Advanced Chemical-Engineered Biochar for the Simultaneous Removal of Toxic Heavy Metals and Complex Organic Pollutants from Water

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Abstract: *The co-occurrence of heavy metals and organic pollutants in aquatic environments has become a critical global concern due to their persistence, toxicity, and complex interactions in multi-contaminant systems. Conventional water treatment technologies often exhibit limited efficiency under simultaneous contamination conditions and may involve high operational costs or secondary pollution. In this context, engineered biochars (E-BCs) has emerged as a promising multifunctional material for sustainable water remediation. This review comprehensively evaluates recent advances in the design, modification, and application of engineered biochar for the simultaneous removal of heavy metals and organic pollutants from water. Various engineering strategies, including metal/metal oxide doping, heteroatom functionalization, magnetic modification, nano-composite formation, and chemical activation, are systematically discussed. The fundamental mechanisms governing pollutant removal are critically analyzed, including ion exchange, surface complexation, electrostatic attraction, precipitation, π–π interactions, hydrogen bonding, hydrophobic interactions, and pore-filling effects. Particular emphasis is placed on competitive and synergistic adsorption behaviors in multi-pollutant systems. Furthermore, the influence of environmental parameters such as pH, temperature, ionic strength, and natural organic matter on adsorption performance is examined. Regeneration capacity, structural stability, environmental safety, and practical applicability in real wastewater matrices are also evaluated. Finally, current challenges and future research directions are highlighted to support the rational development of next-generation multifunctional biochar materials. Engineered biochar demonstrates significant potential as a cost-effective, environmentally friendly, and highly efficient solution for integrated water purification, particularly in complex contamination scenarios.*

Keywords: *Aquatic environments, engineered biochar, heavy metals, organic pollutants, water purification*

1. Introduction

Water contamination has emerged as one of the most critical environmental challenges of the 21st century due to rapid industrialization, agricultural intensification, and urban expansion [1,2]. Aquatic environments increasingly receive complex mixtures of pollutants, including heavy metals, pharmaceuticals, pesticides, dyes, and other persistent organic contaminants [3,4]. Unlike single-contaminant systems traditionally investigated in laboratory studies, real wastewater matrices typically contain multiple classes of pollutants simultaneously, leading to complex physicochemical interactions and increased ecological risks [5]. Among these contaminants, heavy metals such as lead (Pb^{2+}), cadmium (Cd^{2+}), chromium (Cr^{6+}), mercury (Hg^{2+}), and arsenic (As^{3+}/ As^{5+}) are of particular concern due to their toxicity, persistence, and non-biodegradable nature [6,7]. Heavy metals can accumulate in sediments and biota, enter the food chain, and cause severe health effects including neurotoxicity, carcinogenicity, and organ damage [8,9]. Concurrently, organic pollutants, including pesticides, antibiotics, endocrine-disrupting compounds, and polycyclic aromatic hydrocarbons (PAHs), are increasingly detected in surface water, groundwater effluents [10,11]. These organic contaminants may exhibit persistence, bioaccumulation potential, and antibiotic resistance induction effects [12]. The co-existence of heavy metals and organic pollutants in aquatic systems presents a more complicated environmental scenario than individual contamination. Their interactions may alter adsorption behavior, toxicity, speciation, and degradation pathways [13,14]. For instance, heavy metals may compete for active sites on adsorbents, while organic molecules may block pores or form complexes with metal ions, thereby

affecting removal efficiency [15,16]. Therefore, remediation strategies capable of simultaneously removing both pollutant categories are urgently required.

Conventional water treatment technologies such as chemical precipitation [17,18], ion exchange [19], membrane filtration [20-25], coagulation-flocculation [26,27], electrochemical processes [28-31], advanced oxidation processes [32,33], and biological treatments [34,35] have been extensively applied. Although these methods can achieve high removal efficiencies under optimized conditions, they often suffer from limitations including high operational cost, sludge generation, membrane fouling, secondary pollution, and reduced efficiency in multi-contaminant systems. Adsorption has gained significant attention as an attractive alternative due to its simplicity, high efficiency, reusability potential, and economic feasibility [36,37].

In recent years, biochars (BCs), a carbon-rich material produced through the pyrolysis of biomass under limited oxygen conditions, has emerged as a promising adsorbent for environmental remediation [38]. Biochar possesses several advantageous properties, including high surface area, well-developed porosity, surface functional groups (–OH, –COOH, $–NH_2$), and relative environmental compatibility [39]. Pristine biochar has demonstrated effectiveness in removing either heavy metals or organic pollutants individually from aqueous systems [40,41]. However, its performance in simultaneous removal scenarios is often limited due to insufficient surface functionality, low affinity for certain contaminants, and restricted active sites [42].

To overcome these limitations, significant research efforts have focused on the development of E-BCs, which involves physical, chemical, or nanomaterial-based modification to enhance adsorption capacity and selectivity. Engineering strategies include metal oxide loading (e.g., Fe_3O_4, MnO_2, TiO_2), acid/base activation, heteroatom doping (N, S, P), magnetic modification, and composite formation with graphene oxide or nanoparticles. These modifications can increase specific surface area, introduce new functional groups, enhance redox activity, and improve structural stability. Particularly, metal-doped biochars have shown enhanced affinity toward heavy metals through surface complexation, ion exchange, and precipitation mechanisms.

Peng et al. developed a FeS/Fe_3O_4 co-modified biochar via a facile one-step synthesis strategy and applied it for peroxymonosulfate (PMS) activation to degrade quinclorac (QNC) in aqueous systems. The engineered material achieved complete removal (100%) of QNC under optimized laboratory conditions and maintained a high degradation efficiency of 99.31% in real irrigation water, demonstrating strong resistance to interference from coexisting anions and natural organic matter. Ecotoxicity assessment further indicated that the transformation products exhibited lower toxicity compared to the parent herbicide. Their characterization results confirmed the homogeneous dispersion of FeS and Fe_3O_4 nanoparticles on the biochar matrix, providing abundant Fe^{2+} sites for PMS activation and reactive oxygen species (ROS) generation. The Fe^{3+} formed during the reaction was continuously reduced by sulfur species, sustaining an efficient Fe^{2+}/Fe^{3+} redox cycle. Radical quenching and mechanistic analyses revealed the coexistence of •OH, $SO_4•^-$, $^1O_2$, and $O_2•^-$, indicating the simultaneous involvement of radical and non-radical pathways. Density functional theory (DFT) calculations further supported PMS adsorption and charge redistribution processes, while electrochemical tests highlighted the contribution of electron transfer mechanisms to catalytic performance. Overall, Peng et al. demonstrated that co-modified biochar can effectively enhance PMS-based advanced oxidation processes for the removal of refractory organic pollutants in real water matrices [43].

Meanwhile, E-BCs containing aromatic domains and π-electron-rich structures exhibit strong interactions with organic pollutants via π–π stacking, hydrogen bonding, hydrophobic interactions, and pore-filling effects. Li et al. investigated the adsorptive removal of tetracycline (TC) and Hg(II) using ball-milled magnetic nanobiochars (BMBCs) derived from wheat straw. They demonstrated that BMBC700, prepared at 700 °C, could adsorb ≥ 99% of TC and Hg(II) within 12 hours. The maximum adsorption capacities were 268.3 mg/g for TC and 127.4 mg/g for Hg(II). Li and colleagues reported that the adsorption efficiency decreased with increasing ionic strength but increased when the solution temperature rose from 25 °C to 45 °C. Mechanistic analyses showed that TC removal was mainly governed by electrostatic interactions, hydrogen bonding, and Cπ–Cπ interactions, whereas Hg(II) adsorption was primarily controlled by electrostatic attraction, Hg–Cπ bond formation, and surface complexation. They also found that BMBC700 exhibited good recyclability and the advantage of magnetic separation [44].

Additionally, biochar-based nanocomposites integrated with photocatalytic materials such as TiO_2 or ZnO have demonstrated dual adsorption-degradation capabilities, offering synergistic removal performance. Khang et al. demonstrated the synthesis of a BDH/ZnO/TiO_2 nanocomposite via a hydrothermal method, where biochar derived from pyrolyzed biomass was activated with H_3PO_4 and combined with TiO_2 (anatase, 20-35 nm) and ZnO (wurtzite, 100-240 nm). The resulting material exhibited a significantly increased surface area (approximately 5.5 times higher than raw biochar) and enhanced porosity (14.761-34.143 Å). The nanocomposite showed superior photocatalytic and adsorption performance under UV irradiation (365 nm, 100 min) for 10 ppm methylene blue, achieving 98.57% removal and maintaining over 95% efficiency after three regeneration cycles, outperforming the individual TiO_2 (58.52%) and ZnO (40.38%) components. Adsorption data fitted the Freundlich isotherm model, with a maximum adsorption capacity of 52.21 $mg \cdot g^{-1}$, indicating synergistic dual functionality in adsorption and photodegradation [45].

These multifunctional materials hold considerable promise for the remediation of complex wastewater matrices. However, despite notable advancements, several critical challenges remain unresolved. The underlying mechanisms governing simultaneous adsorption of multiple contaminants are not yet fully elucidated, particularly under competitive multi-pollutant conditions. Furthermore, adsorption performance is highly sensitive to environmental factors, including pH, ionic strength, temperature, and the presence of natural organic matter (NOM) [46]. In addition, the long-term regeneration potential, structural integrity, and environmental implications of engineered biochar require comprehensive and systematic investigation to ensure both efficacy and sustainability in practical applications.

This review aims to provide a comprehensive assessment of engineered biochar for the simultaneous removal of heavy metals and organic pollutants from water. The synthesis strategies, physicochemical characteristics, adsorption mechanisms, performance evaluation, influencing factors, regeneration potential, and practical applications are discussed. Furthermore, current limitations and future research perspectives are highlighted to guide the rational design of next-generation multifunctional biochar materials for sustainable water remediation.

2. Methodology of the Review

This review study is prepared by reviewing more than 200 peer-reviewed articles, graduate theses, and meeting proceedings on EPs published from different countries across the world, available from 2020 to 2026. Documents were collected through an exhaustive search in recognized sources of peer-reviewed and other types of scientific information, such as Google Scholar, Science Direct, PubMed, Springer, Wiley, and MDPI. While searching the literature, certain keywords, such as 'engineered biochar', 'removal of heavy metals from water', 'removal of heavy metals and organic pollutants from water' were used. Articles with common information were excluded from the citation list.

3. Engineered Biochars (E-BCs): Synthesis and Characteristics

The performance of engineered biochar (E-BC) is intrinsically linked to its physicochemical properties, including surface area, pore structure, functional group composition, crystallinity, and morphology, which critically influence adsorption capacity, selectivity, and stability. Systematic characterization of these properties is essential to understand contaminant removal mechanisms and optimize biochar design for environmental remediation applications.

Pristine biochar, typically produced through pyrolysis of biomass under limited oxygen conditions, possesses intrinsic adsorption capabilities derived from its porous structure and limited surface functional groups. However, these natural physicochemical properties often constrain performance in complex wastewater treatment, particularly when multiple contaminants coexist. In contrast, E-BC is modified through physical, chemical, or nanomaterial-based strategies to enhance adsorption capacity, selectivity, and stability.

Approaches such as metal doping (e.g., Fe, Mn, Mg), acid/base activation, magnetic modification, and incorporation of nanocomposites introduce additional functional groups, increase surface area, and improve structural properties, rendering engineered biochar a more versatile and effective material for environmental remediation [47].

3.1. Chemical activation

Chemical activation is one of the most widely applied strategies to enhance the physicochemical properties of biochar, particularly its surface area, pore volume, porosity, cation exchange capacity (CEC), and surface functional groups [48]. This approach generally involves treating biomass or pristine biochar with acids (e.g., H_2SO_4, HCl, HNO_3, H_3PO_4), alkalis (e.g., KOH, NaOH), metal salts, or oxidizing agents such as $KMnO_4$ and Fe(III) under controlled thermal conditions and often in an inert atmosphere [49-54]. Activation can be conducted via one-step or two-step processes: in the one-step method, pyrolysis and chemical activation occur simultaneously, whereas in the two-step method, biochar is first produced by pyrolysis and subsequently subjected to chemical activation followed by secondary heat treatment [55]. Comparative studies indicate that the two-step process generally promotes greater surface area and pore structure development than the one-step route. Acid treatments typically enrich oxygen-containing functional groups, while alkaline modification enhances carbon content and microporosity; oxidizing agents further enlarge pore size and specific surface area. Beyond simple acid-base treatments, chemical modification also includes coating and impregnation techniques to produce biochar-based composites. In these methods, high-surface-area biochar serves as a scaffold for clays, carbonaceous materials (e.g., amino-functional polymers, chitosan, carbon nanotubes, graphene oxide), metal oxides, and functional nanoparticles [56,57]. Metal salts may be introduced either by pre-treating the biomass prior to pyrolysis or by post-synthesis impregnation, leading to the in-situ formation of metal hydroxides or nano-metal oxides within the biochar matrix. Although nanoparticles possess high surface reactivity and multiple active sites, their instability can limit direct application; immobilization onto biochar effectively overcomes this drawback while improving porosity, functional group diversity, thermal stability, and contaminant affinity.

More recently, oxygen plasma activation has emerged as an environmentally friendly and efficient alternative to conventional chemical treatments. In this process, oxygen gas is ionized under dielectric barrier discharge conditions, generating reactive species such as electrons and oxygen ions that interact with the biochar surface. This interaction introduces additional oxygen-containing functional groups and increases surface reactivity without extensive chemical consumption.

For example, Wang et al. demonstrated the effectiveness of oxygen plasma treatment as a green activation strategy for raw biochar subsequently applied as an electrode material in electric double-layer capacitors (EDLCs) and capacitive deionization (CDI) systems. Plasma treatment significantly enhanced electrochemical performance, increasing the specific capacitance from 80 to 97.5 F g^{-1}. In addition, the desalination capacity of plasma-activated biochar was approximately 1.2 times higher than that of untreated biochar. These improvements were attributed to the modulation of surface functional groups, surface charge, and textural characteristics induced by plasma activation [58]. These chemical and plasma-based modification strategies enable the tailored design of biochars with enhanced adsorption performance for environmental applications.

3.1.1. Acidic, Alkaline, and Oxidative Modification

Acid treatment primarily aims to remove mineral impurities and metals from the biochar surface while introducing oxygen-containing functional groups such as carboxyl (–COOH), hydroxyl (–OH), phenolic, lactonic, and carbonyl moieties [59]. Common acids used include HCl, HNO_3, H_2SO_4, H_3PO_4, citric acid, and oxalic acid. Acid oxidation generally increases hydrophilicity and may enhance microporosity and specific surface area, although the extent of these changes strongly depends on acid type and concentration. In some cases, substantial improvements in BET surface area have been reported; for example, sulfuric acid activation increased surface area more than 250-fold compared to pristine biochar [60]. However, strong acid treatment can also damage pore structures or reduce mineral components essential for certain adsorption mechanisms. For instance, while HCl modification effectively decreases ash content and removes surface metals, it may not be ideal for heavy metal adsorption, where mineral-mediated precipitation plays a key role. Additionally, excessive oxidation may weaken π–π interactions, potentially reducing adsorption of aromatic organic compounds. Liu et al. investigated the adsorption performance of chemically modified biochars derived from walnut shell (WSC) and wood powder (WPC) prepared by limited-oxygen pyrolysis. The biochars were activated with $ZnCl_2$, KOH, H_2SO_4, and H_3PO_4 and tested for methylene blue (MB) removal. The modified materials exhibited mesoporous structures,

while alkaline activation significantly enhanced pore development and specific surface area, particularly for KOH-modified biochar. The presence of oxygen-containing functional groups further increased the number of active adsorption sites. Wood-derived biochar showed superior performance compared to shell-derived biochar (WPC > WSC), and the effectiveness of activating agents followed the order $ZnCl_2$ > KOH > H_3PO_4 > H_2SO_4. The maximum adsorption capacities reached 850.9 mg g^{-1} for $ZnCl_2$-modified WPC and 701.3 mg·g^{-1} for KOH-modified WSC, highlighting the potential of chemically activated biochars for dye removal from aqueous systems [61]. Jiang et al. developed a phosphoric acid-modified biochar through the co-pyrolysis of agricultural straw and industrial tire wear particles (TWPs) for Cr(VI) removal from aqueous solutions. The optimized material (PBC-3) achieved 90.43% removal efficiency with an adsorption capacity of 10.851 mg·g^{-1}. The adsorption mechanism involved electrostatic attraction, surface complexation, and redox reactions, where Cr(VI) was partially reduced to Cr(III) or metallic Cr and immobilized on the biochar surface, while another fraction interacted with oxygen-containing groups to form CrO_3. The adsorbent also showed good stability and reusability under different environmental conditions, demonstrating the potential of waste-derived biochars for heavy metal remediation [62].

Alkaline activation, typically using KOH or NaOH, is another effective modification strategy [63]. Base treatment often promotes higher aromaticity, increases the N/C ratio, decreases the O/C ratio, and enhances pore development. It may also reduce certain acidic oxygen-containing groups (e.g., C=O) while enriching hydroxyl functionalities. NaOH is considered less corrosive and thermally stable compared to KOH in some applications. Significant surface area enhancement has been observed following alkaline treatment; for example, NaOH-modified coconut biochar exhibited improved surface roughness and adhesion properties. At NaOH concentrations of 4% and 6%, the increased surface roughness enhanced peel strength, reaching 15.6 N and 15.9 N, respectively. However, when the concentration increased to 8%, excessive surface etching reduced the peel strength to 3.7 N. These results indicate that moderate alkaline treatment can enhance surface characteristics and interfacial adhesion, whereas excessive treatment may reduce the effective surface area and adhesion performance [64]. In another study, Su et al. investigated the performance of KOH-modified biochar (KBC) for Zn removal and stabilization in bioretention systems using batch experiments and density functional theory (DFT) calculations. KBC removed 89.0–97.5% of Zn from influent water, mainly through complexation and precipitation, with precipitation being the dominant mechanism. Approximately 67% of Zn was immobilized in the residual fraction, indicating enhanced stabilization. Moreover, KBC significantly suppressed secondary Zn release under acidic and saline runoff conditions, reducing it by 43.6% and 37.08%, respectively. These results suggest that KOH-modified biochar can effectively control Zn-contaminated runoff and mitigate secondary metal release under conditions such as acid rain or snowmelt [65]. Beyond acid and alkaline activations, oxidizing agents such as H_2O_2, $KMnO_4$, and O_3 are used to introduce additional reactive oxygen species onto biochar surfaces. Oxidant-modified biochars often demonstrate improved thermal stability and strong affinity for pollutants. For example, Chang and Li reported that $KMnO_4$-modified biochar derived from cotton stem exhibited abundant surface functional groups and increased surface area, achieving a maximum Pb(II) adsorption capacity of 144.49 mg·g^{-1} at pH 5 [66]. Chemical modification using acid, alkaline, or oxidant treatments effectively enhances biochar surface chemistry and pore structure, improving the removal of metal(loid)s and organic pollutants from wastewater. Large-scale soil applications may be limited by the costs associated with chemical reagents, equipment, and energy requirements.

3.1.2. Iron modification

Iron modification has emerged as one of the most effective and commonly applied approaches to enhance the performance of biochar in large-scale environmental remediation. This is mainly attributed to the natural abundance of iron, its relatively low cost, and its lower environmental risk compared with many other metal-based modifiers. This approach is mainly applied to improve the separation and recyclability of biochar, while simultaneously enhancing its decontamination capacity through interactions between the incorporated and target contaminants [67]. Fe-modified biochars can be synthesized through different preparation techniques such as co-pyrolysis,

precipitation, thermal reduction, and ball-milling, which are generally categorized as either biomass pre-treatment or post-treatment of iron materials [68-73] (Figure 1).

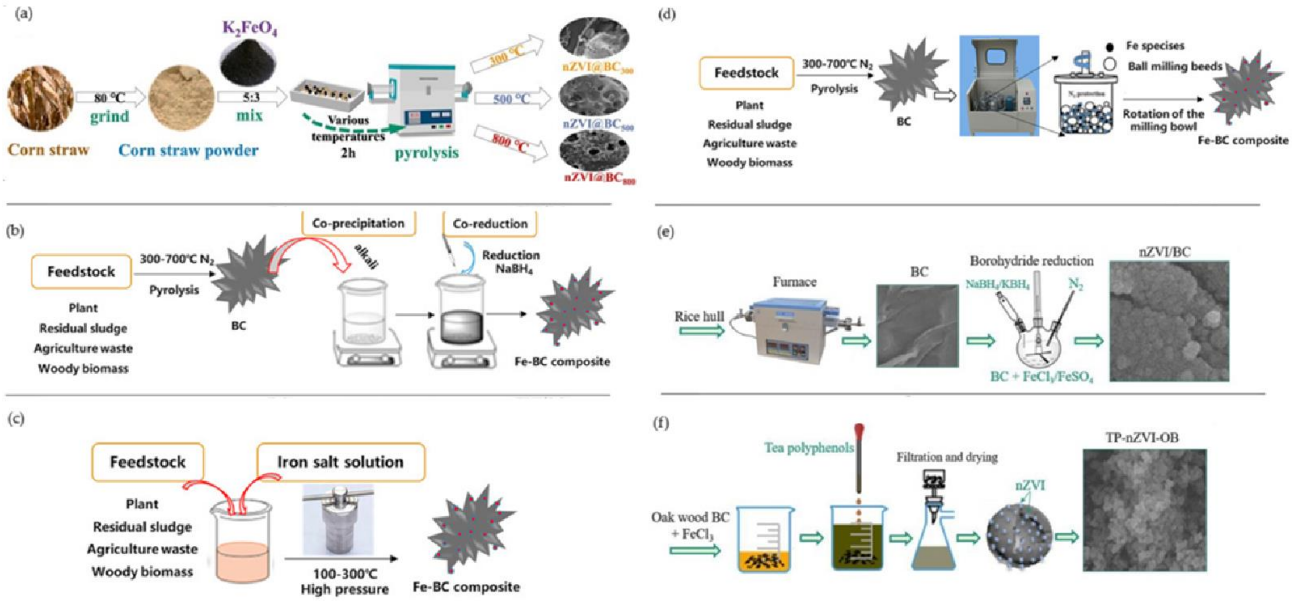

Fig. 1. Methods for preparing iron-based biochar materials: (a) one-step pyrolysis method. Reproduced with permission from ref. [70]. Copyright © 2024 Elsevier, (b) co-precipitation method, (c) hydrothermal carbonization method. Reproduced with permission from ref. [71]. Copyright © 2021 Elsevier; (d) ball milling method (e) chemical reduction method. Reproduced with permission from ref. [72]. Copyright © 2022 Elsevier, and (f) green synthesis Reproduced with permission from ref. [73]. Copyright © 2020 Elsevier.

Various iron compounds, including iron oxides (e.g., hematite (Fe_2O_3) and goethite (α-FeOOH)), iron sulfide (FeS), and nano zero-valent iron (nZVI), have been used to modify biochar [74, 75]. For example, Zhu et al. synthesized α-FeOOH-modified wheat straw biochar (α-FeOOH@BC), which exhibited maximum adsorption capacities of 63 mg g^{-1} for Cd(II) and 78 mg g^{-1} for As(III) [76]. Similarly, Kim et al. modified rice husk biochar through ball-milling with iron-based materials, magnetite (Fe_3O_4) and pyrite (FeS_2), followed by re-pyrolysis at 600 °C to produce Fe_3O_4-BC and FeS_2-BC. In dual-element aqueous systems, Fe_3O_4-BC achieved 99.62% Cd and 62.39% As removal, while FeS_2-BC removed 81.73% Cd and 55.54% As. In comparison, unmodified biochar showed slightly lower efficiencies (99.04% Cd and 54.31% As), indicating the enhancement provided by iron-based modification [77]. Beyond adsorption, Fe-modified biochar can also facilitate redox reactions that reduce the toxicity of contaminants such as As(III), Cr(VI), and U(VI) [78]. Materials modified with nZVI, FeS, or FeOOH can provide reductive species such as Fe^0, Fe(II), or S(II), enabling the transformation of hazardous compounds into less toxic forms. For instance, Zhou et al. reported that nZVI-modified biochar achieved an adsorption capacity of 54.4 mg·g^{-1} for Cr(VI) while simultaneously reducing it to the less toxic Cr(III) [79]. Similarly, Liu et al. also observed that FeS- and starch-modified peanut shell biochar effectively reduced U(VI) to stable U(IV) species, highlighting the role of Fe^0 and S(II) in the reduction mechanism [80]. Due to its electron-transfer capacity, persistent free radicals, and oxygen-containing functional groups, Fe-modified biochar can activate oxidants such as H_2O_2, peroxomonosulfate (HSO_5^-, PMS), peroxodisulfate ($S_2O_8^{2-}$, PDS), and ozone to generate reactive oxygen species (ROS), including •OH, $^1O_2$, and SO_4•$^-$ (Equations (1), (2), (3), (4))). These species contribute to the degradation of various organic pollutants, including tetracycline, bisphenol A, metronidazole, and phthalate esters [81-84]. Therefore, Fe-modified biochar is also widely investigated as a catalyst in advanced oxidation processes, particularly in Fenton-like and persulfate activation systems [85]. For example, Herath et al. developed developed a metal oxide–biochar composite (Fe_2TiO_5/BC) for the simultaneous removal of Pb^{2+}, Cr^{6+}, F^-, and methylene blue (MB) from aqueous solutions. Under acidic conditions (pH 3), partial iron leaching promoted Photo-Fenton degradation of MB. Band gap analysis of Fe_2TiO_5, BC, and Fe_2TiO_5/BC indicated improved photocatalytic activity compared with

conventional TiO_2-based systems. Under UV irradiation (365 nm), MB removal occurred through a combined adsorption–photocatalytic mechanism at pH 3–6. The composite also showed high removal efficiencies for Cr^{6+}, Pb^{2+}, F^-, and MB even in the presence of multiple competing ions in simulated water systems [86].

$$H_2O_2 + Fe^{2+} \rightarrow OH^- + \bullet OH + Fe^3 \quad (1)$$

$$HSO_5^- + Fe^{2+} \rightarrow SO_4^{\bullet-} + OH^- + Fe^{3+} \quad (2)$$

$$HSO_5^- + Fe^{2+} \rightarrow SO_4^{2-} + \bullet OH + Fe^{3+} \quad (3)$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe^{3+} \quad (4)$$

Despite these advantages, conventional iron-based Fenton catalysts tend to aggregate and may suffer from iron ion leaching, which can reduce catalytic efficiency [87]. To address this limitation, various carbon-based supports such as reduced graphene oxide (rGO), carbon nanotubes, and activated carbon have been employed to improve the dispersion of active iron species and enhance catalytic stability [88].

3.1.3. Metal oxides and metal salts

The incorporation of metal oxides or metal salts onto biochar can significantly improve its adsorption performance by introducing additional functional active sites on the surface. Among various metals used for modification, Fe is the most widely studied and has been discussed in detail in Section 3.1.2. In addition to Fe, manganese (Mn) has attracted considerable attention because of its natural abundance, relatively simple preparation procedures, and environmentally friendly characteristics [89]. For instance, Jia et al. synthesized a series of Mn-coated biochars with different Mn-to-biochar mass ratios using $MnSO_4 \cdot H_2O$ as the precursor. The prepared materials exhibited maximum adsorption capacities of 0.94 $mg \cdot g^{-1}$ for Sb(III) and 0.73 $mg \cdot g^{-1}$ for Sb(V). Furthermore, Mn-modified biochar has shown excellent catalytic activity in persulfate activation systems [90]. In addition, Liu et al. reported that Mn-modified nMnOx@RBC biochar achieved nearly 100% removal efficiency of 4-chloro-3-methylphenol (CMP), which was mainly attributed to the generation of reactive oxygen species such as $SO_4\bullet^-$, •OH, and $^1O_2$, promoting the degradation of CMP [91]. Besides Fe and Mn, a variety of other metals have also been explored for biochar modification, including magnesium (Mg) [92], aluminum (Al) [93], copper (Cu) [94], cerium (Ce) [81], lanthanum (La) [95], zirconium (Zr) [96], and bismuth (Bi) [97]. These studies demonstrate that incorporating different metal species into biochar enhances adsorption performance and catalytic activity, highlighting the versatility of metal-modified biochars.

3.1.4. Nonmetallic heteroatoms

Doping biochar with non-metallic heteroatoms has recently gained increasing attention as an effective strategy to tailor the electronic structure and surface chemistry of biochar, thereby improving its adsorption and catalytic capabilities for pollutant removal [47]. Among the various heteroatoms explored, nitrogen (N), sulfur (S), and boron (B) are the most frequently used elements for biochar modification. In addition, phosphorus-doped [98] and iodine-doped biochars [99] have also been reported for the removal of contaminants from aqueous systems.

Nitrogen is the most studied heteroatom in biochar doping, where it integrates into the carbon framework in various configurations, markedly affecting surface chemistry and catalytic properties.

Nitrogen in doped biochar generally exists as amine functional groups, pyridinic N, pyrrolic N, graphitic N, and nitrogen oxide species ($–NO_x$) [100] (Figure 2). Graphitic nitrogen facilitates electron mobility within the carbon matrix, which improves catalytic efficiency during processes such as persulfate activation [101]. In contrast, pyrrolic and pyridinic nitrogen species can donate electrons and generate structural defects, providing additional active sites on the biochar surface. Amine-type nitrogen groups can also serve as coordination sites for metal(loid) ions through chelation interactions [102]. Owing to these characteristics, N-doped biochar has been widely investigated for the removal of various contaminants including antibiotics [103], phenolic compounds [104], dyes [105-107], and heavy metals[108-112].

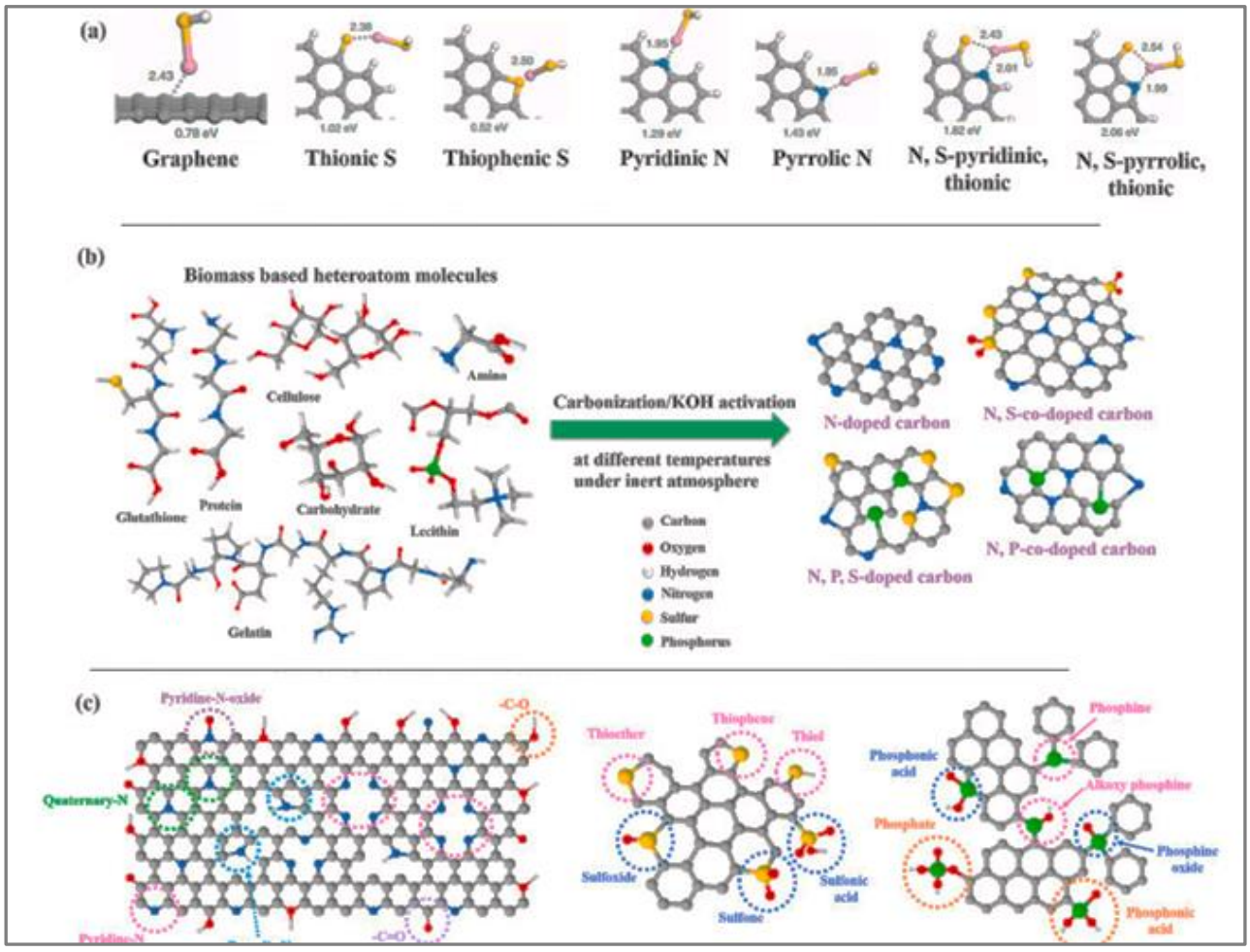

Fig. 2. (a) Model of binding energy of undoped graphene, S-doped graphene, N-doped graphene, and N, S-co-doped graphene with LiSH interaction, (b) schematic illustration of heteroatoms self-doped porous carbon derived from biomass sources; Types of N, P and S in biomass. Reproduced with permission from Ref. [100] Copyright © 2024 Elsevier.

Nitrogen doping enhances biochar properties such as pore structure, surface area, conductivity, catalytic activity, and adsorption capacity, while nitrogen-containing functional groups can actively promote catalytic reactions like ester hydrolysis [113,114]. Similarly, sulfur doping introduces functional groups (C–S, C–S–C, C=S, C–S–O, $–SO_3^{2-}$, $–SO_4^{2-}$) that improve adsorption and catalytic behavior [107,115,116]. For example, Ahmed et al. showed that sulfur-modified sawdust biochar significantly increased Cd adsorption (up to 9-fold), with maximum capacities of 39.38, 20.84, and 34.14 mg g^{-1} depending on the sulfur source, via mechanisms including electrostatic attraction, Cd–π interactions, surface complexation, and ion exchange [117].

Boron doping similarly alters electronic structure, increases defects and active sites, and improves surface chemistry [118]. Boron-modified corn-straw biochar exhibited a high surface area (898 m^2 g^{-1}) and enhanced Fe(II) adsorption via surface complexation, ion exchange, and co-precipitation [118]. Boron incorporation is typically achieved during pyrolysis using boric acid, borax, or boron carbide, or via hydrothermal carbonization followed by doping. For instance, Xue et al. [119] prepared a boron-doped biochar by initially converting *Zoysia sinica* into hydrothermal carbon (HC) through hydrothermal treatment at 180 °C for 4 h. The resulting HC then served as a precursor material for subsequent boron doping and carbonization. Pyrolysis is the most common method for boron incorporation due to its simplicity, scalability, and efficiency. In this process, biomass or pre-activated biochar is thermally treated to integrate boron species, typically sourced from boric acid, sodium tetraborate decahydrate (borax), or boron carbide, into the carbon framework.

Liu et al. [120] demonstrated that when boric acid is mixed with ethanol, a chemical reaction occurs leading to the formation of triethyl borate. During thermal treatment, this compound interacts with hydroxyl groups present in cellulose, hemicellulose, and lignin within the biomass structure.

3.1.5. Carbon nanomaterials

Carbon nanomaterials such as graphene, graphene oxide, carbon nanotubes, and graphitic carbon nitride are widely employed as functional modifiers in the synthesis of biochar-based composites [121]. These materials exhibit a strong affinity toward a wide range of pollutants; therefore, incorporating carbon nanomaterials into biochar structures has attracted considerable attention as a strategy to improve adsorption capacity for toxic contaminants. Among these materials, graphene is a two-dimensional structure composed of sp^2-hybridized carbon atoms arranged in a hexagonal lattice. This unique configuration provides several outstanding physicochemical properties, including high electron mobility, strong π–π interactions, excellent mechanical strength, high biocompatibility, and a remarkably large specific surface area. Owing to these characteristics, graphene demonstrates strong adsorption potential for both organic and inorganic contaminants. Consequently, graphene-modified biochar composites have been explored as effective sorbents for environmental remediation. However, despite their high adsorption capacity, the production of graphene-based biochar often requires extensive pretreatment processes, which significantly increase the cost and limit their feasibility for large-scale applications [122,123].
Graphene oxide (GO) has been extensively investigated as a functional modifier for biochar. Several studies have demonstrated that GO-modified biochar can effectively remove heavy metals such as Cd(II), Cr(VI), As(III) and As(V), and Pb(II), as well as organic contaminants including atrazine. These materials typically interact with pollutants through mechanisms such as complexation, electrostatic attraction, and strong binding with oxygen-containing functional groups present on the graphene-based biochar surface [124]. For example, Liu et al. developed a graphene-modified biochar (GB) supported nanoscale zero-valent iron composite (GB/nZVI) for the simultaneous removal of Cd(II) and As(III) under aerobic conditions. The composite exhibited high sorption capacities of 363 $mg \cdot g^{-1}$ for As(III) at pH 4 and 92.8 $mg \cdot g^{-1}$ for Cd(II) at pH 7, calculated based on the nZVI content. These values were considerably higher than those achieved using GB or nZVI individually, indicating a strong synergistic interaction between the two components. In this system, GB promoted the oxidation of nZVI to iron oxyhydroxides, which also facilitated the conversion of approximately 35% of As(III) to As(V). Moreover, the presence of As(III) further improved Cd(II) removal, reaching 131.8 $mg \cdot g^{-1}$ [125].
Despite these advantages, carbon nanomaterial-coated biochars face limitations, including the lack of comprehensive studies on their long-term stability and environmental impacts in soil systems, which hinders large-scale implementation [126]. Furthermore, many coatings are non-biodegradable and costly to synthesize, limiting their economic feasibility for environmental applications.

3.1.6. Clay minerals

Natural clay minerals such as bentonite, montmorillonite, sepiolite, vermiculite, zeolite, kaolinite, and illite (Figure 3) are abundant, inexpensive, and nontoxic materials widely explored for heavy metal removal due to their layered structures, large surface areas, and ion-exchange capacities. For example, bentonite and montmorillonite exhibit strong electrostatic attraction toward metal ions, while vermiculite and sepiolite provide additional adsorption sites through interlayer interactions and surface complexation. Kaolinite and illite generally show lower adsorption capacities due to tightly bound layers and restricted cation exchange, but their performance can be enhanced via surface modifications or incorporation into biochar composites.
Several studies illustrate the potential of these materials: Ramola et al. demonstrated nearly complete Pb removal using bentonite-biochar composites [127], while Zhang et al. reported effective removal of multiple heavy metals using montmorillonite-based biochar composites [128]. Deng et al. highlighted phosphate removal using sepiolite-modified biochar [129], and Al-Swadi et al. showed pH-dependent adsorption improvements on kaolinite-modified biochar [130].
Integrating clay minerals with biochar enhances porosity, cation exchange capacity, and adsorption efficiency, making clay-biochar composites promising materials for water remediation [131].

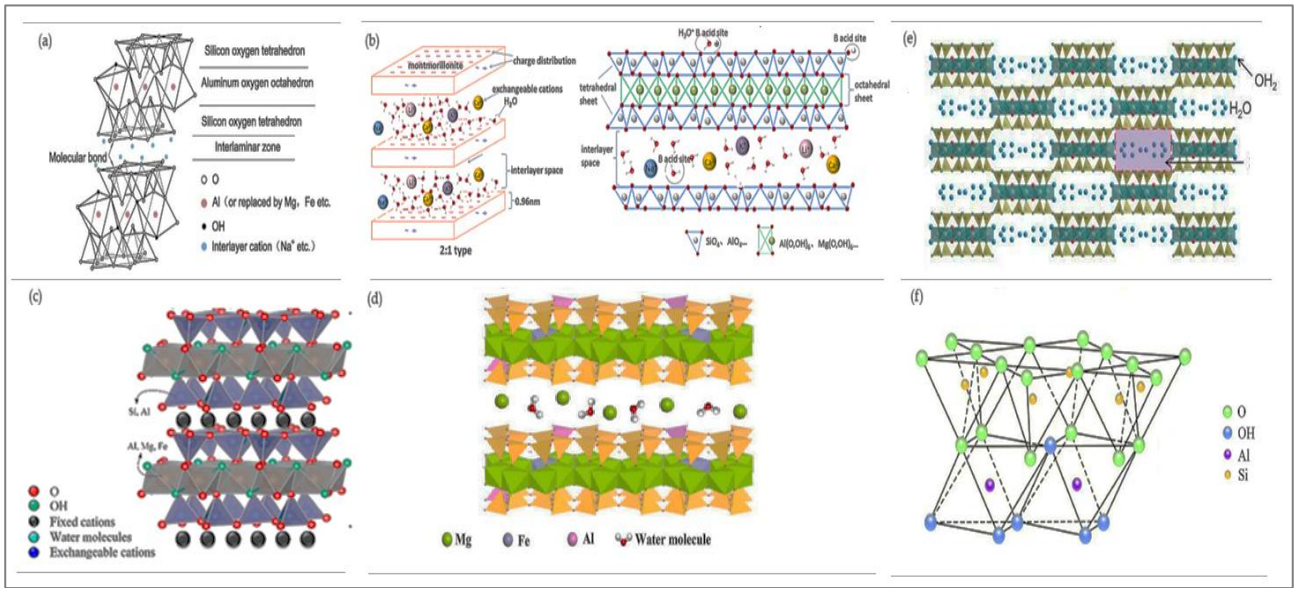

Fig. 3. Crystal structures of (a) bentonite, (b) montmorillonite (MMT), (c) illite, (d) vermiculite, (e) sepiolite and (f) kaolinite. (a) Reproduced with permission from Ref. [132] Copyright © 2024 Elsevier. (b) Reproduced with permission from Ref. [133] Copyright © 2025 Elsevier. (c) Reproduced from [125] under the Creative Commons CC BY license 4.0. (d) Reproduced with permission from Ref. [134] Copyright © 2022 Elsevier. e) sepiolite Reproduced with permission from Ref. [135] Copyright © 2024 Elsevier and (f) Reproduced with permission from Ref. [136] Copyright © 2022 Elsevier

3.1.7. Layer double hydroxides (LDHs)

Layered double hydroxides (LDHs) are effective adsorbents due to their layered structure and strong anion-exchange capability [137]. However, dense stacking can limit adsorption efficiency [138]. To overcome this, LDH nanoparticles are often combined with biochar, resulting in BC/LDH composites with enhanced surface area, functional groups, stability, and overall adsorption performance [139-41]. For example, MgAl-LDH/biochar from engineered wood sawdust efficiently removed Pb and Cr ions [142] (Figure 4a), while ZnCo-LDH/biochar showed improved photocatalytic degradation of antibiotics due to reduced particle aggregation [143]. Wang et al. further demonstrated that E-Mg/Al-LDH-BC removed Pb(II) and Cd(II) via cation exchange, surface complexation, mineral precipitation, and electrostatic interactions [144] (Figure 4b). These results highlight the potential of LDH-biochar composites as multifunctional materials for water remediation.

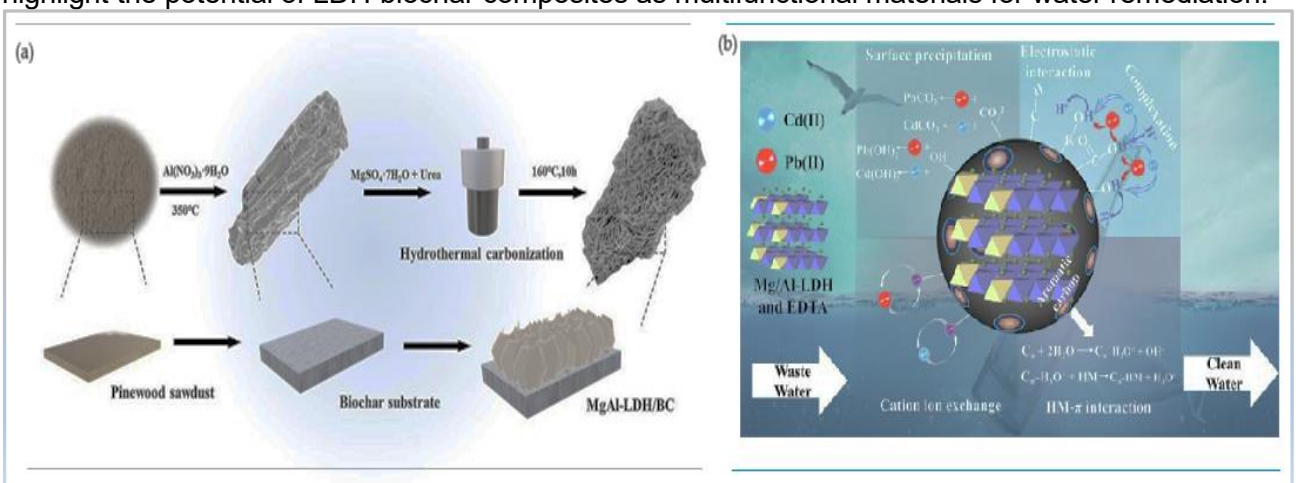

Fig. 4. (a) Preparation of MgAl-LDH/BC and illustration of its structure. Reproduced with permission from Ref. [142] Copyright © 2020 Elsevier. (b) Scenario diagram of the removal mechanism. Reproduced with permission from Ref. [144] Copyright © 2024 Elsevier.

3.1.8. Organic surfactants

Organic surfactants can also modify biochar surface properties, influencing surface area, functional groups, and hydrophobicity. Surfactant molecules attach through electrostatic, hydrogen-bonding, π–π, and hydrophobic interactions, forming mono- or bilayers that enhance adsorption of both inorganic and organic pollutants (Figure 5). For instance, CTAB-functionalized peanut shell biochar improved Cr(VI) removal from 37.47% (pristine) to 79.35% [146]. Similarly, SDS/SAP-modified biochar (SDMBC) significantly increased adsorption capacities for Pb(II), Cd(II), and various organics, maintaining performance even in mixed pollutant systems [145]. Broccoli-derived biochar modified with H_2SO_4 and CTAB achieved removal efficiencies of up to 99.9% for dyes and 98.6% for Pb^{2+} [147]. Non-ionic surfactants like Triton X-100 have been used to improve Pb(II) uptake while sometimes reducing polymer adsorption [148]. These studies illustrate that surfactant modification can tailor biochar properties and create new adsorption pathways, enhancing its versatility for water treatment.

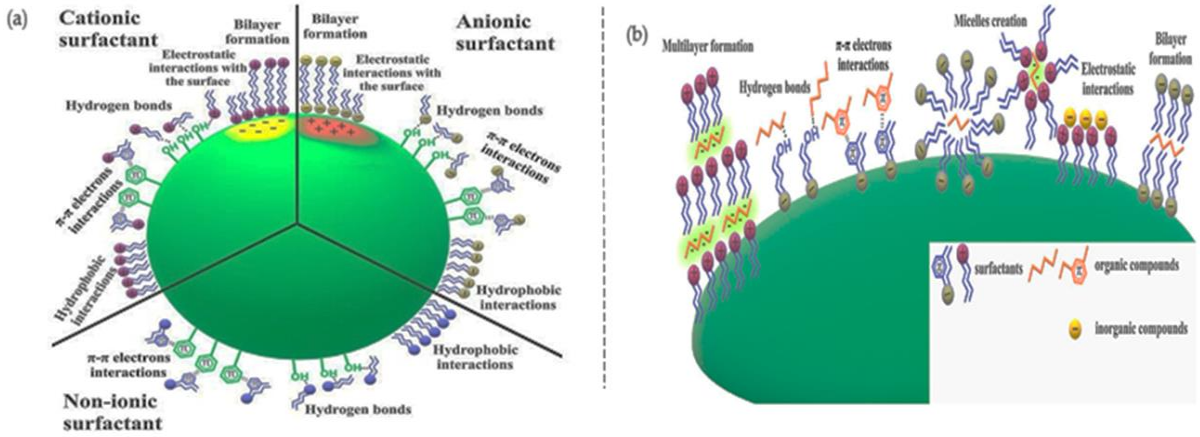

Fig. 5. (a) Possible adsorption mechanisms of surfactants with various ionic character on biochar surface. (b) Possible mechanisms of organic and inorganic compounds adsorption on surfactant-modified biochar surface. Reproduced from [145] under the Creative Commons CC BY license 4.0.

These studies demonstrate that surfactant modification can significantly alter the physicochemical properties of biochar and create new adsorption pathways, thereby improving its effectiveness for the removal of a wide range of organic pollutants and heavy metals from aqueous environments. Similar advancements in adsorption and sensor-based monitoring techniques have been reported for water treatment systems, highlighting the potential of engineered materials for enhanced contaminant removal [149-153].

4. Conclusions

Chemical modification enhances biochar's adsorption, surface functionality, and catalytic activity. Acidic, alkaline, oxidative treatments, and incorporation of metals or metal oxides enable efficient removal of heavy metals and organic pollutants. While laboratory-scale studies show high efficiency and tunable properties, challenges remain in scaling up, ensuring stability, and cost optimization. Chemically modified biochars thus offer a versatile and promising solution for sustainable water and wastewater treatment.

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