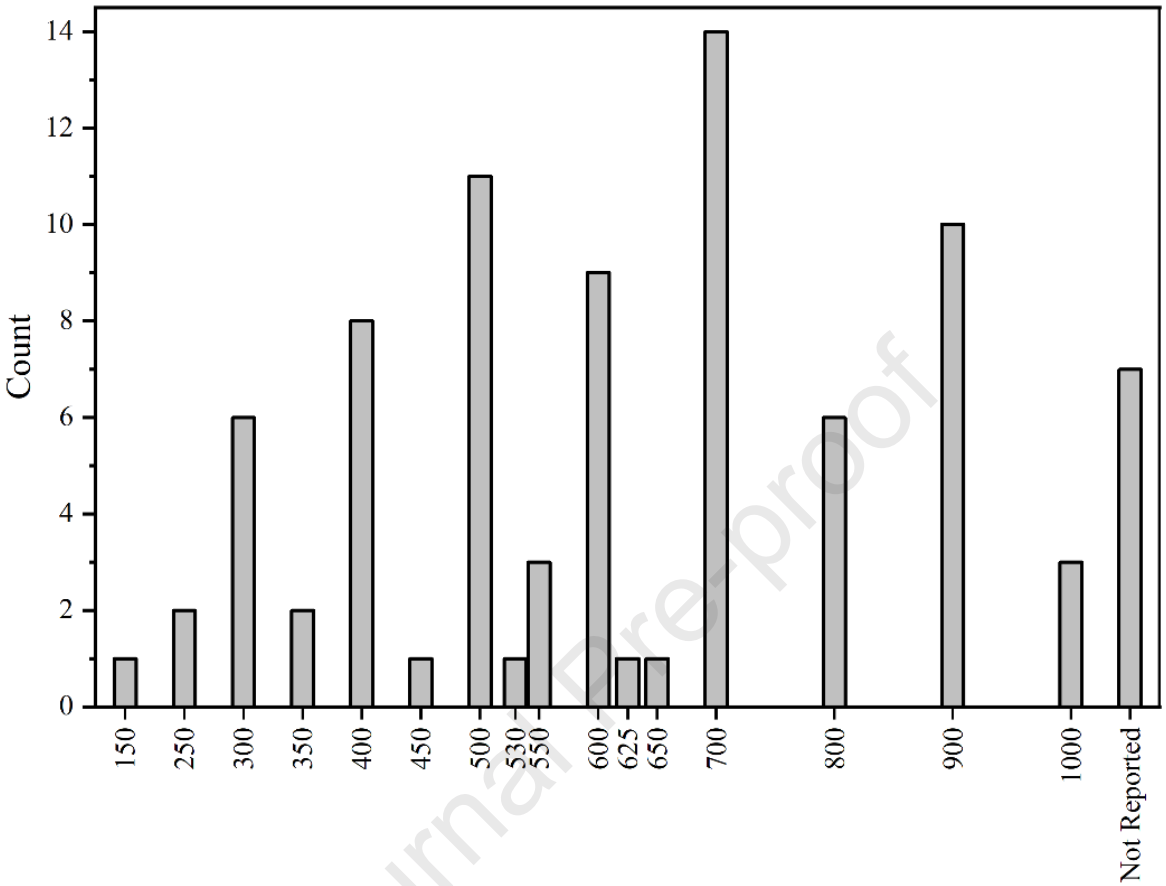

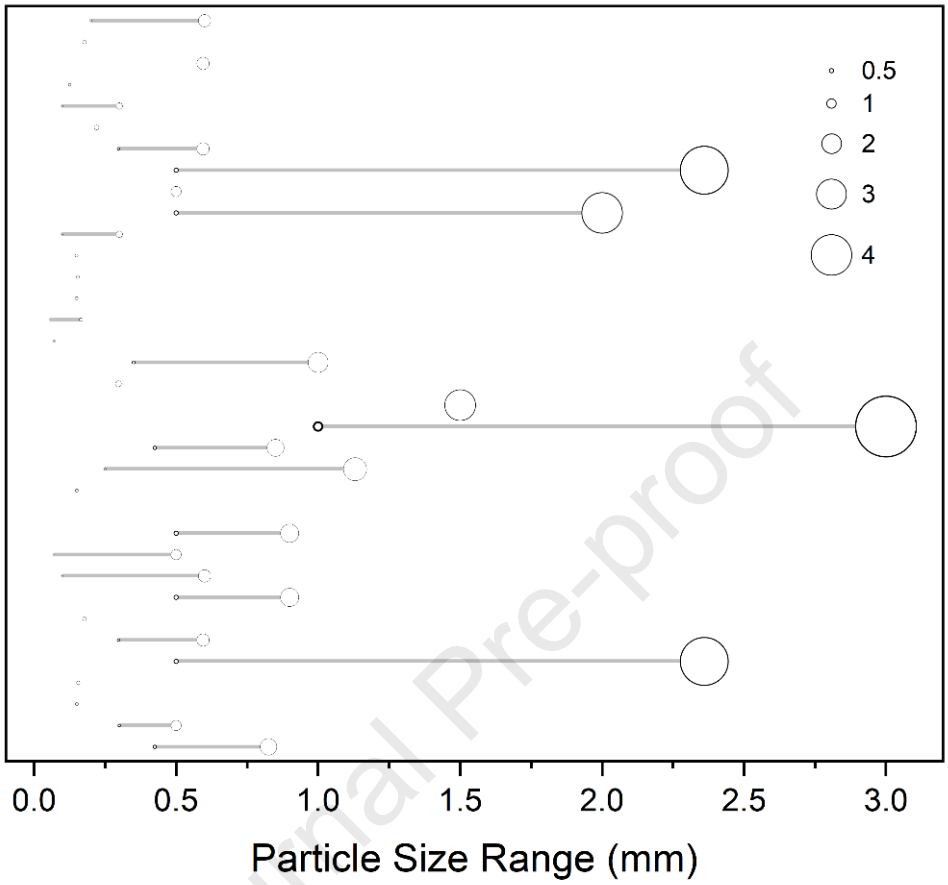

- Long-chain PFAS adsorb more effectively on biochar than short-chain PFAS.
- Functionalized biochar enhances PFAS removal via adsorption mechanisms.
- Pyrolysis temperature, pH, and PFAS chain length affect adsorption efficiency.