

Review

Engineered Biochar for Metal Recycling and Repurposed Applications

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Abstract: Heavy metal pollution is posing significant threats to the environment and human health. Engineered biochar, derived from various biomass sources through thermochemical processes, has emerged as a promising solution for metal pollutant remediation and metal recovery. This review explores the latest advancements in the preparation, characterization, and application of engineered biochar for metal adsorption, recycling, and utilization. It begins by discussing the significance of metal adsorption and providing an overview of biochar properties. The review examines the preparation and characterization techniques, emphasizing feedstock selection, thermochemical conversion methods, and surface modifications. Mechanisms of metal adsorption, such as physical and chemical adsorption, ion exchange, and surface complexation, are critically discussed. Moreover, factors influencing metal adsorption capacity, including biochar properties, metal characteristics, and environmental conditions, are critically analyzed. The efficacy of engineered biochar in adsorbing specific metals, including heavy metals, transition metals, and rare earth elements, is reviewed with recent studies and key findings. Furthermore, the recycling and regeneration of metal-loaded biochar are discussed, focusing on recycling and repurposed application techniques alongside challenges and economic considerations. Finally, future perspectives are provided for the enlightening of future research. This review is unique in addressing the potential of metal-adsorbed biochar as a novel precursor to produce catalytical and electrochemical materials.

Keywords: biomass; biochar; metal; recycling; environmental applications



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1. Introduction

In this era of heavy industrialization, metal resources are playing an increasingly important role in our daily lives for various industrial applications, including electronics, construction, and energy production. The extraction and processing of metal-bearing minerals and the manufacturing, utilization, and recycling of metals are becoming ever more important. The rising levels of heavy metals and other metal-containing contaminants in the environment are alarming due to their potential negative impacts on ecosystems and human health [1]. It has long been known that heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), and chromium (Cr) are nonbiodegradable and persist in the environment, posing long-term risks [2]. Specifically, Pb exposure can cause neurological damage, especially in children, while cadmium and mercury are known carcinogens that can cause kidney damage and other health issues. Cr, in its hexavalent form, is highly toxic and carcinogenic. These metals can accumulate in living organisms, leading to bioaccumulation and biomagnification through the food chain, thereby affecting entire ecosystems [3].

With the fast evolution of the production of electric, such as cell phones, smart home appliances, the booming of electric vehicles, and the development of novel batteries and clean energy technologies (e.g., wind turbines, photovoltaics, energy efficient lighting),

other than the heavy metals, rare earth metals (Li, Ce, Ga, etc.) are emerging as new potential sources of metal pollutions (Figure 1). Let alone the fact that industrial activities, mining operations, agricultural practices, and improper waste disposal contribute significantly to metal pollution. Addressing this challenge is crucial for sustainable development and environmental protection [4]. Moreover, the finite nature of metal resources necessitates efficient recycling and recovery methods to ensure their sustainable use. Metal adsorption using engineered biomass-based carbon materials offers a promising solution for pollution control, value-added biomass utilization, and the potential for recovery of precious metal resources. Carbon-based adsorbents are generally more environmentally friendly and can selectively remove metals from contaminated water, allowing for subsequent recycling and reuse of the adsorbed metals [5]. These dual benefits of pollution mitigation and value-added waste utilization underscore the importance of developing effective carbon-based adsorbents.

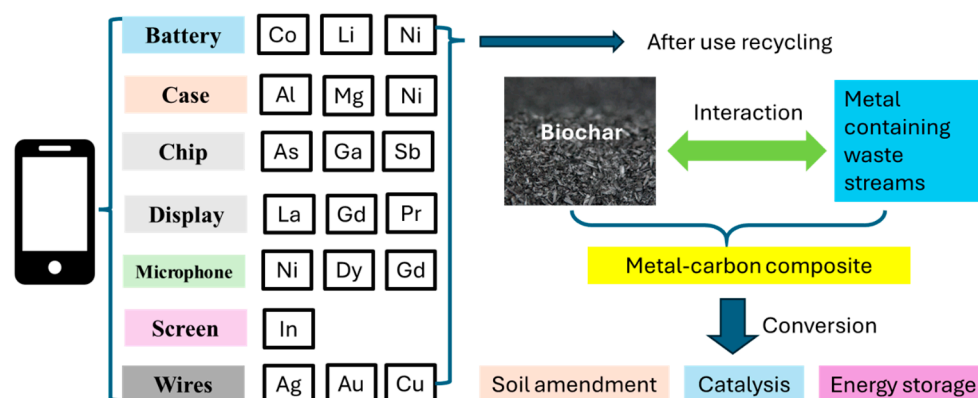


Figure 1. Metal resources used in a smartphone.

Biochar (BC) refers to the carbon-rich material produced from the thermochemical conversion technologies of biomass (i.e., pyrolysis, gasification, and conventional and microwave-assisted hydrothermal processes) and has gained significant attention as a versatile adsorbent for environmental applications [6,7]. The pyrolysis process, which involves the thermal decomposition of biomass in an oxygen-limited environment, transforms organic materials into BC with a high surface area and porous structure [8]. BC's surface is abundant with functional groups such as hydroxyl, carboxyl, and phenolic groups, which facilitate the adsorption of metal ions [9]. Together, these properties, high thermal stability, and biocompatibility make BC an excellent candidate for environmentally friendly metal adsorption applications. BC can be engineered after production to enhance its adsorption capacity through various modification techniques. These modifications include physical activation (e.g., steam or CO₂ activation) and chemical treatments (e.g., acid or base treatments) that increase the surface area, porosity, and functional group density of BC [10–12]. Despite its potential and the tremendous progress being made to evaluate different BC for various metal adsorption, the current understanding of BC's metal adsorption mechanisms and optimization strategies for different metals remains incomplete and is updating very rapidly. Also, to the best of our knowledge of the recycling and regeneration of metal-loaded BC, emphasizing desorption and thermochemical recycling techniques are not previously reported in a summarized manner. Therefore, this review aims to fill these knowledge gaps by providing a comprehensive analysis of the recent advancements in engineered BC for metal adsorption.

The uniqueness of this review lies in its integrated approach, which not only summarizes and upgrades the latest trends in BC engineering research (synthesis, modification, characterization) but also addresses the potential of the metal-adsorbed BC as a novel precursor to produce catalytical and electrochemical materials. In conclusion, this review provides a thorough examination of the current state and prospects of engineered biochar for metal recycling and repurposed applications. By highlighting key findings, addressing

knowledge gaps, and proposing future research directions, it aims to advance BC-based material research.

2. Preparation and Characterization of Engineered Biochar

2.1. Feedstock Selection

The properties of BC are heavily dependent on their sources of feedstock. Careful selection of biomass feedstocks and tailored preparation techniques are crucial for creating engineered BC for specific applications. Since being invented, biochar research has always had a focus on low cost, renewability, low toxicity, easy operation, and broad application prospects for heavy metal removal from wastewater [13–15]. A diverse array of biomass feedstocks is used in BC production, encompassing woody biomass, crops and residues, forestry crops and residues, municipal solid waste, industrial solid waste, animal residues, sewage sludge, algal biomass, seaweeds, and other lignocellulosic materials [16–19]. Woody biomass is characterized by low moisture, low ash content, high density, and high calorific value [3]. Waste biomass, including animal waste, industrial and agricultural solid wastes, and biosolids, is characterized by high ash content, high moisture, low density, and low calorific value [20,21]. The feedstock type influences BC's yield, functional groups, surface area, porosity, elemental composition, carbon content, cation exchange capacity, ash composition, and mineral concentrations, affecting its adsorption potential [17,22–24]. For example, BC from woody biomass is found to be rich in carbon. In contrast, BC from animal manure has a high potassium content and bamboo-derived BC has a higher surface area compared to pig-manure BC when pyrolyzed at the same temperature [25]. Zhao et al. [26] attributed the enhanced properties of BC, such as high carbon content, good cation exchange capacity, and high carbon storage capability to the use of various feedstocks for preparation, such as animal manures, waste wood, crop residues, food waste, aquatic plants, and municipal waste.

In terms of lignocellulosic biomass, the effects of feedstock that precursor composition, including the relative contents of lignin, hemicellulose, cellulose, and inorganic constituents, will significantly influence the effect of BC characteristics. For example, high-lignin content materials such as spruce and pine wood produce BC with higher yields and a high fixed carbon content. Lignin-rich biomaterials i coconut shells and bamboo yield macroporous BC, while cellulose-rich materials like husks produce BC with a high amount of micropores [19]. Leng et al. [27] suggested that lignocellulosic biomass, particularly wood, and woody biomass, is ideal for producing porous BC due to its low ash content, high lignin content, and preservation of the original pore structure. Other important biomasses that have gained significant attention from researchers are algae, fish scales, shells, and kelp, which are excellent feedstocks for BC production due to their high growth rate and seasonal availability [17,28]. Macroalgae BC was found to have high nitrogen, hydrogen, and ash content, high electrical conductivity, low carbon content, and lower cation-exchange capacity compared to lignocellulosic BC [11,17,28].

Yining et al. [29] highlighted the significant impact of feedstock type on BC and hydrochar production, including production rate, thermal stability, and elemental composition. The authors emphasized the challenges of seasonal variation in biomass feedstock availability and the complexities in handling, transportation, storage, and sizing due to different biomasses' diverse physical and chemical characteristics. The nature of the feedstock, particularly its moisture content, strongly impacts the pyrolysis process. High moisture content can reduce BC yield, while low moisture content makes BC production more energy-efficient and commercially viable [30,31]. Efficient pretreatment methods, including physical pretreatments like size reduction, drying, and densification, and chemical treatments such as acid or alkaline treatments, are essential to improve BC quality for certain applications, such as adsorbent for wastewater treatment and soil additives [18]. Therefore, when selecting biomass feedstock for BC production, it is essential to carefully evaluate its composition and morphological structure, which includes the original pore structure and

thermal stability. The unique properties and compositions of each biomass feedstock will partially determine the quality and suitability of BC for heavy metal adsorption.

2.2. Thermochemical Conversion Processes for Biochar Production

Thermochemical conversion produces BC through processes like pyrolysis, hydrothermal carbonization (HTC), gasification, and torrefaction, yielding bio-oil or biosyngas, with BC being a high-carbon, porous material rich in functional groups [32]. Key operational parameters, such as heating rate, temperature, and residence time, must be carefully optimized, as they significantly impact the physicochemical properties of the resulting BC like pore structures, surface area, elemental compositions, and surface functional groups [33,34]. Biochar produced at medium and high pyrolysis temperatures (350–650 °C) increases the release of volatile matter, the surface area, and the carbon content while balancing nitrogen content and effectively removing heavy metals from wastewater. In contrast, lower pyrolysis temperatures (e.g., <300 °C) produce BC with higher yield and moderate stability, making it better suited for agricultural production and soil contamination remediation [35,36]. For instance, corn-straw-derived BC removed Cu²⁺ more efficiently at 800 °C than at 400 °C [37]. Surface functionalization during high-temperature pyrolysis improves reactivity and adsorption capabilities [38]. Wang and Wang [39] reported that BC produced at high temperatures is effective at removing Cr(VI). Microwave-assisted pyrolysis is a novel method that accelerates the process without requiring biomass shredding or drying. This technique uniformly transfers thermal energy to the biomass's functional groups, producing BC with a larger surface area (BET up to 450–800 m²/g) and more functional groups compared to unmodified BC [40]. Kazemi et al. [40] investigated that microwave-engineered BC enhanced heavy metal removal, soil water-holding capacity, and cation exchange capacity. Copyrolysis, involving multiple biomass feedstocks, has recently garnered attention for its ability to influence the pore structure of BC differently than single biomass pyrolysis [18].

The conversion of lignocellulosic biomass into BC involves various reaction parameters and techniques. Cellulose decomposes through slow pyrolysis, which has a longer residence time and lower heating rates, and fast pyrolysis, leading to rapid volatilization and the formation of levoglucosan, which can dehydrate into hydroxymethyl furfural, bio-oil, or syngas. Then, hydroxymethyl furfural undergoes aromatization, condensation, and polymerization to regenerate solid BC. Moreover, hemicellulose decomposes similarly, forming oligosaccharides through decarboxylation and depolymerization at lower temperatures (220–315 °C). Lignin decomposes over a wide range of temperatures (150–900 °C) through complex processes involving β -O-4 bond cleavage and radical formation [30].

Another relatively new technique, HTC, involves dissolving biomass in water and operating temperatures between 180 and 250 °C in a closed reactor, achieving a high carbon yield of 30–50% [41]. Amalina et al. [19] reported that during HTC, char is produced through the depolymerization and cross-linking of intermediates. Alongside pyrolysis, lignin components that remain undissolved in the liquid phase are transformed into hydrochar. Longer hydrothermal treatment reduces polar functional groups in BC, favoring nonpolar ones [42]. Ponnusamy et al. [43] highlighted the disadvantages of HTC such as reduced porosity, limited surface area, thermal resistance, and a less aromatic structure. Biomass gasification involves four stages: drying, pyrolysis, partial oxidation, and reduction. The quantity and quality of the resulting BC depend on the effective control and optimization of these stages [44]. Another method, called torrefaction or low-temperature pyrolysis, produces BC through pyrolysis at lower temperatures (<300 °C), altering biomass properties such as energy density, particle size, surface area, heating time, and moisture content, and generally improves the credibility of the biomass for further processing [45]. Each thermochemical conversion process offers distinct advantages for BC production, contributing to the efficient utilization of biomass resources as heavy metal adsorbents.

2.3. Surface Modification and Functionalization Methods

Biochar is valued for its large specific surface area, highly developed porous structure, and diverse functional groups, including carboxylic, carbonyl, ester, hydroxyl, phenolic, pyridine-N, pyrrole-N, and quaternary-N, which contribute to its efficacy as an adsorbent. Recent research shows that modified BC has a higher adsorption capacity than unmodified BC, driving interest in developing high-performance BC materials through various modification techniques [17,46]. Engineered BC is a biochar that has been deliberately modified through physical, chemical, or biological processes to improve its properties for targeted applications, such as adsorption or soil enhancement. These modifications typically enhance key characteristics like porosity, pH, cation exchange capacity, and specific surface area, leading to superior heavy metal adsorption capabilities compared to untreated BC [27,46]. Kumar et al. [21] reviewed modified agrowaste BC materials, which showed a wide range of adsorption capacities and achieved over 99% removal of toxic heavy metals from aquatic systems. Figure 2 illustrates various modification techniques and their effects on the properties of the engineered BC.

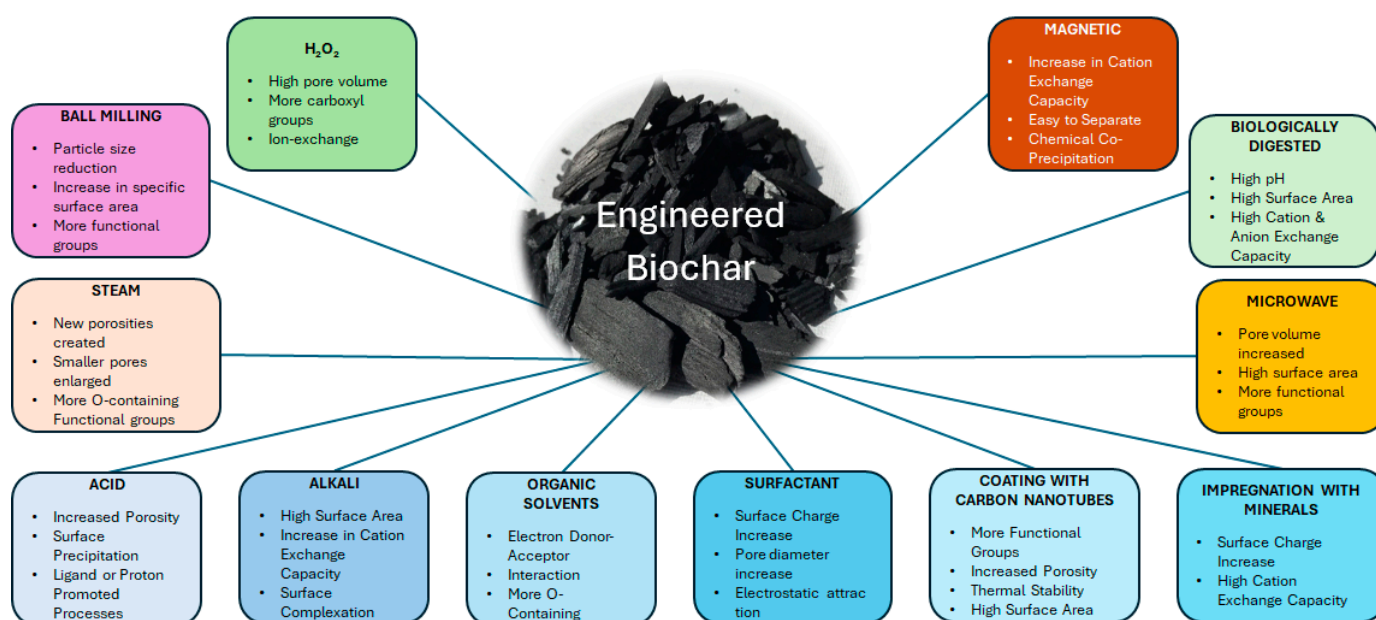


Figure 2. Various modification techniques and their impacts on the properties of engineered biochar [17].

Physical activation techniques like steam, ball milling, magnetization, and microwave modification focus on altering BC's structure and surface properties [24,47]. Steam activation of BC creates new pores and enhances surface functional groups, whereas microwave modification increases both the surface area and functional groups, thereby improving the BC's ability to adsorb heavy metals [24,48]. Using CO₂ as a gas medium or adding chemicals like KHCO₃, K₂CO₃, NaHCO₃, or Na₂CO₃ during pyrolysis is a potentially more cost-effective activation route for creating BC-based materials with a hierarchical porous structure, unlike steam activation, which has higher costs [49,50]. Ball milling reduces particle size, increasing adsorption sites like carbon nanotubes but with better dispersion in water [22,51]. Magnetizing BC enhances its ease of separation, thereby lowering recovery costs. However, caution is needed as magnetization can cause structural deformation and reduction in metal adsorption capacities. Optimizing the timing of magnetization and conducting synthesis in alkaline media can improve its heavy metal removal efficiency [50,52]. Shang et al. [53] magnetized BC derived from herb residues with Fe₃O₄ nanoparticles, achieving efficient Cr(VI) adsorption and easy separation using a magnetic field. Similarly, Wang et al. [54] synthesized magnetic rice husk BC, reporting maximum adsorption capacities of 129 mg/g for Pb(II) and 118 mg/g for U(VI), significantly higher than unmodified

BC. Microwave-assisted pyrolysis is increasingly popular for BC modification due to its rapid heating rate and lower energy consumption, making it more environmentally friendly than conventional methods. Studies have shown that microwave-modified BC has significantly improved microporosity, surface area, and functional group presence, enhancing its yield and adsorption capacity for contaminants like As^{5+} , Zn^{2+} , Cu^{2+} , and silver [55,56]. Chemical activation of BC with oxidants, acids, or alkalis improves the specific surface area, porosity, polarity, charge characteristics, oxygen-containing functional groups, and active sites for the chemisorption of heavy metals [57–59]. However, inappropriate activator concentrations, such as high KOH levels, can hinder heavy metal stabilization by expanding the lignin structure inside BC. Therefore, moderate concentrations of activators are generally recommended [60]. Surface oxidation is widely used to introduce oxygen-containing functional groups to BC, enhancing its specific surface area, pore volume, active sites, and hydrophilicity. This improves its adsorption performance and application properties through reactions such as oxidation, hydroxylation, carboxylation, and aldehydation [61]. Key functional groups like carbonyl, hydroxyl, and carboxyl enhance metal adsorption via hydrogen bonding and electrostatic attraction [62]. Common oxidizing agents include H_2O_2 , O_3 , KMnO_4 , and HNO_3 , which also boost BC's hydrophilicity [63]. For instance, Fan et al. [64] found that $\text{HNO}_3/\text{H}_2\text{SO}_4$ and $\text{NaOH}/\text{H}_2\text{O}_2$ -modified reed BC increased oxygen functional groups, the oxygen-to-carbon ratio, and specific surface area and pore volume. Liu et al. [65] reported an increase in specific surface area from $2.68 \text{ m}^2/\text{g}$ to $86.8 \text{ m}^2/\text{g}$ and an increase in adsorption capacity for $\text{Cr}(\text{VI})$ and Cd^{2+} from $1.29 \text{ mg}/\text{g}$ to $3.20 \text{ mg}/\text{g}$. Biological modification of BC involves producing BC from pretreated feedstocks via anaerobic digestion after biological engineering. This process generates BC with increased surface area, anion exchange capacity, cation exchange capacity, and altered pH values, making it effective for heavy metal adsorption processes in wastewater treatment [66]. BC can serve as a substrate for immobilizing microorganisms and enzymes, creating composite materials. Microbes on BC secrete organic acids and metabolites, introducing new functional groups ($-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$) that enhance adsorption. Some microbes produce biogums, increasing porosity and adsorption capacity. This method uses fewer chemicals, has a milder preparation process, and consumes less energy, aligning with green and low-carbon principles [67,68].

Furthermore, coating BC with metal oxides or graphene can further increase its adsorption capacity and efficiency in removing heavy metals, while utilizing BC as a carrier for nanoparticles enhances their effectiveness in wastewater treatment applications [69,70]. Tho and coauthors [71] reported that modifying cassava root husk-derived BC with ZnO nanoparticles significantly improved its adsorption capacity for $\text{As}(\text{III})$, $\text{Cd}(\text{II})$, $\text{Pb}(\text{II})$, and $\text{Cr}(\text{VI})$. This study demonstrates that incorporating ZnO nanoparticles into BC enhances its ability to remove heavy metals, paving the way for more effective heavy metal removal strategies using modified BC. Despite the benefits of these modification techniques, further research is necessary to understand the effects of modification, the costs, and the potential for secondary pollution in real wastewater treatment applications.

2.4. Characterization Techniques of Biochar Materials

Comprehensive characterization is crucial to decode BC properties and to evaluate BC's suitability for specific applications. Key properties such as surface area, charge, porosity, pH, mineral content, and binding sites are essential to understand, as they influence BC's effectiveness in adsorption mechanisms. Techniques such as scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance spectroscopy (NMR), BET analysis, thermogravimetric analysis (TGA), proximate and ultimate analysis, and Raman spectroscopy are used to examine BC's structure, surface functional groups, and elemental composition (Figure 3) [27,72].

FTIR is used to analyze BC's surface functional groups, which may change significantly when the chars are produced under various temperatures [73]. XPS is used to ascertain

the valence states of chemical elements by examining the energy distribution of emitted photoelectrons. SEM is used to characterize the surface structures of BC, providing detailed images of its microporous and mesoporous distributions and pore configurations [74]. SEM and TEM are useful for elaborating surface morphology before and after adsorption, with TEM offering higher resolution and the ability to assess the electronic state of BC. STEM, like SEM and TEM but with higher resolution, provides atomic-scale BC characterization. SEM combined with EDX (SEM-EDX) is employed to analyze the composition of BC and identify surface components. However, SEM-EDX is incompatible with organic pollutants. EDS, often paired with these microscopes, identifies the molar fraction of surface elements [34].

XRD is widely used to determine the crystallinity and crystal structure of BC. The diffraction pattern shows attributes of amorphous nebulous material formed above 350 °C [17,72]. The nanocrystals produced exhibit a crystalline structure, reflected in sharp and robust XRD peaks, with a particle diameter increasing over time. Thermal analysis, particularly TGA, is used to determine the physicochemical properties of materials as the temperature rises [75]. TGA examines the thermal decomposition/oxidation behavior of various samples and can also help in identifying the ignitability of BC and BC mixtures [76]. It analyzes the synergistic activity between components, aiding in understanding the heating process and sample features [77]. In a typical TGA test, the heating starts at room temperature and increases to 1000 °C, with typical rates between 10 and 20 °C/min [78]. NMR spectroscopy is used to determine the structural composition of BC by analyzing the resonance frequencies of atomic nuclei using a magnetic field and RF pulses. It identifies carbon functional groups, aromatic ring formation, and overall BC molecule structure [73,79]. NMR distinguishes aliphatic and aromatic hydrocarbons and compares the stability and carbonization of different biochars. However, ferromagnetic minerals in BC and low signal-to-noise ratios in high-temperature pyrolysis products can interfere with NMR signals [80].

Surface area, total pore volume, and pore diameter were determined using the Brunauer–Emmett–Teller (BET) method with a surface area and porosity analyzer. In this method, nitrogen adsorption isotherms were utilized to measure the surface area of BC by assessing the multilayer adsorption capacity at varying nitrogen partial pressures [19].

Proximate analysis, which includes measuring moisture content, fixed carbon, and volatile matter, follows different standard methods like British Standards (BS), Chinese Standards, ASTM (American Society for Testing and Materials), and ISO (International Organization for Standardization). Residual matter was calculated by the difference. Electrical conductivity (EC) and pH were measured in a 1:10 DI water suspension. Cation exchange capacity (CEC) was determined using the ammonium acetate extraction method. Elemental analysis quantifies elements like nitrogen (N), hydrogen (H), carbon (C), and sulfur (S) using sophisticated instruments based on complete combustion in oxygen. Atomic ratios of elements like O/C and H/C were calculated to indicate the polarity and aromaticity of the BC materials [81]. These comprehensive characterization techniques can provide valuable data to confirm whether the characterized BC is optimized for specific applications.

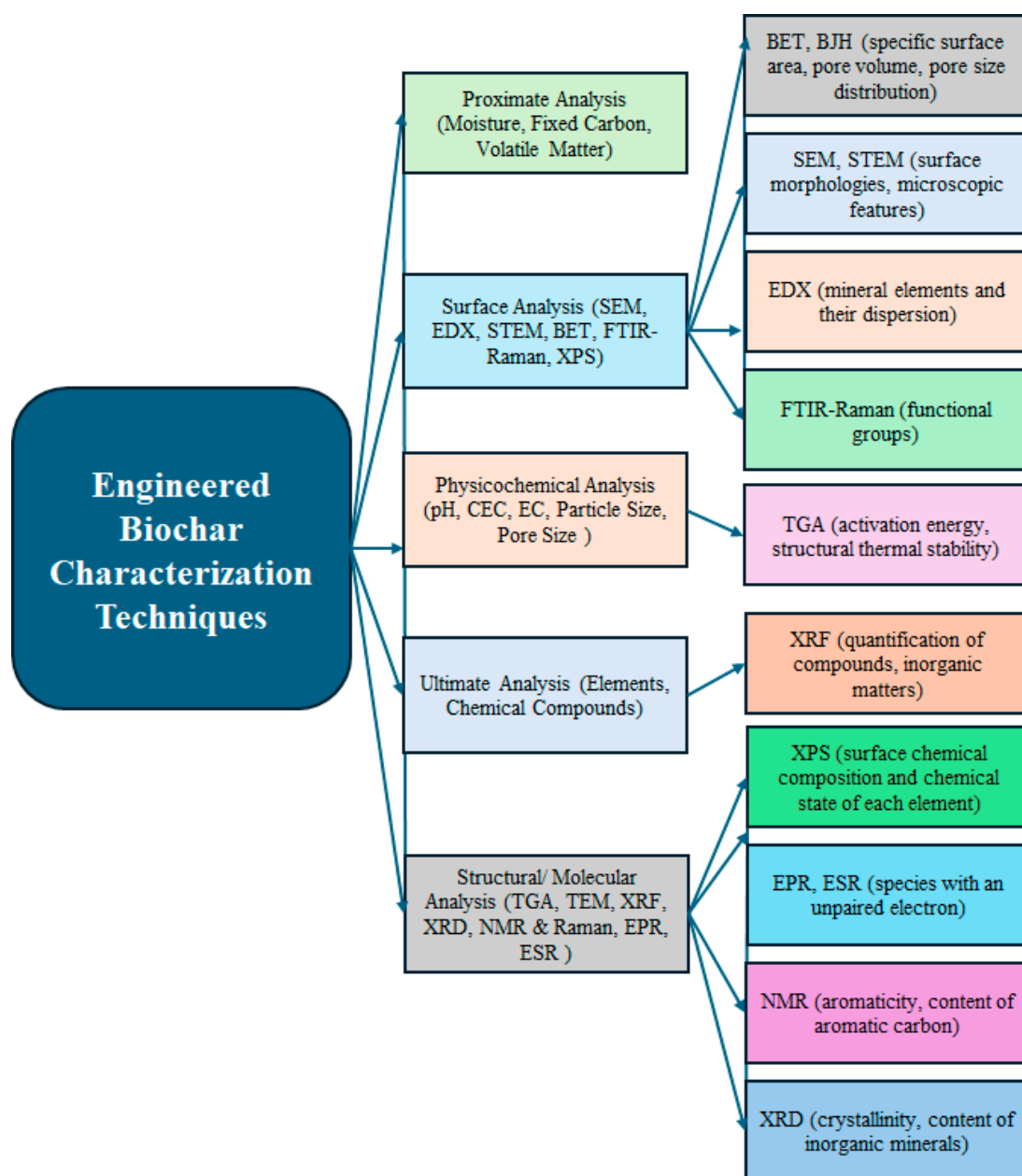


Figure 3. Overview of engineered biochar characterization techniques [73,81,82].

3. Mechanisms of Metal Adsorption on Biochar

Various mechanisms, such as physical adsorption, chemical adsorption, and other potential processes, contribute to metal adsorption by engineered BC (Figure 4).

3.1. Physical Adsorption

Physical adsorption, known as physisorption, occurs when metal ions adhere to the BC surface through Van der Waals forces [83]. This process is typically weak and reversible, with adsorption and desorption continuously competing at varying rates depending on the specific conditions of the system [84]. This process largely depends on the BC's surface area and pore structure, with higher surface areas and well-developed micro-, meso-, and macropores enhancing adsorption capacity. BC activation/modification processes can increase these properties, improving adsorption efficiency [10,27]. Liu et al. [85] prepared BC from rice straw biogas residue modified with KOH, which demonstrated that KOH

modification significantly enhanced the specific surface area (from 273.26 to 2372.51 m²/g) and pore volume (from 0.24 to 1.20 cm³/g), resulting in the creation of BC with numerous adsorption sites and a high adsorption capacity (209.65 mg/g) of mercury.

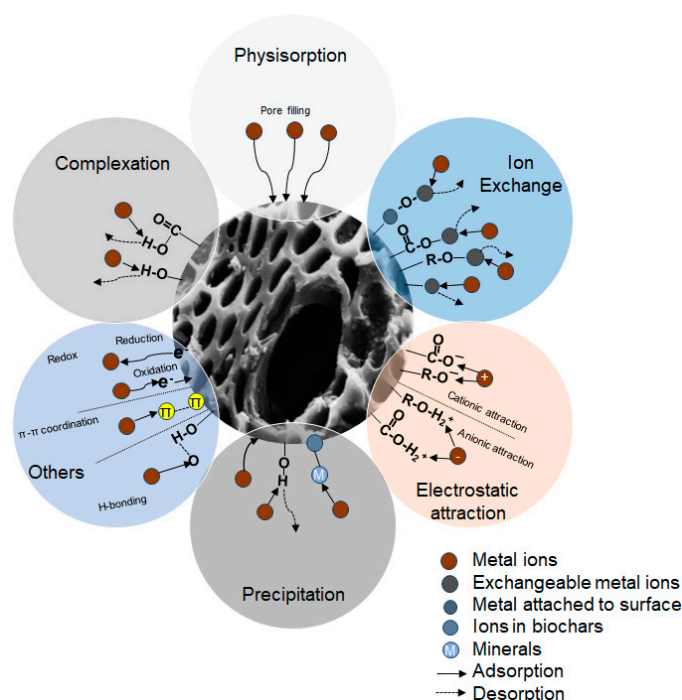


Figure 4. Schematic representation of metal adsorption mechanism on engineered biochar.

3.2. Chemical Adsorption

Chemical adsorption, or chemisorption, involves the formation of stronger bonds between metal ions and functional groups on the BC surface. This process is typically irreversible and significantly depends on the BC's chemical composition and surface properties. Various mechanisms can contribute to chemical adsorption, including ion exchange, complexation, electrostatic attraction, and precipitation.

3.2.1. Ion Exchange

Ion exchange is a process in which metal ions in the solution replace ions originating from the BC surface. This mechanism is facilitated by the presence of exchangeable cations like H⁺, Na⁺, K⁺, Ca²⁺, and Mg²⁺ on BC. The efficiency of ion exchange depends on the BC's cation exchange capacity (CEC), which is influenced by its surface functional groups and the degree of activation. A higher cation exchange capacity (CEC) correlates with an increased rate of adsorption [86]. Wu et al. [87] showed that MgCl₂ modification of coconut shell BC significantly enhanced the release of Mg²⁺ ions into the solution, leading to a substantial increase in adsorption capacities (q_e) for Pb (192.36 mg/g) and Cd (105.46 mg/g) compared to unmodified BC (Pb 3.93 mg/g and Cd 1.78 mg/g), thus improving its ion exchange capacity [87]. In aqueous solutions, metal ions like Cd²⁺ and Pb²⁺ replace exchangeable cations such as H⁺ and Na⁺ on the surface of BC. These metal ions then attach to functional groups, including carboxyl (-COOH) and hydroxyl (-OH) groups. Studies have shown that BC produced from palm leaves, rich in oxygen-containing functional groups, effectively exchanges ions with heavy metals like chromium (Cr³⁺) and lead (Pb²⁺), reducing their concentration in contaminated water [88]. Another study demonstrated that ion exchange and precipitation were the predominant mechanisms for the adsorption of heavy metals (Pb, Cd, and Ni), as these metals effectively exchanged ions with the mineral constituents of the BC [89].

3.2.2. Complexation

Complexation involves the formation of stable, often covalent, bonds between metal ions and functional groups on the BC surface [90]. This mechanism significantly enhances the stability and retention of metal ions in BC. Metal ions (e.g., Cu^{2+} , Fe^{3+}) interact with specific functional groups such as carboxyl, hydroxyl, amino ($-\text{NH}_2$), and thiol ($-\text{SH}$) groups to form metal-ligand complexes. For instance, Pb(II) and Cd(II) have been shown to form strong complexes with oxygen, nitrogen, and sulfur functional groups on BC derived from *A. compressus* and reed straw, leading to the efficient removal of these metals [90,91]. Similarly, BC modified with FeCl_3 has demonstrated effective complexation with As(V) by forming complex compounds with iron ions [92]. The stability of these complexes depends on the metal ions and the specific functional groups present and thus effectively removes heavy metals from contaminated aqueous solutions.

3.2.3. Electrostatic Attraction

Electrostatic attraction occurs when metal ions are attracted to oppositely charged sites on the BC surface. This mechanism is particularly effective for adsorbing cationic metals and is influenced by the surface charge of the BC, which is determined by its pH and functional groups. Negatively charged sites on the BC surface, such as deprotonated carboxyl and hydroxyl groups, attract positively charged metal ions like Ni^{2+} and Zn^{2+} . As an example, a study by Chen et al. [93] indicated that Zeta potential (ZP) values, which indicate the electrostatic potential of biomaterials in various pH solutions, significantly decreased between pH 2 and 4 and stabilized around -30 mV at pH 4–10, suggesting that the negatively charged surfaces of pomelo-peel-derived BC facilitate the adsorption of Pb(II) and Cu(II) through electrostatic attraction. The authors also reported that the BC surface was negatively charged and contained carboxyl and hydroxyl functional groups, suggesting that electrostatic attraction was the dominant mechanism in removing those pollutants. Similarly, Li et al. [94] demonstrated that the adsorbents exhibited a negative charge when the pH of the solution exceeded the point of zero charge (pH_{pzc}), facilitating the electrostatic binding of acetate-based novel BC to Pb(II) and Cu(II) .

3.2.4. Precipitation

Precipitation is a mechanism by which BC adsorbs heavy metals. It involves the transformation of dissolved metal ions into insoluble solid phases on the BC surface. This process is influenced by the chemical composition of the BC, including the presence of mineral components and functional groups that can induce nucleation and growth of metal precipitates. BC has a high mineral content, such as calcium, magnesium, potassium, phosphorus, etc. [95]. BC's high mineral content, mainly when derived from feedstocks rich in inorganic components, provides a favorable environment for precipitation reactions. These minerals can react with metal ions to form insoluble hydroxides, carbonates, or phosphates, which are then deposited onto the BC surface. For example, BC derived from coconut shells demonstrated that anions (e.g., CO_3^{2-} , PO_4^{3-} , and OH^-) released from the BC reacted with metal ions (Pb , Cd) to form mineral precipitates such as PbCO_3 , $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, $\text{Pb}(\text{H}_2\text{PO}_4)_2$, CdCO_3 , $\text{Cd}_3(\text{PO}_4)_2$, $\text{Cd}(\text{OH})_2$, and Cd_3SiO_5 [87]. The surface functional groups of BC, such as carboxyl ($-\text{COOH}$) and hydroxyl ($-\text{OH}$) groups, also play a significant role in the precipitation mechanism. Cr(III) reacts with ($-\text{OH}$) of BC and forms $\text{Cr}(\text{OH})_3$ precipitation and thus helps immobilize Cr(III) [96]. These groups can bind metal ions, forming stable metal-organic complexes that act as precursors for further precipitation. Studies have shown that Mg -loaded BC can enhance the precipitation of Cd(II) and Cu(II) by forming stable CdCO_3 and $\text{Cu}_2\text{Cl}(\text{OH})_3$ complexes, respectively [97].

3.2.5. Other Mechanisms

Biochar adsorbs heavy metals through several mechanisms beyond these dominant mechanisms. Redox reactions involve the reduction in metal ions facilitated by BC's surface functional groups and redox-active components. For example, the redox reaction

between oxygen-containing functional groups on the BC surface and Cr(VI) significantly contributes to adsorption, where these functional groups donate electrons to reduce Cr(VI) to Cr(III), which can then be released into the solution through ion exchange with K^+ in the BC [98]. π - π interactions occur when metal ions coordinate with the aromatic rings of BC. Liu et al. [99] demonstrated that BC derived from banana stems and leaves effectively adsorbed Pb and Cd, as indicated by FTIR analysis showing reduced -CH, C=C, and C=O groups postadsorption, suggesting that these metal ions interacted with the π electrons during the adsorption process. Hydrogen bonding involves metal ions forming bonds with hydroxyl and carboxyl groups in BC, enhancing adsorption. A study showed that As(V) was adsorbed onto the BC surface via hydrogen bonding with the -COOH groups present on the BC [100]. These mechanisms collectively contribute to the effective removal and stabilization of heavy metals in contaminated environments.

4. Factors Influencing Metal Adsorption Capacity of Biochar

Various factors, including the properties of BC, the characteristics of the metal ions, and the environmental conditions, influence the ability of BC to adsorb heavy metals. Fundamental BC properties include surface area, porosity, functional groups, and cation exchange capacity, which collectively determine its affinity for metal ions [101]. Additionally, the ionic radius, charge, and redox potential of the metal ions significantly impact their adsorption behavior [102–104]. Environmental conditions, including pH, temperature, competing ions, etc., further influence the interaction between BC and metal ions, thereby modulating the overall adsorption capacity. A summary of the factors influencing metal adsorption capacity is shown in Table 1.

4.1. Effect of Biochar Properties on Metal Adsorption

The efficacy of BC as an adsorbent for metal ions is profoundly affected by its inherent properties. These properties determine the interaction between BC and metal ions, affecting overall adsorption capacity.

4.1.1. Surface Area and Porosity

The surface area and porosity of BC are fundamental determinants of its adsorption capacity. An increased surface area offers a greater number of active sites available for metal ion binding, while higher porosity, particularly the presence of micropores and mesopores, enhances accessibility and facilitates ion transport for adsorption [105,106]. For instance, BC derived from bamboo and modified with guanidine phosphate demonstrated an increase in surface area from 196 to 458 m^2/g , which markedly enhanced its adsorption capacities for Pb(II) (166.2 mg/g), Cu(II) (81.7 mg/g), and Cd(II) (60.3 mg/g) [107]. This modification not only increased the surface area but also enhanced the porosity, thereby providing more pathways for metal ions to reach the active sites on the BC.

4.1.2. Surface Functional Groups

Functional groups on BC surfaces significantly influence their metal adsorption capacity through mechanisms such as complexation, ion exchange, and electrostatic interactions. Carboxyl (-COOH) and hydroxyl (-OH) groups are particularly influential in enhancing metal adsorption. These functional groups can form strong complexes with metal ions, facilitating their removal from aqueous solutions. Zeng et al. [108] demonstrated that oxygen-containing functional groups (COOH and -OH) on BC surfaces act as electron donors, reducing Cr(VI) to Cr(III) and resulting in the formation of Cr precipitates and complexes. Amino (-NH₂) groups are particularly beneficial for removing heavy metals such as Pb²⁺ and Cd²⁺ due to their chelating properties, which enable the formation of strong metal-ligand complexes [109,110]. Phosphate groups (-PO₄³⁻) on BC surfaces are advantageous for removing metals like Pb²⁺ and Cd²⁺ through precipitation reactions. Deng et al. [111] demonstrated that incorporating chloro-phosphate into BC significantly en-

hances the adsorption efficiency of heavy metals (Pb^{2+} , Cd^{2+} , and Cu^{2+}) due to the specific precipitation mechanisms, forming $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$, $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$, and $\text{Cu}_3(\text{PO}_4)_2$ precipitates.

4.2. Effect of Metal Characteristics

The characteristics of metal ions, including ionic radius, charge, speciation, and oxidation state, significantly influence their adsorption capacity on biochar. Ionic radius and charge are crucial determinants of metal ion interactions with BC surfaces. Metal ions with smaller ionic radii and higher charges typically exhibit stronger adsorption due to the higher charge density, which enhances electrostatic interactions and complexation with functional groups in BC. For example, in a study, Cr(III) demonstrated more effective adsorption onto Fe_3O_4 -loaded BC due to its smaller ionic radius (0.0615 nm) compared to that of Cu(II) (0.073 nm) and Zn(II) (0.074 nm) [102].

The speciation and oxidation state of metal ions also play a vital role in adsorption. Metal ions in different oxidation states exhibit varying affinities for BC surfaces. Cr(VI) and Cr(III), for example, display distinct adsorption behaviors; Cr(VI) is often adsorbed through reduction to Cr(III) on BC surfaces, followed by complexation or precipitation. Additionally, the speciation of metal ions, which is dependent upon pH and the presence of other ligands, influences their availability and reactivity toward BC [112]. For example, the speciation of As and Cr significantly affects their adsorption capacity, with As(V) and Cr(III) generally exhibiting higher adsorption efficiencies compared to As(III) and Cr(VI) due to differences in their chemical stability and reactivity [100,113].

4.3. Environmental Conditions

4.3.1. Effect of pH

The pH of the medium significantly impacts the metal adsorption capacity of BC by affecting both the surface charge of BC and the speciation of metal ions. The point of zero charge (pH_{pzc}) is crucial in determining the surface charge of BC; at pH values above the pH_{pzc} , the BC surface becomes negatively charged, which enhances the electrostatic attraction of positively charged metal ions. Conversely, at pH values below the pH_{pzc} , the BC surface is positively charged, reducing the adsorption capacity for cationic metals due to electrostatic repulsion. For instance, Biswal et al. [114] showed that polymer-modified BC exhibited enhanced Cr(VI) adsorption at low pH (pH 2) due to the protonation of surface functional groups, resulting in strong electrostatic attraction with anionic Cr(VI) species and its reduction to Cr(III). In contrast, the adsorption capacity for cationic metals such as Cu^{2+} increases with higher pH, as shown by Zhang et al. [115], where cow manure BC achieved peak adsorption at the pH of 5. However, a further increase in pH reduced the adsorption slightly due to the formation of metal hydroxides. This trend is further supported by studies on the removal of contaminants like textile dyes, where higher pH (7) levels enhanced the adsorption due to increased negative charges on BC surfaces, facilitating the attraction of positively charged dyes [116].

4.3.2. Effect of Temperature

Temperature significantly influences the adsorption capacity of BC for heavy metals, with most studies indicating an endothermic process [117–119]. The adsorption rate and capacity significantly increase with rising temperatures due to the higher kinetic energy of adsorbate molecules, which enhances the ion transfer rate [120]. For instance, Zhang et al. [118] demonstrated that the adsorption capacity of Pb(II) and Cd(II) onto magnetized activated carbon (MAC) derived from rape straw powder increased significantly as the temperature rose from 24.8 to 44.85 °C. Researchers also concluded that, as temperature increased, the adsorption spontaneity rose (ΔG^0), with positive enthalpy changes (ΔH^0) for Pb(II) and Cd(II) adsorption by MAC (18.02 kJ/mol and 15.32 kJ/mol, respectively), indicating an endothermic process favoring higher temperatures. Similarly, Xu et al. [117] found that higher temperatures (39.85 °C) improved the adsorption capacity (160 mg/g) of U(VI) by BC derived from water hyacinth.

However, some studies suggest an exothermic process, where adsorption decreases with increasing temperature. Harsha et al. [121] reported a decline in Cu(II) adsorption by H₂SO₄-modified *Annona reticulata* seed-based BC as temperature increased from 26.85 to 56.85 °C. He proposed that increased temperature enhances cation movement and desorption, with optimal cation separation by BC observed at 30 °C, indicating that lower temperatures are more favorable for removal. Singh et al. [122] observed that Cr(VI) adsorption efficiency decreased with rising temperature for both BCs, indicating an exothermic process. The optimal temperature for Cr(VI) adsorption onto bacterial BC was found to be 24.85 °C, as higher temperatures reduce adsorption forces and efficiency due to increased molecular separation and decreased solution viscosity. These results indicate that the adsorption process can exhibit either endothermic or exothermic behavior, depending on the specific interactions between BC and metal ions.

4.3.3. Effect of Competing Ions

In wastewater or natural water environments, the presence of various competing ions such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl[−], NO₃[−], and SO₄^{2−} can significantly influence the adsorption capacity [123]. These competing ions coexist in the solution and their concentrations can influence the adsorption efficiency. These competing ions have high bonding affinities toward BC and occupy or block a greater number of adsorption sites on the BC surface, resulting in a substantial decrease in its adsorption capacity [124].

For instance, Wang et al. [125] investigated the effects of various ions (K⁺, Fe³⁺, Ca²⁺, and Mg²⁺) on the adsorption of Cr(VI) by modified BC. The authors found that the presence of K⁺ ions reduced the adsorption capacity of BC. Additionally, Ca²⁺ and Mg²⁺ had little impact on the adsorption. The competitive adsorption process is attributed to the intrinsic ions occupying the available adsorption sites on the BC surface, thereby diminishing the removal efficiency of heavy metal ions.

Table 1. Summary of factors influencing metal adsorption capacity.

Factors	Description	Impact on Metal Adsorption	Example	Reference
Surface area	Total area available for metal ion binding on the BC surface	A larger surface area increases the number of active sites, enhancing adsorption	Increased surface area from 273.26 to 2372.51 m ² /g improved Hg adsorption capacity	[85]
Porosity	Micropores and mesopores in BC affect the accessibility of adsorption sites	Higher porosity improves accessibility and adsorption capacity	Alkali treatment of BC from Douglas fir enlarged micropores to mesopores, enhancing adsorption. The KOH-activated BC effectively adsorbed Cr(VI), Pb(II), and Cd(II) with capacities of 127.2, 140.0, and 29.0 mg/g, respectively	[126]
Functional groups	The chemical groups on BC that interact with metal ions	Different functional groups enhance interaction with specific metals	Cr(III) immobilized through complexation with the -COOH group of the modified BC	[127]
Cation exchange capacity (CEC)	BC's ability to exchange cations with metal ions	Higher CEC improves the BC's ability to adsorb metal ions	CEC of all BC samples increased by 1.33 to 2.40 times post-modification, enhancing the immobilization efficiency for Cd(II) and Cu(II)	[59]
Ionic radius	The size of the metal ion affects how easily it can fit into adsorption sites on BC	Smaller ionic radius may enhance adsorption due to better site fit	Cr(III) exhibited higher adsorption efficiency due to its smaller ionic radius (0.0615 nm) compared to Cu(II) (0.073 nm) and Zn(II) (0.074 nm)	[102]

Table 1. Cont.

Factors	Description	Impact on Metal Adsorption	Example	Reference
Charge	The electrical charge of metal ions influencing electrostatic interactions with BC	A higher charge can lead to stronger electrostatic attraction	The crayfish shell BC possessed a higher positive charge, resulting in stronger electrostatic interactions with As	[128]
Speciation	The chemical form of the metal ion in solution, which affects its interaction with BC	Different species may have varying adsorption efficiencies	The speciation of arsenic significantly influences its removal efficiency; As(V) is more readily adsorbed compared to As(III) due to its greater stability and inertness	[100]
Oxidation state	The oxidation state of the metal ion, which affects its reactivity and interaction with functional groups on BC	Different oxidation states influence the adsorption mechanisms	Cr(VI) reduction to Cr(III) impacts its adsorption on BC	[113]
pH of the medium	The acidity or alkalinity of the solution affects the ionization of functional groups and metal speciation	pH changes can enhance or reduce adsorption depending on the metal type	Cationic metals such as Cu^{2+} increase with higher pH, while Cr(VI) adsorption decreases	[114,115]
Temperature	The thermal condition of the environment affecting adsorption kinetics and capacity	Increased temperature can enhance or reduce adsorption depending on the process	Higher temperatures improved the adsorption capacity (160 mg/g) of U(VI) by BC	[117]
Competing ions	The presence of other ions in the solution that can compete with metal ions for adsorption sites	A high concentration of competing ions can decrease metal adsorption	Anions (Cl^- , SO_4^{2-} , PO_4^{3-} , and NO_3^-) in wastewater competed with Cr(VI) for adsorption sites, leading to a reduction in adsorption capacity	[127]

5. Engineered Biochar for the Adsorption of Specific Types of Metals

5.1. Adsorption of Heavy Metals

Heavy metals such as Pb, Cd, Hg, and Cr are persistent pollutants that can contaminate soil, water, and air, posing severe risks to ecosystems and human health [129]. This underscores the critical necessity for implementing effective treatment technologies to safeguard environmental sustainability and public health. There are several methods for removing heavy metals from various sources, which can be divided into three main categories: physical, chemical, and biological. These include precipitation/coagulation, ion exchange, adsorption, membrane filtration, electrochemical treatment, bioremediation, chelation, phytoremediation, chemical oxidation/reduction, and acid/base treatment [130]. Each method has specific advantages and applications in environmental cleanup. BC offers a multifaceted approach to heavy metal remediation with several advantages. It is not only more cost-effective compared to technologies like membrane filtration and electrochemical treatment due to lower operational and maintenance costs but it also can be regenerated and reused multiple times by desorption of heavy metals using appropriate eluents, extending its lifecycle and reducing waste generation [131]. Moreover, once heavy metals are adsorbed onto BC, they are generally immobilized and less prone to leaching or release back into the environment, providing long-term effectiveness [132]. Table 2 presents the adsorption capacities of different engineered BC for heavy metal removal.

Biochar from rice husks and sunflower husks was obtained using stepwise pyrolysis, with temperatures reaching up to 750 °C, resulting in 34% and 32% BC yields, respectively. Sorption isotherm experiments demonstrated high adsorption capacities for heavy metals

(Cu, Zn, Pb) due to the BC's porosity and specific surface area [133]. Moreover, BC derived from secondary sedimentation (SS) and kitchen waste (KW) were evaluated for their heavy metal (HM) adsorption capacities, with KW-derived BC, notably KO-700, demonstrating significant efficacy in removing copper (Cu) and lead (Pb) from aqueous solutions (Cu: 1.25 mg/L after 72 h; Pb: 1.04 mg/L after four h). Characterization emphasized BC properties such as specific surface area, pore volume, and surface functional groups, elucidating their role in adsorption mechanisms, including electrostatic attraction and chemical precipitation [134]. Another study compared BC from waste biomass and plastic char from PET, PE, and PVC and confirmed the efficiency of these chars in removing heavy metals. Biochars showed the highest sorption capacities for heavy metals: SC 11 absorbed Ni (99.01%), Cu (91.60%), Cd (99.24%), Fe (10.95%), Pb (95.52%), and BC 11 absorbed Cr (99.06%). For plastic chars, PV 11 absorbed Ni (43.32%) and Cu (90.96%), while PT 11 absorbed Cd (28.31%), Fe (4.0%), Pb (70.07%), and Cr (99.01%) [135]. Biochars had higher metal adsorption capacities than plastic chars, even without activation. Derived sustainably from biomass like rice and sunflower husks, BC exhibits high adsorption capacities for metals such as Cu, Zn, and Pb due to its porous structure. It offers cost-effective and reusable capabilities, immobilizing metals effectively to prevent environmental leaching. Challenges include variability in BC properties and the need for optimized production processes. Despite these, BC demonstrates superior efficacy over plastic-derived pyrolysis chars for metal adsorption, highlighting its potential as a sustainable solution for environmental remediation efforts.

Table 2. Summary of heavy metals adsorption capacities of different engineered biochars.

Biochar Sources	Temperature (°C)	Procedure	Pollutant	Adsorption Capacity (mg/g)	Sorption Mechanism	Reference
Rice straw	100–700	Stepwise pyrolysis, including drying, grinding, and slow pyrolysis under anaerobic conditions. The BC was sonicated to form colloids	Cr(III)	2.4–14.1	Physical adsorption due to high specific surface area and functional groups	[136]
Eupatorium adenophorum	500	Mixed with magnesium nitrate and ferric chloride, dried, and then pyrolyzed in an oxygen-free environment	Pb(II)	252.70	Precipitation and cation exchange	[137]
Eupatorium adenophorumj	500	Mixed with magnesium nitrate and ferric chloride, dried, and then pyrolyzed in an oxygen-free environment	Cd(II)	156.60	Precipitation and cation exchange	[137]
Sargassum hemiphyllum	700	Dried, ground, sieved, pyrolyzed in muffle furnace 10 °C·min ^{−1}	Cu(II)	75–120	Physical sorption, ion exchange, surface complexation, surface precipitation, electrostatic interaction, metal– π interaction	[138]
HFO-BC (BC with Fe(III) and NaOH treatment)	-	Treated with 1 mol/L FeCl ₃ solution, stirred in 5% NaOH solution, washed, dried	Cd(II), Cu(II)	29.9, 34.1	Inner-sphere complexation, migration from solution to adsorbent surface, pore diffusion	[139]

Table 2. Cont.

Biochar Sources	Temperature (°C)	Procedure	Pollutant	Adsorption Capacity (mg/g)	Sorption Mechanism	Reference
Sulfonated BC (SBC)	180	Carbonization and sulfonation with A. compressus, H ₂ SO ₄ treatment, washing, and drying	Pb(II), Cd(II)	191.07, 85.76	Complexation, ion exchange, electrostatic interaction	[90]
Nix-MnO ₂ /BC	-	Hybrid BC precursor from CS and RH biomasses pyrolysis; surface-functionalized with Ni-MnO ₂ nanorods via ultrasonication, hydrothermal treatment, and calcination	Li ⁺	89.2	Physisorption via electrostatic attractive forces; monolayer adsorption according to Langmuir model	[140]
Magnetic EP BC	400, 800	Enteromorpha prolifera biomass (126 g) treated with 120 mL FeCl ₃ (2 mol/L) solution, stirred at 80 °C for 2 h. Ferric hydroxide-coated biomass separated via centrifugation, dried at 80 °C overnight. Pyrolysis at 400 or 800 °C under N ₂ with heating rate of 5 °C/min and N ₂ flow rate of 300 mL/min. Washed with 1 M HCl and distilled water, dried at 80 °C	Cr(VI)	95.23	Enhanced adsorption due to increased surface polarity and specific surface; likely includes physical adsorption due to magnetic modification	[141]
Coffee ground	650	SCG/FO mixtures pyrolyzed in a quartz tube furnace with CO ₂ atmosphere. Mixtures of SCG and FO in mass ratios SCG1/FO0.33, SCG1/FO0.5, SCG1/FO1, and SCG1/FO2. Pyrolysis at 10 °C/min heating rate to 650 °C, held for 60 min, cooled to 25 ± 2 °C	Sb(V), Cd(II), Ni(II)	Sb(V): 7.0 (single mode), 9.3 (multiple mode); Cd(II): 12.7; Ni(II): 16.8	Ternary complexation on iron oxides surface; competition for adsorption sites in multiple mode reduces Cd(II) and Ni(II) uptake but enhances Sb(V) removal	[142]
Porous BC	600	Corn straw powder soaked in 25% ZnCl ₂ for 20 h, dried, pyrolyzed at 600 °C for 1.5 h with N ₂ , mixed with Fe(NO ₃) ₃ and Zn(NO ₃) ₂ , pH adjusted to 11, stirred, red-brown precipitate formed	Ce(IV)	453.518	Chemisorption via surface active sites fits quasisecundary kinetic model better; adsorption influenced by temperature and is heat absorbing	[143]
Palm tree fronds	650	Carbonization at 650 °C under inert N ₂ atmosphere. Oxidation with 8 M HNO ₃	Eu ³⁺	123	Reaction equation: Proposed two-step mechanism: Cation exchange of carboxylic protons with Eu ³⁺ , followed by complexation of Eu ³⁺ with carboxylate groups	[144]

Table 2. Cont.

Biochar Sources	Temperature (°C)	Procedure	Pollutant	Adsorption Capacity (mg/g)	Sorption Mechanism	Reference
Orange peel	600	Orange peel cut, washed, oven-dried at 60 °C, heated at 600 °C under oxygen-limited conditions for 2 h, ground and sieved to <0.15 mm	La(III)	55.57	High adsorption capacity; mesoporous structure with well-developed porosity and surface functional groups	[145]
Corn cob	600	A mixture of 6.5 g KCl/NaCl (1:1) and 3 g corncob powder was dissolved in 30 mL DI water and soaked for 12 h at 50 °C. In the final hour, 1 g of Na ₂ S, Na ₂ S ₂ O ₃ , Na ₂ SO ₃ , or Na ₂ SO ₄ was added. The precursors were then filtered, dried at 80 °C for 12 h	Pb(II), Cu(II)	421.8 for Pb(II), 185 for Cu	Ion exchange, electrostatic interaction, cation- π interaction	[146]
Apple wood	700	-	Cr(VI)	5	Electrostatic interactions, ion exchange, complexation	[147]
Food waste	300	Food waste was mixed, oven-dried (105 °C), ground (10-mesh sieve), and stored in a sealed container at room temperature	Cd(II), Pb(II)	Cd 16.86, Pb 12.41	Surface complexation, cation- π interaction, precipitation, electrostatic interaction	[148]
Sewage sludge-coconut fiber	600	Copyrolysis	Cu(II), Zn(II), Ni(II), Cd(II)	-	Electrostatic interaction, complexation, π - π interaction, H-bond, pore filling, crystal lattices	[149]
Modified pineapple pulp	400	-	Cu(II)	41.9	Ion exchange, complexation, electrostatic attraction	[150]

5.2. Adsorption of Transition Metals

Transition metals such as copper (Cu), zinc (Zn), nickel (Ni), and cobalt (Co) are indispensable in various industrial processes and essential for biological functions. However, their accumulation in the environment beyond permissible levels poses significant hazards. These metals are persistent pollutants that can contaminate soil, water, and air, damaging ecosystems and human health [151]. For instance, Cu and Zn are essential micronutrients but excess levels can disrupt aquatic life and soil microbial communities. Ni and Co, used in alloys and batteries, are toxic at elevated concentrations, impacting organisms' growth and reproduction. Engineered BC has emerged as a promising solution due to its unique properties. Biochar, derived from biomass through pyrolysis, offers a highly porous structure with a large surface area and functional groups such as carboxyl, hydroxyl, and phenolic moieties [19]. Recent research has stated that BC production methods encompass various factors, including characterization, stability, and potential applications in promoting regenerative economic sustainability [30]. The resulting BC loaded with Fe-Mn binary oxides demonstrated a maximum adsorption capacity of 95.7 mg/g, which surpassed those loaded

with individual oxides and pristine BC, showing potential for effective water remediation applications [152]. In exploring the pH-dependent adsorption behaviors of As(V) and Ni(II) using Fe-BC composites produced under N₂ and CO₂ environments, it was found that adsorption of As(V) increased significantly with the final pH from 3.0 to 5.8, reaching up to 20.1 mg/g for Fe-C-N₂ and 18.7 mg/g for Fe-C-CO₂, but decreased linearly thereafter. This trend is attributed to electrostatic repulsion between As(V) ions and the surface of magnetite and Fe as the pH exceeded 5.8 [153]. Continued research and innovation in BC technology are crucial for optimizing its effectiveness and sustainability in mitigating the adverse impacts of transition metal pollution on ecosystems and human well-being.

5.3. Adsorption of Rare Earth Metals

Rare earth elements (REEs), first discovered in 1794 by Finnish scholar John Gadolin, are defined by the IUPAC as comprising 15 lanthanides and two transition elements with similar chemical properties and they exhibit “lanthanide shrinkage” due to their decreasing atomic radius with increasing atomic numbers. Rare earth metals also can be found in secondary sources such as industrial byproducts (e.g., coal ash), electronic waste, and other residues [4]. Due to their unique chemical and physical properties, REEs are essential in various industries, including electronics, green energy, and agriculture. However, their environmental impacts and toxicological effects remain under-researched and poorly understood [154]. Studies have evaluated the profitability of various extraction methods from specific secondary sources. Understanding both the quality (concentration) and quantity of REEs in these sources is crucial; for instance, coal ash can contain concentrations ranging from 0.9% to 1.3% of total REEs. Techno-economic analysis (TEA) plays a pivotal role in assessing the economic feasibility of scaling up these extraction processes from lab to industrial scales [4]. There is another study that extensively reviews environmental considerations in rare earth mining, emphasizing techniques such as selective precipitation, solvent extraction, and ion exchange for thorium and uranium removal. These methods, particularly solvent extraction using tertiary and primary amines, offer effective separation capabilities. However, challenges remain in scaling up applications for commercial use and addressing similar adsorption behaviors between REEs and uranium [155].

According to the study [156], BC-FeNPs exhibited significant advantages in adsorbing rare earth elements (REEs) compared to FeNPs and BC alone. The adsorption efficiencies for REEs increased over time to a maximum, contrasting with the unchanged efficiency for Zn(II). At equilibrium, BC-FeNPs achieved a maximum adsorption efficiency of 88.4% for Lu(III), far surpassing the 8.7% efficiency observed for Zn(II). This demonstrated BC-FeNPs' superior selectivity for REEs over Zn(II) in mine wastewater [156]. In another study [157], the structural analysis of BC before and after adsorption experiments revealed significant changes under scanning electron microscopy, utilizing an accelerating voltage of 10.0 kV and a working distance of 15.55 mm for enhanced resolution and depth. This study also employed infrared spectroscopy to examine surface functional groups of BC, highlighting key spectral features in the range of 450 to 4000 cm⁻¹. Kinetic studies on the adsorption of rare earth elements using pseudo-second order and intraparticle diffusion models indicated that resonant vibratory mixing (RVM) enhanced adsorption efficiency more effectively than stirring, as evidenced by higher K² values and better model fits.

Recent advancements in rare earth element (REEs) research emphasize their pivotal role in electronics, green energy, and agricultural technologies. Notably, innovative adsorption technologies, such as BC-supported iron nanoparticles (BC-FeNPs), have demonstrated superior REE adsorption capabilities compared to traditional methods, underpinned by sophisticated analytical techniques to elucidate structural changes and surface interactions during adsorption processes.

6. Recycling and Regeneration of Metal-Loaded Biochar

6.1. Chemical Regeneration Techniques

After a certain period of use, BC's adsorption capacity diminishes as its active sites become saturated with heavy metals, necessitating regeneration. Additionally, heavy-metal-adsorbed BC, when discarded, particularly in acidic conditions, can release these metals as secondary pollutants, posing a long-term environmental hazard. Spent BC can often be regenerated through multiple adsorption-desorption cycles without significantly altering its physicochemical properties. Understanding the desorption process is crucial for evaluating BC's adsorption efficiency and recycling potential. Effective desorption methods include thermal, solvent, chemical, microwave, and supercritical fluid treatments, with acids and complexing agents being particularly efficient [55,70].

Common chemical agents for regeneration include inorganic acids (HCl, HNO₃, H₂SO₄), organic acids (formic acid, acetic acid), and alkaline solutions (NaOH, KOH). These agents, also known as stripping agents, are usually applied at lower concentrations (0.1–0.2 M) to avoid altering BC's properties [152]. Additionally, complexing agents like ethylenediaminetetraacetic acid (EDTA) and salts such as NaCl, KNO₃, NaNO₃, and Ca (NO₃)₂ are employed for desorption [114,158]. Several studies have demonstrated the effectiveness of regenerating BC through various techniques. For instance, HCl has shown a desorption efficiency of 10–93%, outperforming HNO₃ and NaOH due to the Cl[−] ion's similar ionic radius to metal ions [159]. Another study found EDTA-2Na to be the most effective desorbing agent for lead-loaded magnetic BC, with a desorption efficiency of 91.1%. Furthermore, microwave irradiation combined with chemical reagents like NaOH improved desorption rates, achieving up to 73% efficiency [160].

Poonam et al. [161] found that bagasse agricultural waste, modified through various physicochemical methods, was used to remove lead ions (Pb²⁺) from industrial wastewater. After adsorption, the saturated BC was treated with 0.1 M HNO₃, achieving approximately 90% regeneration. Similarly, magnetic nanocomposites made from camel bone BC demonstrated efficient desorption of heavy metals like cadmium (Cd²⁺), cobalt (Co²⁺), and lead (Pb²⁺) using 0.01 M HCl [162]. Furthermore, nano zinc/bagasse BC showed an increased adsorption capacity for chromium (Cr⁶⁺) at 102.66 mg/g and maintained high heavy metal adsorption ability after six desorption cycles [163]. Additionally, water hyacinth BC exhibited significant regeneration potential following removing cadmium and lead when desorbing with 0.5 mol/L HCl [164]. The effectiveness of chemical-reagent-based regeneration methods depends on factors such as surface functional groups, pore structure, and changes in active sites. While effective, these methods can produce secondary contamination due to the potential leaching of sorbed contaminants. Among the various methods, acidic solutions are particularly effective at desorbing heavy metal ions [114].

6.2. Thermochemical Recycling Techniques

Regeneration using mineral acids, alkalis, and inorganic salts extends the BC's service life. However, the adsorption capacity of regenerated BC decreases with each cycle, and waste BC disposal remains an issue. Additionally, wastewater generated during BC regeneration requires proper treatment [165]. Incineration is a prevalent thermochemical method for processing spent BC, but it does not regenerate BC. This process decreases both the mass and volume of the spent BC while facilitating thermal energy recovery. In contrast, pyrolysis is seen as a more effective method for the safe treatment and regeneration of exhausted BC [114]. Cui et al. [165] found that pyrolysis at 500 °C effectively removed Cd from the hyperaccumulator, producing more valuable BC than incineration-derived ash. The authors also investigated the pyrolysis of exhausted BC adsorbent at 300–900 °C, examining Cd behavior and the physicochemical properties and environmental applications of the regenerated BC [165]. Increasing pyrolysis temperatures greatly enhanced the vaporization of Cd, with almost no Cd in BC regenerated at 700–900 °C. The regenerated BC exhibited higher pH, ash content, and carbon content but lower hydrogen and oxygen contents compared to raw hydrochar. The toxicity and mobility of Cd were significantly

reduced after pyrolysis and the regenerated BC showed a much higher Cd adsorption capacity (26.05–30.24 mg/g) compared to raw hydrochar (6.70 mg/g). Surface complexation with oxygen-containing functional groups was the primary Cd adsorption mechanism for hydrochar while precipitation with carbonates dominated Cd removal in regenerated BC. Yang et al. [166] stabilized spent rice straw BC loaded with cobalt and nickel through hydrothermal carbonization, creating a stable structure with a low leaching rate, which was reused as a catalyst for pollutant degradation. Pan et al. [167] used spent magnetic BC with adsorbed Cu^{2+} to improve peroxymonosulfate activation and norfloxacin degradation, enhancing the BC's properties. Chen et al. [168] converted spent BC into heterostructured electrocatalysts, showing good performance in oxygen evolution reactions. The advanced oxidation process for removing organic pollutants can also utilize regenerated BC. Mer et al. [169] used BC loaded with lead and nickel to generate reactive hydroxyl radicals. Their findings suggest that the effectiveness of the advanced oxidation process relies on the structure of the carbon material and the type and amount of metal complexes it contains. Anton Zubrik et al. [170] found that microwave irradiation significantly enhances the desorption rate of As^{5+} from magnetic BC. These findings demonstrate that thermochemical processes are an effective technique for safely disposing of exhausted BC adsorbents and regenerating valuable BC.

6.3. Limitations in Recycling and Environmental Considerations

Disposing of or reusing heavy-metal-loaded BC presents a significant challenge, with no effective large-scale recycling strategy currently available. Stabilizing heavy metals on spent BC is difficult and improper treatment can result in secondary pollution [70]. Proper management and reuse are crucial to prevent secondary pollution when regenerating spent BC is not feasible. A resource utilization strategy can repurpose heavy-metal-laden spent BC, aligning with circular economy principles by transforming waste into valuable products. This approach creates economic opportunities and promotes sustainable resource use [169]. The reuse options for spent BC, as described in the subsequent section, include applications in energy storage devices, supercapacitors, catalysts, and construction materials. These applications align with circular economy principles and contribute to the reduction of carbon footprints by capturing CO_2 from the atmosphere [114]. Therefore, developing convenient and economical recycling technologies reduces the production costs of adsorbents and minimizes waste generated from metal-loaded adsorbents. However, challenges like loss and structural degradation during recycling limit their effective reuse over multiple cycles in laboratory-scale studies [171]. Incineration offers waste-to-energy benefits, reducing the mass and volume of spent adsorbents while recovering thermal energy but it is not capable of regenerating BC. Landfilling, although a last option, may require pretreatments to reduce heavy metal content to comply with local regulations or USEPA standards for hazardous waste [114]. Thus, advancing technologies for the recovery, regeneration, and recycling of adsorbents is crucial for scaling up adsorption engineering applications.

7. Applications of Metal-Loaded Biochar

7.1. Soil Amendment and Fertilization

The application of metal-loaded BC in soil amendment and fertilization offers promising benefits for enhancing soil properties and promoting agricultural productivity. BC, a carbon-rich material from biomass pyrolysis, is widely recognized for enhancing soil structure, nutrient retention, and plant growth, serving primarily as a soil amendment to improve agricultural conditions [172]. When loaded with metal ions through adsorption processes, BC can also address soil contamination issues and provide additional nutrients for crops. Metal-loaded BC can be used as a soil amendment to address deficiencies in essential trace elements and improve soil fertility. For example, iron-loaded BC can enhance soil fertility and nutrient absorption efficiency, effectively delivering nutrients to plants [173].

The introduction of metal-loaded BC into soil can enhance nutrient availability, improve soil pH, and increase soil cation exchange capacity, thereby fostering better crop yields.

Furthermore, BC amended with heavy metals can aid in the remediation of contaminated soils. For instance, BC loaded with Pb and Cd has been employed to immobilize these toxic metals in polluted soils, reducing their bioavailability and mitigating potential risks to plant and human health [174]. This immobilization process occurs through various mechanisms, including adsorption and chemical stabilization, thereby decreasing mobility and toxicity. Studies have demonstrated that metal-loaded BC can also contribute to improved soil fertility. For example, BC loaded with Cu and Zn enhanced bean production and micronutrient uptake, particularly Zn, outperforming traditional fertilizers [175]. BC contains a significant concentration of trace elements such as Fe, Cu, B, Zn, and Mn, which can enhance plant nutrient uptake and contribute to disease resistance mechanisms [176]. Similarly, the use of metal-loaded BC has been reported to improve soil quality and water-holding capacity, which can be particularly beneficial in drought-prone areas [177].

7.2. Catalytic Applications

Biochar has gained significant attention as a versatile support for metal-loaded catalysts, presenting numerous innovative applications across environmental, energy, and chemical sectors. The high surface area, porosity, thermal stability, and diverse functional groups of BC make it an excellent candidate for dispersing and stabilizing metal nanoparticles, enhancing their catalytic efficiency [178]. In environmental remediation, metal-loaded BC catalysts are effectively used in water treatment processes to adsorb and degrade pollutants such as heavy metals, textile dyes, and organic contaminants [97,179–182]. For energy production, these catalysts play a critical role in biofuel synthesis by improving the conversion efficiency of biomass into valuable fuels and chemicals through processes like pyrolysis, gasification, and hydrothermal liquefaction. Additionally, metal-loaded BC catalysts facilitate the production of hydrogen via catalytic reforming of bio-oil or methane, contributing to cleaner energy solutions [183,184]. In chemical synthesis, they are employed to enhance the production of fine chemicals and pharmaceuticals due to their high catalytic activity and selectivity. For instance, alkaline earth metals and transition metals like iron (Fe), nickel (Ni), cobalt (Co), and copper (Cu) loaded BC are favored for their cost-effectiveness and catalytic properties. Bimetallic and multimetallic combinations of BC further improve catalytic performance through synergistic effects. Preparation methods such as impregnation, coprecipitation, and the sol-gel process ensure uniform metal distribution and enhanced interaction with the BC matrix. Overall, metal-loaded BC catalysts represent a sustainable and efficient approach to addressing contemporary industrial and environmental challenges.

7.2.1. Application for Wastewater Treatment

Metal-loaded BC catalysts have emerged as a highly effective solution for wastewater treatment, leveraging the unique properties of BC to enhance the removal of inorganic and organic contaminants. These catalysts excel in adsorbing and degrading a wide range of pollutants, including heavy metals, dyes, pharmaceuticals, and organic contaminants, through processes like adsorption, reduction, and oxidation [185–188]. For example, iron-loaded BC can effectively remove arsenic and lead from wastewater [189,190] while copper-loaded BC excels in breaking down complex organic compounds [185]. Additionally, the catalytic properties of metal-loaded BC enable advanced oxidation processes (AOPs), such as Fenton-like reactions, which generate reactive oxygen species to degrade persistent pollutants [180,182]. The use of metal-loaded BC in wastewater treatment not only improves water quality but also offers a sustainable approach by utilizing waste biomass for BC production and reducing reliance on traditional, more hazardous chemical treatments. This innovative application highlights the potential of metal-loaded BC catalysts to address pressing environmental challenges and enhance the efficiency of wastewater purification systems.

The list of recent studies on metal-loaded BC is presented in Table 3 for the removal and degradation of inorganic and organic pollutants from wastewater. Ouyang et al. and Wu, Jia et al. investigated the degradation of tetracycline (TC) and bisphenol A (BPA) using MoO₂-loaded BC as a cocatalyst to enhance Fe³⁺/Fe²⁺ cycling, achieving removal efficiencies of 90.9% for TC and over 96% for BPA within 60 min [188,191]. In both studies, Mo- and iron-loaded BC were prepared through impregnation with iron salts, pyrolysis at 600–800 °C, and subsequent autoclaving at 180 °C with ammonium molybdate. However, these multistage processes could increase operational costs. In another separate study, Coloaded BC was prepared from cherry kernels for efficient removal of BPA with the aid of peroxydisulfate (PMS) and persulfate (PDS) [186]. The optimal concentrations of PMS and PDS were found to be 0.25 g L^{−1} and 1.0 g L^{−1}, respectively, when using Coloaded BC. Increasing the temperature from 15 to 45 °C improved the BPA removal efficiency, which was highest at pH 7 and lowest at pH 3. The removal efficiency of BPA remained above 90% after five cycles, indicating economic viability. Transition metals, carbon materials, heat, UV radiation, and ultrasound can activate PDS, while PMS activation by Fe²⁺ for organic contaminant removal can be enhanced by the active MoO₂ surface [181,192]. A recent study highlighted the superior performance of Cu-loaded BC (BC-Cu, 1:4) in activating PMS [180]. The prepared BC-Cu composite achieved a remarkable 99.99% removal rate of ciprofloxacin, with an initial concentration of 20 mg·L^{−1} within 40 min. Additionally, the BC-Cu sample demonstrated significant activity across a wide pH range (4–12) and exhibited an “anti-anion interference” capability [180]. Another unconventional modified BC was prepared in recent years by autoclaving of corn stalks in sulfuric acid followed by copyrolysis with KOH (1:1 with the hydro char) and finally wet impregnation of the BC with FeCl₃·6H₂O at room temperature in an inert environment. The produced hydrophilic BC had excellent removal efficiency of Pb²⁺ (99.8%) due to the synergetic effect with the zero-valent iron (Fe⁰) [193].

Table 3. Recent studies of the application of metal-loaded biochar for wastewater treatment.

Raw Materials	Metal Compounds	Process	Remarks	References
Calamus	MoO ₂ -enhanced Fe ²⁺ /Fe ³⁺	Impregnation and followed by pyrolysis, 600 °C	Degradation of tetracycline, 90.9%	[188]
Rice straw	MoO ₂ -enhanced Fe ²⁺ /Fe ³⁺	Impregnation and followed by pyrolysis, 800 °C	Degradation of BPA, >96%	[191]
Cherry kernel	CoCl ₂ ·6H ₂ O	Impregnation and followed by pyrolysis, 800 °C	Degradation of BPA, ~100%	[186]
Rice straw	CuCl ₂ ·2H ₂ O	Impregnation and followed by pyrolysis, 800 °C	Degradation of ciprofloxacin, ~100%	[180]
Rice straw	FeCl ₃ ·6H ₂ O/LaCl ₃ ·7H ₂ O	Pyrolysis, 450 °C	Adsorption of phosphorus, 52 mg P/g	[182]
Corn stalks	KOH, FeCl ₃ ·6H ₂ O	Autoclave at 200 °C, Copyrolysis (800 °C) with KOH and impregnation in FeCl ₃ ·6H ₂ O solution	480.9 mg g ^{−1} of Pb ²⁺ adsorption capacity	[193]
Sewage sludge	Zero valent iron	Copyrolysis 500 °C	83.4% degradation of sulfamethoxazole	[194]
Municipal sludge	FeCl ₃ ·6H ₂ O	Impregnation and followed by pyrolysis, 400 °C	99.8% degradation of thiamethoxam	[195]

Moreover, iron-loaded BC has been studied for Fenton-like catalytic reactions for the degradation of organic pollutants in wastewater [194,195]. The Fenton reaction, which involves the combination of Fe²⁺ and H₂O₂, has attracted increased attention due to its potent free radical oxidation capabilities and environmental benefits. Iron-loaded magnetic biochar has been identified as an effective catalyst for activating hydrogen peroxide (H₂O₂)

to generate hydroxyl radicals ($\bullet\text{OH}$). Both radical quenching experiments and electron paramagnetic resonance exposure have confirmed the generation of $\bullet\text{OH}$ and its significant role in the oxidative degradation of thiamethoxam [195]. Previous research indicates that an acidic pH optimizes Fenton activity, with pH levels above 4 hindering the $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycle due to the formation of inactive iron complexes. Additionally, increasing the catalytic dosage to 1.5 g/L and raising the adsorption batch temperature to 45 °C have demonstrated superior degradation capabilities for sulfamethoxazole [194].

Phosphorus (P) removal from wastewater has also been a focus of recent research. It was found that raw BC has a limited capacity for P removal, necessitating further modification. Previous studies identified $\text{La}(\text{OH})_3$ as an effective compound for P removal, achieving nearly 100% removal efficiency [182,196]. Building on this, Sun, Zhang, et al. developed a novel rice-straw-based BC, which was subsequently mixed with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ salt solutions to create a composite granule with montmorillonite, demonstrating efficient phosphorus removal [182].

7.2.2. Applications for Catalytic Bio-Oil Production

Transitional metal ion-loaded BC has demonstrated significant potential in enhancing the production of bio-oil and biochemicals, offering an innovative and sustainable approach to biomass conversion [197–200]. These metals are well regarded for their catalytic properties in various thermochemical processes. When loaded onto BC, these metal ions can significantly improve the efficiency of biomass conversion techniques like pyrolysis, gasification, and hydrothermal liquefaction. For instance, nickel-loaded BC serves as an effective catalyst in the pyrolysis process, enhancing the yield and quality of bio-oil by promoting the breakdown of complex organic polymers such as lignin and cellulose, etc. into simpler, more valuable hydrocarbons [198,199]. Similarly, iron and Mn-loaded BC catalysts facilitate the gasification process, aiding in the production of syngas, which can be further processed into a variety of biochemicals and fuels [201,202].

The presence of these metal ions not only accelerates the reaction rates but also aids in the selective formation of desired products, reducing the formation of unwanted by-products such as tar. The synergistic effect between BC and transitional metals enhances catalytic stability and longevity, making these catalysts more effective and economically viable for large-scale applications. A few recent studies on the production of biofuel by using metal-loaded BC as a catalyst are listed in Table 4.

The superior catalytic activity and notable recyclability of iron enhance its industrial application value compared to other metals. During the thermochemical conversion of biomass, the produced bio-oil is enriched with phenolic/aromatic compounds. Lignin has been identified as the primary source of phenolic compounds in bio-oil [203]. Cellulose undergoes dehydration, decarboxylation, decarboxylation, and cyclization reactions, leading to the formation of cyclic oxygen-containing compounds such as furan derivatives, which subsequently transform into phenolic compounds [204,205]. Specifically, anhydro sugars derived from cellulose are converted into furans through dehydration and structural rearrangements. Additionally, C5 compounds are produced via dehydration and decarboxylation processes that release gases like carbon monoxide, methane, and water. These reactions occur at the catalytic sites of BC through mechanisms such as Diels–Alder reactions, decarboxylation, and oligomerization, eventually reforming into phenols [203]. Hemicellulose, upon aromatization, can also be converted into phenolic compounds [206]. In this context, iron-loaded cellulose BC effectively facilitates the transformation of aldehydes and ketones present in corncob bio-oil, significantly enhancing the phenolic compound content [200,203]. Nickel-based catalysts are extensively employed in the hydrogenolysis of lignin and its model compounds due to their exceptional hydrogenation capabilities and cost-effectiveness [197–199]. These catalysts, often supported on materials like BC, can selectively cleave the C–O linkages in β -O-4 and α -O-4 bonds within lignin and model compounds such as diphenyl ether, resulting in the formation of phenolic compounds [198]. Nickel-supported activated carbon (AC) has demonstrated significant efficacy in breaking

the C-O bonds of diaryl ethers, yielding high concentrations of aromatic and phenolic compounds. In a previous study, BC derived from various carbon sources, including cellulose, lignin, and hemicellulose, was used to support a Ni catalyst for the catalytic hydrogenolysis of lignin model compounds (e.g., diphenyl ether) [199]. The study indicated that Ni/AC derived from cellulose exhibited the highest catalytic activity in converting lignin-derived compounds into aromatic products. The uniform pore sizes and structural characteristics of the cellulose-derived BC were identified as critical factors enhancing the dispersion of Ni while the sulfur-free nature of cellulose contributed to increased catalytic activity of the Ni/AC [199].

The industrial synthesis of biodiesel typically involves the homogeneous transesterification of vegetable oils and animal fats, catalyzed by strong acids and bases such as KOH, NaOH, and H₂SO₄ [207]. However, these strong acids and bases are generally avoided due to their corrosive nature. As an alternative, CaO has been employed in biodiesel production, owing to its basicity and low cost. Nevertheless, the stability of CaO can diminish due to its transformation into Ca(OH)₂ and CaCO₃, which reduces catalytic activity [207]. In this context, BC can serve as an effective carrier for CaO, helping to maintain catalyst activity during the transesterification reaction. Recent studies have developed efficient Ca-BC composite catalysts using rice husk and municipal sludge as carriers. These materials are rich in silica, which can form Ca-O-Si bonds on the BC surface, enhancing catalyst stability [207,208]. Postactivation with KOH significantly increases the porosity of BC, resulting in a high biodiesel yield of 93–94% due to the catalyst's high basicity. Comparisons between the newly synthesized catalyst and pure CaO revealed that rice husk BC is an effective carrier, with the Ca-O-Si bond formation contributing to both catalytic activity and stability [209].

Table 4. Recent studies of the application of metal-loaded biochar for bio-oil production.

Feedstock for BC	Process for BC Catalyst	Metal Ion Sources	Feedstock for Biofuel	Process for Biofuel	Remarks	References
Rice husk	Microwave-assisted catalytic pyrolysis, 550 °C	Fe(NO ₃) ₃ , impregnation and calcined with BC	Corn cob	MW-assisted torrefaction	Increased phenol compounds in bio-oil up to 60%	[200]
Cellulose powder	Pyrolysis, 600 °C	Ni(NO ₃) ₂ ·6H ₂ O, impregnation and calcined with cellulose powder BC (CPB)	Lignin model compounds	Hydrogenolysis, 140 °C	Increased yield of phenol (12.5%) and cyclohexanol (80.7%)	[199]
Peanut shell	Microwave-assisted Pyrolysis, 550 °C	FeCl ₂ ·4H ₂ O and FeCl ₃ (1:1 ratio), impregnation and calcined, 450 °C	Peanut shell	Pyrolysis	Total bio-oil 24.3% where 27% aliphatic and 18% aromatic hydrocarbon selectivity	[201]
Rice husk	Pyrolysis, 700 °C	CaO (30 wt%), impregnation and calcined (700 °C) with rice husk BC	Palm oil	Transesterification reaction, 65 °C	Biodiesel yields up to 93.4%	[209]
Municipal sludge	Pyrolysis, 800 °C	CaO (20 wt%), impregnation and calcined (700 °C) with the BC	Palm oil	Transesterification reaction, 65 °C	Biodiesel yields up to 93.8%	[207]

Table 4. Cont.

Feedstock for BC	Process for BC Catalyst	Metal Ion Sources	Feedstock for Biofuel	Process for Biofuel	Remarks	References
Peanut shell	Pyrolysis, 700 °C	FeCl ₃ ·4H ₂ O, MnCl ₂ ·4H ₂ O, NaCl; impregnation and calcined with BC	Peanut shell	Pyrolysis, 440–660 °C	8% phenolic selectivity over Fe ³⁺	[202]
Pine tree needles	Impregnation with ZnCl ₂ (1:1 biomass to ZnCl ₂ weight ratio) and Pyrolysis, 700 °C	Ni(NO ₃) ₂ ·6H ₂ O, Impregnation and calcined with the modified BC, 500 °C	Pine tree needles	Pyrolysis, 550 °C	Increased the aromatic selectivity to ~36%	[197]

7.3. Electrochemical Applications

By increasing the porosity, surface area, graphitization, or doping with heteroatoms, BC can be tuned into a suitable for energy storage applications in supercapacitors, batteries, and hydrogen storage [210]. BC derived from manure and sewage sludge, after microwave oxidation to reduce carbon content and increase oxygen content, showed enhanced stability in specific capacitance, power density, and charge–discharge capacities when used as supercapacitor materials loaded with Ni²⁺, forming NiO and NiOOH [211]. Spent BC has been used to create supercapacitor electrodes, addressing the demand for green energy. For instance, cobalt-doped BC exhibited remarkable electrochemical properties, making it suitable for energy storage [212]. Deping Li et al. [213] converted waste Ni-laden BC into pseudocapacitive materials via hydrothermal treatment. The optimized temperature (90–180 °C) and Ni content (100 and 500 mg/g) revealed that nickel can amplify the graphite layer and improve the stability of BC-based pseudocapacitive material during hydrothermal treatment. Rawat et al. [210] reported that optimizing BC for energy storage in batteries and supercapacitors requires a careful selection of additives, conducting polymers, solvents, and electrolytes to enhance overall device performance and justify costs. Comprehensive performance evaluation and testing are necessary to develop better alternatives to traditional batteries and accelerate research and development. During this review, we were not able to find lots of reports in this area but with the rapid increase in the demand for energy storage devices, we believe this is an interesting area that is worth exploring.

8. Future Research Directions

Most studies use pristine BC for heavy metal removal from groundwater and wastewater sources. However, further research is needed to evaluate the application of engineered BC under diverse conditions, accounting for all potential influencing factors in water and wastewater. Future studies should focus on enhancing BC adsorption capacity by incorporating functional groups and novel substances to improve its physical and chemical properties for targeted heavy metal removal. Current research on biomass-based BC often uses synthetic wastewater containing a limited number of metals. Investigating real wastewater with multiple metals is crucial to understanding adsorption interactions and competitive effects. Additionally, exploring BC's efficacy in treating acid mine drainage and combining it with other treatments could optimize heavy metal remediation [30].

BC-based heavy metal removal has predominantly been investigated at the laboratory scale. While many studies have demonstrated effective removal, the transition to the industrial application has been limited due to a lack of engagement from entrepreneurs and industry personnel. Collaborating with industry and large-scale pilot trials is essential to advance BC as a cost-effective and efficient adsorbent to assess its stability and performance under real-world conditions. Sustainable adsorption technologies require

low-cost adsorbents. Comparative cost-benefit analyses between biomass-based BC and conventional adsorbents along with comprehensive life cycle assessments are necessary to evaluate environmental sustainability. Employing artificial neural networks can model and predict BC performance under varying conditions and hopefully enhance adsorption efficiency [18,21]. Specifically, artificial neural networks (ANNs) are powerful tools for modeling and predicting BC performance by analyzing complex data patterns. They can optimize BC properties for enhanced adsorption efficiency by training on historical data to understand relationships between BC characteristics and performance under various conditions. Once trained, ANNs can predict how different conditions affect performance, facilitating the development of more efficient BCs and guiding improvements based on complex, nonlinear interactions that are challenging to model with traditional methods.

Furthermore, challenges related to the regeneration, reuse, and proper disposal of spent BC must be addressed. There is limited research on regenerating spent BC to extend its lifespan and reduce operational costs. Future studies should focus on developing efficient, low-cost, and environmentally friendly regeneration techniques. Spent BC with heavy metals cannot be directly disposed of due to the risk of secondary pollution. There is limited information on the toxic effects of disposing of metal-impregnated BC, necessitating the development of effective stabilization and desorption methods. Eco-friendly decontamination methods using natural micro-organisms or plants should be developed [70,114].

Additionally, novel methods for reusing spent BC for energy recovery or converting it into value-added and energy storage should be explored to support circular economy principles. Converting spent BC into electrode materials for supercapacitors and catalysts supports sustainable energy solutions. This highlights the need for further exploration of the relationship between biomass waste precursors and carbonaceous electrochemical materials [114].

9. Conclusions

The use of engineered BC derived from waste biomass for heavy metal adsorption offers significant environmental benefits, such as waste reduction and improved sustainability. This review examines the current progress in developing engineered BC for effective heavy metal remediation and the repurposed applications of metal-loaded BC. However, challenges persist in terms of scalability, regeneration, disposal, and system compatibility. Future research should focus on green functionalization methods and evaluate their environmental and economic feasibility. Overcoming these challenges will allow engineered BC to play a more significant role in creating a cleaner and more sustainable future.

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