

Review

# Preparation and Modification of Biochar Materials and their Application in Soil Remediation

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**Abstract:** As a new functional material, biochar was usually prepared from biomass and solid wastes such as agricultural and forestry waste, sludge, livestock, and poultry manure. The wide application of biochar is due to its abilities to remove pollutants, remediate contaminated soil, and reduce greenhouse gas emissions. In this paper, the influence of preparation methods, process parameters, and modification methods on the physicochemical properties of biochar were discussed, as well as the mechanisms of biochar in the remediation of soil pollution. The biochar applications in soil remediation in the past years were summarized, such as the removal of heavy metals and persistent organic pollutants (POPs), and the improvement of soil quality. Finally, the potential risks of biochar application and the future research directions were analyzed.

**Keywords:** biochar preparation; soil pollution; remediation

## 1. Introduction

With the development of industry and high-intensity human activities in China, soil pollution is becoming more and more serious, mainly due to the reduction of soil area and pollution by chemical compounds such as pesticides, petroleum, heavy metals, persistent organic matter, and acidic substances [1].

Pollutants in soil mainly include heavy metals and organic compounds, such as Cd, Pb, Cr, pesticides, fertilizers, antibiotics, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), etc. [2,3]. These pollutants not only affect the decline of crop yield and quality, resulting in further deterioration of the atmospheric and water environment quality, but also have carcinogenic, teratogenic, mutagenic effects, and genotoxicity, which endanger human health through the food chain [4].

The remediation methods of contaminated soil are mainly divided into physical, chemical, biological, and plant methods. Physical remediation technologies mainly include soil leaching, thermal desorption, steam extraction, and off-site landfill [5]. But the disadvantages are its high costs and the risk of secondary diffusion. Chemical remediation technologies mainly include immobilization-stabilization techniques, redox, chemical modification, surfactant cleaning, and organic matter improvement [6,7], but the chemicals used may cause secondary pollution to the environment. There is a long repair cycle in bioremediation technology and the repair effect is susceptible to external environmental factors.

Since Lehmann proposed the efficacy of Amazon black soil [8], scholars have found that the biochar produced by the lack of oxygen through pyrolysis of agricultural and forestry wastes is a material with well-developed pore structure, large specific surface area, abundant oxygen-containing functional groups, and excellent adsorption performance [9,10]. Biochar remediation technology is

between physical remediation and chemical remediation. On one hand, inorganic pollutants could be removed by physical adsorption, and organic pollutants could be removed by distribution. On the other hand, the application of biochar affects the solubility, valence, and existence of heavy metals in the soil, thus immobilizing the heavy metals in the soil. Finally, toxicity of heavy metals was fixed or reduced [9]. Due to its remarkable effect, low cost, and convenient operation, biochar has advantages in the treatment of heavy metal and organic pollution [11].

Before summarizing the application of biochar in soil remediation, this paper summarized the preparation and modification methods of biochar and analyzed the influence of different processes on the physicochemical properties of biochar to deepen the understanding of biochar. As the adsorbing material, the removal of heavy metals and organic compounds from soil and the main mechanism of biochar were reviewed. As a soil improver, the improvement of soil pH, nutrient, nitrogen, and phosphorus loss by biochar, and the application trend in the future, were summarized. At the same time, the potential risks of biochar were analyzed to effectively avoid the possible harm to the environment.

## 2. Preparation and Modification of Biochar

### 2.1. Preparation of Biochar

The preparation methods of biochar are mainly divided into pyrolysis [12], hydrothermal carbonization (HTC) [13], and microwave carbonization [14]. Different preparation methods affect the physical and chemical properties of biochar, such as yield, ash, specific surface area, pore structure, type and number of functional groups, and cation exchange capacity. Compared with the pyrolysis, HTC does not require drying step and has a higher biochar yield [15]. The advantages of microwave carbonization are controllable process, no hysteresis, rapid heating, and energy efficiency [16,17]. However, biochar prepared through HTC and microwave contained high concentrations of organics, which are not actually considered soil remediation material.

#### 2.1.1. Pyrolysis

Pyrolysis, also known as the thermal decomposition under oxygen-free conditions, is the most common method for preparing biochar. In general, pyrolysis involves the heating of organic materials to temperatures greater than 400 °C under inert atmospheres by electric heating or high-temperature medium. There are many parameters influence physicochemical properties of biochar, such as raw material, reaction temperature, heating rate, residence time, and reaction atmosphere.

#### 2.1.2. Factors Affecting the Pyrolysis Process

The raw materials for the preparation of biochar are abundant. Basically, any form of organic materials can be pyrolyzed [18]. Due to the large output of biomass solid waste resources, biomass is a common raw material for biochar, mainly including wheat straw, corn straw, wood chips, melon seed shell, peanut shell, rice husk, livestock and poultry manure, kitchen waste, sludge, fruit skin, etc. [19]. Biochar prepared from different materials contains different proportions of cellulose, hemicellulose, and lignin, so its yield, element composition, and ash content are different [20,21]. Enders et al. [22] found that the ash content of straw biochar is higher than that of other biochar, which is mainly caused by the high Si content of straw. Yuan et al. [23] compared the physicochemical properties of biochar prepared from different feedstocks (the straws of canola, corn, soybean, and peanut). The ash content of biochar from corn straw prepared at 700 °C was the highest (73.30%), compared to canola, soybean, and peanut straw biochar (28.55%, 23.70%, 38.50%, respectively).

The reaction temperature ranges of high temperature anoxic, hydrothermal synthesis, and flash carbonization for the preparation of biochar are 400–900 °C, 180–250 °C, and 300–600 °C, respectively [11]. In general, with the increase of pyrolysis temperature, the yield of biochar and the number of acidic functional groups (-COOH, -OH) decreased, while the alkaline functional groups, ash content, and pH increased. In addition, the effects of pyrolysis temperature on the surface area and

pore volume are especially significant. Park et al. [24] showed that the specific surface area and total pore volume of sesame straw biochar increased from 46.9 to 289.2  $\text{m}^2 \cdot \text{g}^{-1}$ , 0.0716 to 0.1433  $\text{cm}^3 \cdot \text{g}^{-1}$ , respectively, with the pyrolysis temperature increased from 500 to 600 °C.

According to the different heating rate, it could be divided into slow pyrolysis (SP) and fast pyrolysis (FP) [25]. SP is characterized by slow heating (minutes to hours) of the organic material in the oxygen-depleted atmosphere and relatively long solids and gas residence times [26,27]. During the SP process, liquid and solid products such as char, bio-oil, and syngas ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ) are produced. The FP involves blowing small particles of organic material into a thermal reactor and exposing it to heat transfer in milliseconds to seconds [18]. Modern FP often takes place in fluidized bed systems, systems using ablative reactors, and systems using pyrolysis centrifuge reactors (PCR) [28]. Slow and fast pyrolysis results in biochars with different physicochemical properties, thus providing different effects on the soil environment upon application. Compared with the FP-biochar contained labile un-pyrolyzed biomass fraction, the SP-biochar can be pyrolyzed completely [26].

At the same pyrolysis temperature, the yield of biochar decreases with the increase of residence time. Chen et al. [29] prepared orange peel biochar with the pyrolysis temperature of 700 °C and residence time of 6 h, and the biochar yield was only 5.93%. The specific surface area and pores of biochar increased with the extension of residence time. But the residence time is not as long as possible. Lu et al. [30] found that the specific surface area and pores decreased from 2 to 3 h. The reason is that the increase of residence time is conducive to the development of biochar pores, but excessive residence time may cause damage to the pore structure [31].

The reaction atmosphere studied by scholars is dominated by inert gas, such as  $\text{N}_2$ , Ar, which mainly act to isolate oxygen. Besides, the atmosphere of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{O}_3$  [32] is also used to prepare biochar, which is known as physical activation, also called gas activation. The gases selectively decompose the non-structural components of the biochar surface, open its internal pores, and increase the specific surface area and pore volume [11]. Table 1 lists the biochar prepared by different process parameters.

### 2.1.3. Other New Methods

In addition to the pyrolysis, hydrothermal carbonization, and microwave carbonization discussed above, flash carbonization and torrefaction [33] are other methods of biomass transformation. During the flash carbonization process, the flash fire is ignited at a high pressure (1–2 Mpa) on the biomass packed bed to convert the biomass into the gas and solid phase products [11]. It is reported that about 40% of biomass is converted to solid phase products (biochar) at 1 Mpa [34]. In addition to microwave, new pyrolysis technologies such as laser and plasma cracking technologies have also been developed. The sample usage of laser pyrolysis technology is small, and rapid heating and cooling can be carried out, which can effectively avoid the occurrence of secondary reactions [35]. Plasma pyrolysis technology is mainly applied in the preparation of syngas and coke. Compared with the traditional cracking technology, it can greatly increase the syngas and reduce the yield of bio-oil [36,37]. However, it is difficult to popularize the new pyrolysis technology due to its high cost and energy consumption.

**Table 1.** Physicochemical properties of biochar prepared by different methods and process parameters.

Raw Material	Atmosphere	Temperature (°C)	Heating Rate (°C/min)	Residence Time (h)	Yield (%)	pH	Ash Content (%)	Surface Area (m <sup>2</sup> ·g <sup>-1</sup> )	Total Pore Volume (cm <sup>3</sup> ·g <sup>-1</sup> )	Pore Diameter (nm)	Reference
Herb residue	N <sub>2</sub>	400	10	3	37.9	10.2	28.3	49.2	0.042	3.39	[38]
		600			31.2	10.1	31.1	51.3	0.051	3.99	
		800			29.1	10.6	37.1	70.3	0.068	3.87	
Sesame straw	oxygen-limited	400	5	2	35.6	10.0	30.77	37.2	0.0542	23.7	[24]
		500			28.2		28.54	46.9	0.0716		
		600			22.9		21.98	289.2	0.1433		
Corn straw	N <sub>2</sub>	600		3		10.0	5.02	61.0	0.036		[39]
Pine cone	N <sub>2</sub>	500		1		4.66	2.13	6.6	0.016		[40]
Rice-husk		450–500				7.0	42.2	34.4	0.028		[41]
Hickory wood	N <sub>2</sub>	450	10	2	28.5	7.9	6.47	12.9			
		600			22.7	8.4	4.18	401.0			
Bagasse	N <sub>2</sub>	450	10	2	28.0	7.5	13.68	13.6			[42]
		600			26.5	7.5	15.36	388.3			
Bamboo	N <sub>2</sub>	450		2	26.3	8.5	8.83	10.2			
		600		2	24.0	9.2	11.86	375.5			
Poplar chips	N <sub>2</sub>	550		2	23.18		7.56	212.58	0.356	6.70	[43]
Burcucumber plants	oxygen-limited	700		2	27.52	12.23	43.72	2.31	0.008	6.780	[44]
Pine wood	N <sub>2</sub>	600		1			4.02	209.6	0.003		[45]
Orange peel	oxygen-limited	400		6	11.3		6.93	28.1	0.0409	2.9	[29]
		700		6	5.93		14.9	501	0.390	1.6	
Marine macroalgae	N <sub>2</sub>	450		2				1.05	0.007	30.41	[46]
Municipal solid waste	N <sub>2</sub>	400		0.5		8.0	6.1	20.7	0.027		[47]
		500		0.5		8.5	9.2	29.1	0.039		
		600		0.5		9.0	6.2	29.8	0.038		
Rice straw	oxygen-limited	700		2			58.97	369.26	0.23		[48]
Swine manure	oxygen-limited	700		2			60.73	227.56	0.14		
Auricularia auricula dreg		400		2			0.55	77.64	0.0612	4.837	[49]
Thalia dealbata	N <sub>2</sub>	500		4		10.09	22.0	7.1			[50]
Corn straw	N <sub>2</sub>	500		1.5			41.0	32.85	0.0148	5.01	[51]

Table 1. Cont.

Raw Material	Atmosphere	Temperature (°C)	Heating Rate (°C/min)	Residence Time (h)	Yield (%)	pH	Ash Content (%)	Surface Area (m <sup>2</sup> ·g <sup>-1</sup> )	Total Pore Volume (cm <sup>3</sup> ·g <sup>-1</sup> )	Pore Diameter (nm)	Reference
Pitch pine	oxygen-free	400		2 s	33.5		7.9	4.8			[52]
		500		2 s	14.4		7.7	175.4			
Wheat straw	N <sub>2</sub>	600	10	3			5.65	38.1	0.051	19.9	[53]
Rice straw	N <sub>2</sub>	600	10	3			0.03	27.4	0.040	15.8	
Digested sugar beet tailing	N <sub>2</sub>	600	10	2	45.5	9.95		336.0			[54]
Raw sugar beet tailing	N <sub>2</sub>	600	10	2	36.3	9.45		2.6			
tea waste	oxygen-limited	700	7	2	28.35		10.87	342.22	0.0219	1.756	[55]
		700	7	2	22.35		11.60	421.31	0.0576	1.904	

## 2.2. Modification of Biochar

In order to obtain biochar with superior properties, scholars studied the effects of different modification methods on biochar. Modification refers to the activation of the original biochar through physical and chemical methods, so as to achieve the desired purpose. The type of activator, soaking time, activation time, and activation temperature all affect the properties of biochar. Table 2 lists the biochar prepared from different modified.

### 2.2.1. Chemical Oxidation

Chemical oxidation refers to the oxidation of the biochar surface to increase the oxygen-containing functional groups such as -OH, -COOH, etc., thereby its hydrophilicity is increased. At the same time, the pore size and structure of the biochar would be changed, and, finally, its adsorption capacity for the polar adsorbate would be enhanced. The commonly used oxidants are HCl, HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, etc. [56–60]. Although the specific surface area of biochar modified by HCl, HNO<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub> has little difference, compared with biochar modified by HCl, the biochar modified by HNO<sub>3</sub> contains more acidic oxygen-containing functional groups [61] and has stronger adsorption capacity for NH<sub>3</sub>-N. Compared with other acids, biochar modified by H<sub>3</sub>PO<sub>4</sub> has more advantages in removing Pb pollution. The increased specific surface area and pore volume, as well as the role of phosphate precipitation, increase the biochar adsorption capacity of Pb [60].

### 2.2.2. Chemical Reduction

Chemical reduction is also known as alkali modification method. The reducing agent was used to reduce functional groups on the surface of biochar, so as to improve its non-polarity. Meanwhile, chemical modification also can improve porosity and specific surface area of biochar. Finally, adsorption capacity of biochar for pollutants is enhanced, especially for non-polar adsorbates. The commonly used reducing agents are NaOH [62], KOH [63], NH<sub>4</sub>OH [64], etc. [65]. Different reducing agents have different modification effects. In order to determine suitable modified biochar for improving adsorption capacity of volatile organic compounds (VOCs), Li et al. [64] used NH<sub>4</sub>OH, NaOH, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub> to carry out chemical treatment on coconut shell-based carbon. The results showed that, compared with the poor adsorption capacity of acid-treated carbon, high adsorption capacity was obtained for alkali-treated carbon. The reason is that surface area and pore volume increased and total oxygen containing function groups were diminished when treated by alkalis, while acid treatment was the opposite. Pouretedal et al. [66] found that the process of biochar activation by KOH and NaOH is different. Atomic species, K, formed in situ during KOH activation intercalates between the layers of the carbon crystallite, while there is hardly any evidence for the intercalation of Na with carbon.

### 2.2.3. Metal Impregnation

Metal impregnation refers to the adsorption of some heteroatoms or metal ions into the surface and pores of the biochar. On one hand, the specific surface area is increased, and on the other hand, metal ions are combined with the adsorbate to improve the adsorption performance. Common metal ions are iron [67], magnesium [68], silver [69], zinc [70], etc. Some scholars have combined the advantages of chemical reagents to achieve better adsorption performance. Lyu et al. [71] prepared a novel biochar material (CMC-FeS@biochar) via combining carboxymethyl cellulose (CMC) and iron sulfide (FeS), and demonstrated the effective sorbent of CMC-FeS@biochar composite for removal Cr(VI).

**Table 2.** Preparation of different modified biochar.

Raw Material	Reagent	Pollutant	Modification Method	Modification Effects	Reference
Bamboo hardwoods	NaOH, CS <sub>2</sub>	Cd	The composition of sulfur modified mixture solution was obtained by stirring NaOH and CS <sub>2</sub> . Biochar and sulfur modified mixture solution stirred at 45 °C for 8 h.	Sulfur-modified biochar (S-BC) has more roughness, with a more granular massive structure than that seen on the pristine biochar.	[76]
	FeSO <sub>4</sub>		S-BC was added to FeSO <sub>4</sub> solution and then stirred for 16 h with magnetic stirrer at 40 °C, and cooled slowly to room temperature and filtered through 0.45 µm filters. The feedstock was oven-dried at 40 °C.	Successful impregnation of sulfur and iron onto the SF-BC surface, and it showed various atomic proportions of sulfur and iron, with biochar ranging from 0.48% to 4.66% and 0.44% to 22.25%, respectively.	
Poplar chips	AlCl <sub>3</sub>	NO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup>	The poplar pieces were impregnated into AlCl <sub>3</sub> solutions with different concentrations for 6 h. The mixtures were dried at 80 °C for 48 h. The pretreated pristine poplars were pyrolyzed under the N <sub>2</sub> atmosphere at 550 °C with a heating rate of 5 °C/min, and the peak temperature was maintained for 2 h.	The biochar yield increased after modification with Al. The carbon content of the Al-modified biochar significantly decreased compared with the pristine biochar. The BET surface area significantly increased with the Al content of the biochar. NO <sub>3</sub> <sup>-</sup> and PO <sub>4</sub> <sup>3-</sup> adsorptions significantly improved on the Al-modified biochar.	[43]
Rice straw, swine manure	H <sub>3</sub> PO <sub>4</sub>	Tetracycline (TC)	Biochars were immersed in H <sub>3</sub> PO <sub>4</sub> solution for 24 h at 25 °C. Then, the H <sub>3</sub> PO <sub>4</sub> modified biochars were washed by distilled water until the pH of supernatants was stable. Finally, the supernatants were discarded and the biochars were oven-dried overnight at 105 °C.	The H <sub>3</sub> PO <sub>4</sub> modification enhanced the surface area of biochars produced from rice straw biochar (RC) and swine manure biochar (SC). Compared with SC, modified SC presented higher total pore, micropore and mesopore volume by 0.25 to 0.14, 0.09 to 0.07, 0.17 to 0.07 cm <sup>3</sup> ·g <sup>-1</sup> ), but there was no change between RC and RCA modification.	[48]
Wheat straw, cow manure	HNO <sub>3</sub>	U(VI)	Biochar powders were treated with 300 mL 25% HNO <sub>3</sub> solution at 90 °C for 4 h. The excess acid was removed by centrifugation. All oxidized biochar samples were washed with deionized distilled water, freeze-dried, and milled to <0.25 mm.	Owing to the higher contents of surface COO groups and more negative surface charge, the modified biochar showed enhanced U(VI) adsorption ability than the unmodified biochar. The maximum adsorption capacity of U(VI) by the oxidized wheat straw biochar showed an improvement of 40 times relative to the untreated biochar.	[77]



Table 2. Cont.

Raw Material	Reagent	Pollutant	Modification Method	Modification Effects	Reference
Auricularia auricular dreg (AAD)	cetyltrimethyl ammonium bromide (CTAB)	Cr(VI)	Mixed 5 g of dried AAD biochar with 250 mL of 3.0% CTAB solution in 25 °C for 2 h. Residual CTAB rinsed with deionized water and the material was dried at 70 °C until the weight remained constant.	After modification, the surface area increased 6.1% and the average pore diameter increased 16.5% (77.64 m <sup>2</sup> /g and 48.37 Å). Moreover, the number of mesoporous and micropores in unit area increased obviously. The adsorption rate and quantity of modified AAD biochar were 6.4% and 8.0% higher than those of AAD biochar, respectively.	[49]
Thalia dealbata	MgCl <sub>2</sub>	sulfamethoxazole (SMX), Cd	Thalia dealbata were soaked in 100 mL 1 M MgCl <sub>2</sub> solution, after 0.5 h mixing under magnetic stirring, the pre-treated biomass was then separated from the solution and pyrolyzed at 500 °C.	The surface area of MgCl <sub>2</sub> modified biochar (BCM, 110.6 m <sup>2</sup> ·g <sup>-1</sup> ) was higher than untreated biochar (BC, 7.1 m <sup>2</sup> ·g <sup>-1</sup> ). The addition of BCM increased the sorption of SMX (by 50.8–58.6%) and Cd (by 24.2–25.6%) as compared with BC. In situ remediation with BCM decreased the mobility and bioavailability of SMX and Cd in sediments.	[50]
Corn straw	Na <sub>2</sub> S and KOH	Hg(II), atrazine	Biochar were mixed with 500 mL of 2 M Na <sub>2</sub> S or 2 M KOH solution and stirred for 4 h. The suspension was then filtered and washed with deionized water for several times until the pH of the filtrate was nearly 7. The washed biochar was dried overnight in an oven at 105 °C.	Sulfur content significantly increased by 101.29% under Na <sub>2</sub> S modification. Compared to untreated biochar (BC, 32.85 m <sup>2</sup> ·g <sup>-1</sup> ), chemical modification increased the BET surface area which was 55.58 and 59.23 m <sup>2</sup> ·g <sup>-1</sup> for Na <sub>2</sub> S modified biochar (BS), KOH modified biochar (BK), respectively. In comparison to BC, the sorption capacity of BS and BK for Hg (II) increased by 76.95%, 32.12%, while that for atrazine increased by 38.66%, 46.39%, respectively.	[51]
Coconut shell	HCl+ultrasonication	Cd, Ni and Zn	5 g of CS biochar and 250 mL of 1 M HCl were mixed in beaker and ultrasonicated for 3 h with interval stirring. Then, the material was filtered, washed, and dried to constant weight.	Modified coconut shell biochar (MCSB) improved surface functional groups and microcosmic pore structure of pristine biochar (CSB).	[78]
Dairy manure	NaOH	Pb and Cd	Biochar and 2 M NaOH were thoroughly mixed with a solid–liquid ratio of 1:5 and then were re-suspended for 12 h with a speed of 30 r min <sup>-1</sup> at 65 °C. After that, the mixture was filtered, and the precipitate was collected and rinsed with deionized. Finally, material was dried at 105 °C.	The NaOH treatment increased the specific surface area, ion-exchange capacity, and the number of oxygen-containing functional groups of biochar. The adsorption capacities of biochar for Pb and Cd increased after modification. The highest sorption capacities were 175.53 and 68.08 mg·g <sup>-1</sup> , for Pb and Cd, respectively.	[79]



#### 2.2.4. Other Modification Methods

In addition to the above three modification methods, modification methods such as low-temperature plasma [72,73], organic matter grafting [74], and ozone oxidation [32] have also been studied. Low-temperature plasma modification means that plasmas generated by glow, microwave, and corona were collided with C=C on the surface of biochar, and plasmas were oxidized to the oxygen-containing functional group, and enhanced the polarity of biochar [75]. However, such methods have not been widely used due to high cost and complicated operation.

### 3. Removal Mechanism of Major Pollutants by Biochar

The remediation mechanisms of soil pollution by biochar include ion exchange, physical adsorption, electrostatic interaction, precipitation, and complexation [9].

#### 3.1. Ion Exchange

Ion exchange means the process that acidic oxygen-containing functional groups on the surface of biochar, such as carboxyl groups, carbonyl groups, and hydroxyl groups, can ionize  $H^+$  or surface base ions such as  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , etc., to exchange with heavy metal ions or cationic organic pollutants [80].

#### 3.2. Physical Adsorption

Physical adsorption means that biochar utilizes its surface characteristics, namely porosity and large specific surface area, so that pollutants such as heavy metals or organic substances could be adsorbed on its surface or diffused into the micropores. The diameter of the heavy metal ions is smaller than the average pore diameter of the biochar. Generally, the smaller the diameter of the heavy metal, the more the pores penetrate into the pores of the biochar, thereby increasing the adsorption capacity [81,82]. The intensity of physical adsorption is closely related to the properties and specific surface area of biochar, the properties and concentration of pollutants, and the temperature during adsorption process. Physical adsorption kinetics is usually fitted by pseudo-first-order and pseudo-second-order kinetic models [83,84]. Physical adsorption can be either single-layer adsorption or multi-layer adsorption, which is usually fitted by Langmuir and Freundlich model [85,86].

#### 3.3. Electrostatic Interaction

Electrostatic interaction refers to the electrostatic adsorption between the surface charge of biochar and heavy metal ions. When the pH value of solution is greater than the charge point of biochar ( $pH_{pzc}$ ), the negative charge on the surface of biochar and the heavy metal with positive charge causes electrostatic adsorption. Heavy metal ions with positive charge on the surface of biochar combine with oxygen-containing functional groups such as carboxyl, carbonyl, and hydroxyl [87–91].

#### 3.4. Precipitation

Mineral components in biochar, such as  $CO_3^{2-}$ ,  $PO_4^{3-}$ ,  $SiO_3^{4-}$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $SO_3^{2-}$ , and  $OH^-$ , combine with heavy metal ions to form water insoluble substances such as metal oxides, metal phosphates, and metal carbonates, which promote the adsorption and immobilization of heavy metals. Xu et al. [92] believed that the adsorption of Cu, Zn, and Cd by fertilizer biochar was mainly attributed to the precipitation of  $CO_3^{2-}$  and  $PO_4^{3-}$ , while the electron surface complexation via -OH groups or delocalized  $\pi$  was less.

#### 3.5. Complexation

Complexation refers to the interaction between oxygen-containing functional groups on the surface of biochar and heavy metals to form complexes, which could be fixed. Qian et al. [93] studied the aluminum phytotoxicity of cow manure biochar to wheat and concluded that the adsorption of

aluminum by biochar was mainly through the complexation of carboxyl group with  $[Al(OH)]^{2+}$  and its monomer surface, rather than through the electrostatic attraction of  $Al^{3+}$  with negative charge sites. Jia et al. [94] believed that the adsorption of oxytetracycline by biochar was mainly mediated by  $\pi$ - $\pi$  interaction and metal bridge, with surface complexation as the main factor, and cationic exchange might exist.

In the process of adsorption, it is often not a single mechanism, but a combination of multiple adsorption mechanisms. Table 3 summarizes the adsorption mechanism of biochar for pollution restoration.

**Table 3.** Adsorption mechanism of biochar for pollution remediation.

Raw Material	Pollutant	Mechanism	Reference
Municipal sewage sludge	Cd	Surface precipitation under alkaline conditions and exchange of exchangeable cations with Cd.	[95]
Fertilizer	Cu, Zn and Cd	Precipitate from $\text{CO}_3^{2-}$ , $\text{PO}_4^{3-}$ on the surface of the biochar, partially by surface complexing with -OH group or delocalized $\pi$ electron.	[92]
Rice husk loaded with manganese oxide	Pb	Oxide spherical complexes and biochar surface oxygen complexes; the $\pi$ -band electron density of graphene-based carbon in the $\pi$ -electron cloud system reduces vacancies on the surface of biochar, thereby adsorbing $\text{Pb}^{2+}$ .	[96]
Wheat straw, pine needles	Zn	The components of -OH, $\text{CO}_3^{2-}$ , and Si in biochar can form precipitates with $\text{Zn}^{2+}$ .	[97]
Bamboo, eucalyptus	chloramphenicol	Electron-donor-acceptor (EDA) interaction with $\text{pH} < 2.0$ , also forms charge-assisted hydrogen bonds (CAHB) and hydrogen bonds at $\text{pH} 4.0\text{--}4.5$ , and interaction with CAHB and EDA at $\text{pH} > 7.0$ .	[98]
Corn straw	Hg(II), atrazine	After $\text{Na}_2\text{S}$ modification, sulfur impregnated onto the biochar reacted with Hg(II) to form HgS, which greatly facilitated the sorption of Hg(II). Formation of surface complexes between Hg(II) and the functional groups of sorbent, such as phenolic hydroxyl, carboxylic groups. These oxygen-containing functional groups exchanged ion with Hg(II). The electrostatic and EDA interaction also participated in Hg(II) sorption.	[51]
Dairy manure	Pb and Cd	Because of the easy hydrolysis of Pb at low pH, biochar has a higher affinity for Pb than Cd. Besides, precipitation as carbonate minerals ( $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ and $\text{CdCO}_3$ ) and complexation with functional groups such as carboxyl and hydroxyl, were also important for adsorption of Pb and Cd by biochar.	[79]
Rice straw, swine manure	Tetracycline (TC)	The H-bonding, electrostatic attraction and EDA interaction might be the primary mechanism during adsorption process.	[48]
Sugar beet tailing (SBT)	Cr(VI)	First, SBT biochar reduced Cr(VI) to Cr(III) by electrostatic adsorption. Second, with the participation of hydrogen ions and the electron donors from SBT biochar, Cr(VI) was reduced to Cr(III). Then, the function groups on the SBT biochar complexed with Cr(III).	[99]
Empty fruit bunch, rice husk	As(III), As(V)	Surface complexes were formed between As(III) and As(V) and the functional groups (hydroxyl, carboxyl, and C-O ester of alcohols) of the two biochars.	[100,101]
Bamboo biomass	Sulfathiazole, sulfamethoxazole, sulfamethazine	The sorption of neutral sulfonamide species occurred mainly due to H-bonds followed by EDA, and by Lewis acid-base interaction. EDA was the main mechanism for the sorption of positive sulfonamides species. The sorption of negative species was mainly due to proton exchange with water forming negative CAHB, followed by the neutralization of -OH groups by $\text{H}^+$ released from functionalized biochar surface, and $\pi$ - $\pi$ electron-acceptor-acceptor (EAA) interaction.	[102]

## 4. Application of Biochar in Soil Remediation

### 4.1. Removal of Heavy Metals

The removal of heavy metals by biochar is mainly reflected in two aspects: One is the adsorption of heavy metals in the pores of biochar to reduce the residual amount in the soil; the other is the ion exchange or redox reaction between the effective components in biochar and heavy metal ions to stabilize the formation of heavy metal precipitates or to reduce toxicity by transforming them into low-valent states.

Boostani et al. [103] investigated the effect of sheep and earthworm manure biochars on Pb immobilization in a contaminated calcareous soil. The addition of biochars resulted in a significant increase in the Pb content in the residual state, which reduced the Pb activity in the soil. Chen et al. [79] studied the adsorption mechanisms for removal Pb and Cd with dairy manure biochar. The extractable Pb and Cd contents decreased significantly and were converted to the precipitation as carbonate minerals. However, it may also be due to the lack of selective adsorption capability of biochar, which adsorbs nitrogen in the soil, resulting in a decrease in soil nutrients [104]. When the soil pollution is contaminated by complex heavy metals, although biochar reduces the concentration of extractable heavy metals, biochar has different adsorption effects on different heavy metals due to competitive adsorption. Yang et al. [105] showed that straw and bamboo biochar are more effective than Zn in reducing extractable Cu and Pb. Zhou et al. [106] also reached a similar conclusion. In the single metal adsorption test, the adsorption capacity of sludge biochar to Zn was the largest, while in the polymetallic adsorption test, the adsorption capacity of Mn, Cu, and Zn decreased, but the adsorption capacity of Cr increased. Table 4 shows the research on removing heavy metals in soil by using biochar in the past two years.

**Table 4.** Study on the application of biochar to the remediation of heavy metal pollution in soil.

Raw Material	Tested Soil	Pollutant	Remediation Effect	Reference
Bamboo, rice straw, and Chinese walnut shell	industrial contaminated soil	Cu	Cu uptake in roots was reduced by 15%, 35%, and 26%, respectively. Rice straw biochar reduced solubility of Cu and Pb.	[107]
Sewage sludge	Brazil soil	Cd, Pb, and Zn	Biochar reduced the concentration and bioavailable levels of Cd, Pb, and Zn of in the leachates.	[108]
Poultry litter	paddy soil near Zn and Pb mines	Cd, Cu, Zn, Pb	Acid-soluble Cd in soils amended with poultry litter biochar was 8% to 10% lower than in the control polluted soil.	[109]
Wheat straw	acid soil	Cd and Cu	Cu concentration in wheat roots was reduced most efficiently to 40.9% by biochar. Available Cd and Cu in soil added biochar decreased 18.8% and 18.6%.	[110]
Rice husk	saturated soil, dryland soil	Cd	The adsorption of Cd on saturated soil increased by 21–41%, and that on dryland soil increased by 38–54%.	[111]
Gliricidia sepium	shooting range soil	Pb, Cu	The addition of biochar to the soil reduced the dissolution rates of Pb and Cu by 10.0–99.5% and 15.6–99.5%, respectively, and was able to fix Pb and Cu released by protons and ligands in the soil.	[112]
Poultry manure, cow manure, and sheep manure	farmland soil	Cr(VI)	Poultry manure decreased 61.54 mg·kg <sup>-1</sup> Cr(VI) in acidic soil and 73.93 mg·kg <sup>-1</sup> Cr(VI) in alkaline soil. Cow and Sheep manure decreased by 66.61, 58.67, and 57.81, 68.15 mg·kg <sup>-1</sup> Cr(VI) in acidic and alkaline soil, respectively.	[113]

In order to achieve better remediation effect, scholars gradually carry out research on the modification of biochar. Modification refers to the activation of the original biochar through physical and chemical methods, so as to achieve the desired purpose. The modification methods of surface structure characteristics are generally divided into physical method, chemical method, and combined method [65]. In the early stage, Monser et al. [114] modified activated carbon with sodium dodecyl sulfonate to reduce the heavy metal content in phosphoric acid and reduce the content of cadmium and chromium. Scholars have modified biochar similarly to activated carbon, mainly by chemical modification, through adding acid, alkali, oxidants, and supporting various metal oxides to aminated, acidify, and alkalinize biochar. Oxidation, etc., increase the surface oxygen-containing functional groups, thereby achieving a good repair effect. Studies on the adsorption effect of modified biochar are dominated by heavy metals, followed by organics, and most of them are adsorption of heavy metals in aqueous solution. Table 5 provides a summary of studies on soil pollution remediation by various types of modified biochar in recent years.

**Table 5.** The remediation of soil pollution by various types of modified biochar.

Raw Material	Modification	Pollutant	Tested Soil	Remediation Effect	Reference
Bamboo hardwoods	sulfur-iron	Cr	plant farmland	Sulfur-modified biochar (S-BC) and sulfur-iron modified biochar (SF-BC) addition increased the content of soil organic matter, alpha diversity indices, and changed soil bacterial community structure. The exchangeable Cd in soil was decreased by 12.54%, 29.71%, 18.53% under the treatments of BC, S-BC, SF-BC, respectively.	[76]
Poultry, cow, sheep manure	Chitosan, ZVI	Cr	uncontaminated surface soil	Modified sheep manure biochar reduced Cr(VI) by 55%, and poultry manure modified biochar reduced Cr(VI) by 48%.	[113]
corn straw	Fe-Mn	As	paddy soil	Modified biochar decreased the content of available As, increased the residual, amorphous hydrous oxide-bound, and crystalline hydrous oxide-bound As forms.	[115]
Eucalyptus wood and poultry litter	iron	Cd, Cu, Zn, Pb	paddy soil near Zn and Pb mines	Acid-soluble Cd, Zn, Cu in soils amended with poultry litter biochar (PLB) was 8% to 10%, 27% to 29%, 59% to 63%, respectively, lower than in the control polluted soil. Plant biomass increased by 32% in the treatments containing magnetic PLB.	[109]
Coconut shell	HCl + ultrasonication	Cd, Ni, and Zn	topsoil of paddy fields	In groups with 5% MCSB addition, the acid soluble Cd, Ni and Zn decreased by 30.1%, 57.2%, and 12.7%, respectively.	[78]
Rice husk	Sulfur	Hg	Hg contaminated soil	Modification increased the Hg <sup>2+</sup> adsorptive capacity of biochar by 73%, to 67.11 mg·g <sup>-1</sup> . And freely available Hg in TCLP (toxicity characterization leaching procedure) leachates by 95.4%, 97.4%, and 99.3%, respectively, compared to untreated soil.	[116]
Corn straw	MnO	As	red soil	Modified biochar (MBC) in red soil had a much greater sorption capacity for As(III) than pristine biochar, although both enhanced the sorption of As(III) in red soil.	[117]



#### 4.2. Removal of Persistent Organic Pollutants (POPs)

The persistent organochlorine pesticides in farmland soils are still seriously polluted, and the polycyclic aromatic hydrocarbon pollution caused by sewage irrigation cannot be ignored. Biochar has a strong adsorption capacity for organic pollutants, and the process can be understood as the accumulation and collection of organic pollutants on biochar. Table 6 shows the research on the removal of POPs from soil by using biochar in the past two years.

**Table 6.** Study on the application of biochar to remove persistent organic pollutants (POPs) in soil.

Raw Material	Tested Soil	Pollutants	Remediation Effect	Reference
Fir wood chips	rice soil	2,4-dichlorophenol, phenanthrene	Reduced the degradation and mineralization of both pollutants. Increased the accumulation of their metabolites in soil.	[118]
Mixed wood shavings Rice husk	loamy agricultural soil	Pyrene, polychlorinated biphenyl and dichlorodiphenyldichloroethylene (DDE)	At the biochar dose of 10%, bioavailability and accessibility by 37% and 41%, respectively, compared to unamended soil.	[119]
Rice hull	loamy clay, sandy loam, clay loam	oxyfluorfen	Oxyfluorfen degraded faster in biochar amended soil than in unamended soil. Biochar decreased the oxyfluorfen uptake by soybean plants by 18–63%, and the adsorption capacity of oxyfluorfen by soybean decreased.	[120]
Orchard pruning biomass	vineyard	PAHs	During the investigated period, PAH concentrations decreased with time and the change resulted more intense for light PAHs. The soil properties (TOC, pH, CEC, bulk density) were modified after two consecutive applications	[121]
Corn straw and bamboo	soil contaminated with PAHs	PAHs	The bioaccumulation of PAHs in rice roots was reduced, especially high molecular weight PAHs. The total and bioavailable concentration of PAHs in the soil treated with corn straw biochar were both lower than that of the control group.	[100]

Koltowski et al. [122] studied the removal effect of PAHs in soil by microwave, CO<sub>2</sub>, and H<sub>2</sub>O activation of willow biochar. The results showed that the biochar samples with the best effect after activation reduced the concentration of PAHs dissolved in the coal plant soil (near cooking plant battery) and bitumen plant soil from 153 to 22 ng/L and 174 to 24 ng/L, respectively, and the PAHs concentration decreased by 86%. The concentration of PAHs dissolved in the asphalt soil (from an industrial waste deposit) decreased from 52 to 16 ng/L, and bioacceptable PAHs reduced to almost zero. Zhang et al. [123] applied biochar from corn straw and pig manure to black soil containing thiacloprid, and explored the adsorption and degradation process of thiacloprid. The results showed that the biochar changed the microbial community of soil by changing the physicochemical properties of the soil, thus promoting the biodegradation of thiacloprid.

In general, biochar can enhance the adsorption capacity of soil for organic pollutants, reduce their activities of desorption and flow in the soil, and bioavailability in soil pore water, provide essential nutrients to improve soil microbial activity, and improve soil physical and chemical properties, etc. [124].

#### 4.3. Amelioration of Soil

The improvement of soil by biochar is mainly reflected in the improvement of soil organic matter content, the increase of nitrogen, potassium, and other nutrients contents and utilization rate, and the improvement of soil erosion and acid soil.

The application of biochar can significantly increase the content of soil organic matter, alkali-hydrolyzed nitrogen, ammonium nitrogen, and available potassium, but the more biochar added is not better. Excessive application of biochar can inhibit the content of nutrients. Bayabil et al. [125] mixed acacia, croton, and eucalyptus charcoal into the soil in a basin of the Ethiopian plateau, and found through laboratory and field experiments that it had a good improvement on the water conservancy characteristics of degraded soil, so as to reduce runoff and erosion. Biochar is mostly alkaline, which can improve the utilization and absorption of nutrients in rice by increasing the pH value of acid soil [126]. In addition, the effect of biochar on soil cation exchange capacity was significant. Agegnehu et al. [127] found that biochar, compost, and their compounds significantly improved the availability and use of plant nutrients: Soil organic carbon, moisture content, CEC, and peanut yield all increased, and greenhouse gas emissions decreased.

Nitrogen is an essential nutrient for plant growth. The application of nitrogen fertilizer could replenish soil nitrogen and maintain land productivity. However, over-application will cause a large loss of soil nitrogen, reduce the efficiency and utilization of nitrogen fertilizer, and aggravate the eutrophication pollution degree of surrounding water environment such as rivers and lakes. The inhibition of nitrogen and phosphorus leaching by biochar is considered as follows: Biochar changed the microbial-mediated reactions in soil nitrogen and phosphorus cycles, namely N<sub>2</sub> fixation, nitrogen and phosphorus mineralization, nitrification, ammonia volatilization, and denitrification. At the same time, biochar provided a reactive surface in which nitrogen and phosphorus ions remain in the soil microbial biomass and exchange sites, both of which regulate crop nitrogen and phosphorus availability [128].

#### 4.4. Potential Risk of Biochar

Although biochar has great advantages in remediation of soil pollution, improvement of soil quality, increase of crop yield, and reduction of greenhouse gas emissions, these studies are all short-term and the long-term effects of biochar on soil are still ambiguous. Therefore, in order to make better use of biochar and reduce its possible risks, the long-term effects and risk assessment of biochar on soil should be paid more attention. Studies have shown that, although the application of biochar improved soil quality and crop yield, biochar reduced the efficacy of herbicide and increased weed growth by 200% [129]. The reduction of herbicide efficacy must increase the use of herbicide, which may increase the residual concentration of herbicide in the soil and cause more serious pollution

to the soil. In addition, biochar, which is mostly prepared from crop waste, may contain heavy metals on its own and could release pollutants if it gets into the soil. Due to the weathering and aging, biochar would undergo physical, chemical, and biological degradation. Finally, it would form colloids, nanoparticles, and smaller fragments that alter the microbial community in the soil. However, the interaction between these components of biochar and soil, the internal mechanism of microbial transformation and geochemical circulation still need to be further studied [130].

## 5. Conclusions

In this paper, the effects of preparation, process parameters, and modification of biochar on its physicochemical properties were reviewed. The mechanism of biochar remediation for soil pollution was summarized, the application status of biochar in soil remediation was analyzed, and the research articles on the removal of heavy metals and organic pollutants by biochar in the past two years were listed; lastly, the possible risks in the application of biochar were proposed. The application of biochar in soil remediation can not only reduce the damage of soil wastes to the atmosphere and water environment, but also remove the pollutants in the soil and improve the soil quality. In addition, biochar has advantages in dealing with water pollution and reducing greenhouse gas emissions, so the research on the application of biochar is of great significance to sustainable development.

At present, the following problems still exist in the application of biochar: (i) Although studies are on the same type of biochar to repair the same kind of pollution, the mechanism of action, adsorption kinetics, thermodynamics, etc., are different; (ii) in terms of the characterization of biochar, there is no unified standard, which is difficult to compare; (iii) the number of indoor tests is much more than of field outdoor tests, which results in the incomplete considered factors and difficult practical application; (iv) the research on the mechanism of biochar on compound pollution is not thorough enough; (v) the study on the long-term effects and negative effects of biochar is not well studied; and (vi) there is little research about life cycle assessment of biochar and the overall economic value of biochar applications is not clearly enough.

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