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Review

Modified Biochar as a More Promising Amendment Agent for Remediation of Pesticide-Contaminated Soils: Modification Methods, Mechanisms, Applications, and Future Perspectives

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Abstract: With the acceleration of the process of agricultural modernization, many pesticides (insecticides, fungicides, and herbicides) are applied to the field and finally brought into the soils, causing serious damage to the environment. The problem of pesticide pollution has become increasingly prominent. This has highlighted the urgent need for effective and efficient remediation treatment technology for pesticide-contaminated soils. Biochar has a high specific surface area, high porosity, and strong adsorption capacity, making it a soil amendment agent and carbon fixation agent that can improve soil health and enhance adsorption capacity for pesticides to remediate contaminated soils. Recently, efforts have been made to enhance the physicochemical and adsorption properties of biochar by preparing modified biochar, and it has been developed to expand the application of biochar. Specifically, the following aspects were reviewed and discussed: (i) source and modification methods of biochar for pesticide remediation; (ii) the effect of biochar on the environmental fate of remediating pesticides; (iii) the effect of biochar on pesticide-contaminated soils; and (iv) potential problems for the large-scale promotion and application of biochar remediation of pesticides. In conclusion, this review may serve as a reference and guide for pesticide remediation, hence reducing the environmental concerns associated with pesticides in soil.

Keywords: biochar; soil; pesticide; modified biochar; remediation; environmental fate

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1. Introduction

1.1. Application of Pesticides and Soil Pollution

Pesticides are widely used to prevent and control crop pests all over the world, ensuring the improvement of yield and quality and playing a great role in producing food to meet global demand [1]. However, there are benefits and drawbacks when using pesticides in agriculture. Increasingly, pesticides are applied to control various pests, diseases, and weeds, though most of these pesticides remain in the environment, posing a potential risk to the whole agricultural ecosystem [2]. Pesticides' environmental contamination is raising concerns because of their negative effects on nontarget organisms in the soil and even the entire ecosystem in the world [3]. Pesticides are a vital pollutant of nonpoint source pollution and can contaminate soil in a variety of ways [4]. After applying pesticides, only a small proportion remains in the plant, and the majority remains in the soil [5,6]. Excessive use of pesticides in the past several decades has caused the pesticides' residues accumulation problem, which often exceeds the self-purification capacity of the soil. This further leads to increasing soil pollution and soil quality deterioration. Due to their high solubility in water, pesticides with high water solubility have a high risk of leaching into the soil, which is the primary reason for pesticide misuse in agricultural fields [7].

1.2. Soil Pollution Remediation

The removal of pesticide contamination from soil and the possible detrimental effects of pesticides on the environment have received more attention in recent years. Considering the toxicity generated by excessive pesticide use during crop management, there is an urgent demand to find environmentally safe, cost-effective, and appropriate remediation techniques [8]. Currently, the main relevant techniques are physical and chemical remediation and bioremediation [9,10]. For example, electrochemical degradation, bioremediation, membrane filtration, photocatalytic degradation, and adsorption have been explored for the pesticide remediation in contaminated environments [11]. In view of the long cycles and low efficiency, some of the methods are difficult and even impractical to apply in soil remediation with severe pesticide pollution [12]. Chemical extraction methods are conventionally used to extract contaminants from the environment [13]. However, some effective methods are constrained in large agricultural fields by a lot of factors, such as expensive costs, fertility loss, soil erosion, and potential environmental risks. Exploring an environment-friendly and sustainable approach to counteract soil pesticide contamination is promising with the absence of remediation technologies that have been tested at full scale [14]. Generally, the adsorption method is relatively simple, low-cost, and low-energy-consumption for contamination remediation [15].

1.3. Biochar

Biochar, usually produced by a pyrolysis process with lack of oxygen, has a high specific surface area, high porosity, and strong adsorption capacity at a relatively lower cost [16]. It is an excellent soil amendment agent and carbon fixation agent that can improve soil health and enhance adsorption capacity for pesticides to remediate contaminated soils [17,18]. At the same time, it can add soil organic matter and provide extra refugia for beneficial microorganisms in the soil [19]. Soil properties can affect the application of biochar, and attention should be paid when using a specific biochar for a specific soil property improvement [20,21]. Therefore, a clear understanding of its effects and mechanisms is necessary to engineer biochar production with desirable properties [22]. Improving the soil's ability to immobilize pesticides would restrict pesticide movement and lessen the likelihood of pesticides seeping into the environment. In conclusion, this review could provide a reference and guidance for remediation of pesticides to reduce the environmental risks of pesticides in the soils.

2. Source and Modification Methods of Biochar for Pesticide Remediation

2.1. Biochar Production

Numerous organic resources, including agricultural residues, forest residues, livestock manure, culinary wastes, industrial biowastes, municipal biowastes, and animal carcasses, can be utilized as feedstocks to create biochar for a variety of applications [23]. Biochar is a carbon-rich byproduct of biomass pyrolysis that is produced in a reactor with a limited oxygen supply and moderate temperature conditions (<700 °C). The traditional preparation method of biochar limits the application of biochar. In recent years, more and more chemical modification methods are used to improve the properties of biochar. Various different agricultural waste is selected as raw materials, dried by natural air, ground by a high-speed crusher, screened, and burned into carbon in the furnace. The prepared biochar is washed with deionized water and dried to remove surface impurities and ash. The laboratory and industrial production methods are both shown in Figure 1. Biochar characteristics include porosity (comprising several pore sizes), a large surface area, pH, ash, cation exchange capacity (CEC), electrical conductivity (EC), and nutrient level, which improve its sorption abilities with the pesticides. Due to its extremely porous structure and diverse functional groups, biochar has received attention for its involvement in the sorption and immobilization of organic pollutants in soil [24]. However, the efficiency of biochar is greatly dependent on its manufacturing factors, which include feedstock type, manufacturing methods, and processing conditions, all of which play a part in the processes. Table 1 is shown below.

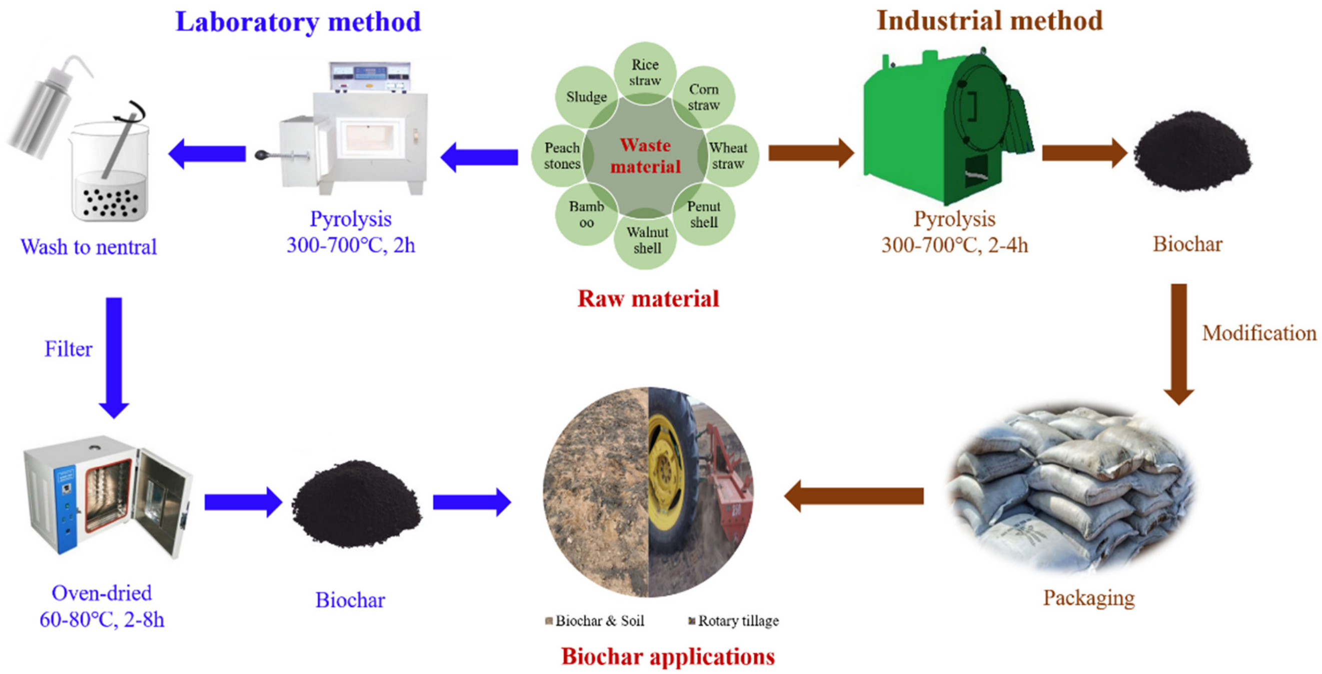

Figure 1. Procedure for biochar preparation and application.

Table 1. Effect of biochar source on adsorption capacity and removal rate.

Raw Material	Pyrolysis Temperature °C	pH	Specific Surface Area ($m^2 \cdot g^{-1}$)	Organic Carbon Content%	Maximum Adsorption Capacity ($mg \cdot g^{-1}$)	Maximum Removal Rate%	Contaminant (Pesticide)	Principle	Adsorption Kinetics	Adsorption Isotherm	Active Matrix	Reference
rice hull	500	6.96	95.67	33.6	—	increase by 2 to 3.2 fold	Oxyfluorfen (herbicide)	surface polarity mechanism, the pore-filling mechanism, hydrophobic and π-π interaction	The first-order kinetics	Freundlich	soil	[25]
cassava	750	9.55	430.37	62.38	125	86.64%	atrazine (herbicide)	via a pore-filling mechanism	pseudo-second order	Freundlich	soil	[26]
red gum wood	500	7.8	—	—	—	49.8%	isoproturon (herbicide)	—	The first-order kinetics	Freundlich	soil	[27]
wood chip	>500	10.8	28.8	73.9	—	82%-85%	aminocyclopyrachlor (herbicide)	—	—	Freundlich	soil	[28]
woodchip	725	7.39	3.72	85.76	11.8–21.5	—	4-chloro-2-methylphenoxyacetic acid (MCPA) (herbicide)	—	—	—	soil	[29]
pine-wood shavings	400	—	—	—	—	95%	atrazine (herbicide)	—	—	Freundlich	soil	[30]
poultry litter	550	8.9	3.14	—	increase by 448%	—	diuron (herbicide)	—	—	Freundlich	soil	[31]
wood pellet	500	6.02	1.25	81.39	3	—	methyl isothiocyanate (fumigant)	—	The first-order kinetics	—	soil	[32]
rice husk	700	9.87	377.00	47.71	9.6 ± 0.2	47.7%	carbofuran (insecticide)	the pore-filling mechanism, π-π interaction, Van der Waals' forces, H-bond, electrostatic interaction	The first-order kinetics	—	water	[33]
rice husk	750	10.51	53.08	64.08	9.5	95%	metolachlor (herbicide)	the pore-filling mechanism, H-bond	intra-particle diffusion	Freundlich	water	[34]
magnolia wood	700	10.14	364.63	83.55	—	81.10%	ethiprole (insecticide)	π-π interaction, the pore-filling mechanism	The first-order kinetics	Freundlich	water	[35]
pine needle	700	—	390.52	93.67	105	75.04%	trichloroethylene (TCE) (insecticide)	the pore-filling mechanism	—	Temkin Dubinin-Radushkevich	water	[36]

Table 1. *Cont.*

Raw Material	Pyrolysis Temperature °C	pH	Specific Surface Area ($m^2 \cdot g^{-1}$)	Organic Carbon Content%	Maximum Adsorption Capacity ($mg \cdot g^{-1}$)	Maximum Removal Rate%	Contaminant (Pesticide)	Principle	Adsorption Kinetics	Adsorption Isotherm	Active Matrix	Reference
soybeans	450	9.21	17.5	57.52	1.5	—	atrazine (herbicide)	physical adsorption, chemical adsorption	—	Freundlich	water	[37]
azadirachta indica	300	—	30.43	42.89	79.40	80%	bentazone (herbicide)	H-bond, electrostatic interaction and ion exchange	pseudo-second order	Freundlich	water	[38]
pig manure stock	700	8.7	218.1	81.83	2.872	71.80%	carbaryl (insecticide)	the pore-filling mechanism, π-π electron interaction	—	Freundlich	water	[39]
Herb Dangshen and Danggui	750	9.75	85.3	79.09	3.09	91%	metolachlor (herbicide)	the pore-filling mechanism, hydrophobic effect and π-bond	—	Freundlich	water	[40]
greenwaste	450	—	7.56 ± 0.29	71.18	1.066	95%	simazine (herbicide)	—	—	Freundlich	water	[41]
switchgrass	425	—	1.1	—	50	90%	MCPA (herbicide)	H-bond, van der Waals and π-π interaction	pseudo-second order	Redlich-Peterson	water	[42]
walnut shells	700	—	358.67	82.53	44.67	87.89%	metolachlor (MET) (insecticide)	the pore-filling mechanism, H-bond, and π-π electron donor–acceptor	pseudo-second order	Langmuir	water	[43]
crofton weed	500	10.53	382.21	86.48	—	90% (pH = 2)	flubendiamide (insecticide)	π-π interaction	The first-order kinetics	Freundlich	water	[44]

The physical and chemical properties of biochar vary with the types of raw materials, and the preparation conditions are summarized in Table 1. The physical and chemical properties and structures and the surface adsorption capacity of biochar surface are varied with pyrolysis temperatures [45]. Pyrolysis usually includes fast pyrolysis and slow pyrolysis. Fast pyrolysis means keeping the raw material for only a few seconds after the temperature reaches the set value, while slow pyrolysis means keeping it from half an hour to several hours [46]. Compared with rapid pyrolysis, high temperature and slow pyrolysis are more conducive to the improvement of biochar yield and performance [47]. However, the relative content of biochar pyrolysis products prepared at different temperatures is obviously different. As shown in Table 1, different temperatures ranging from 300 to 750 °C, different pH values ranging from 6.02 to 10.8, and the responding specific surface area (SSA) ranging from 1.1 to 430.37 $m^2 \cdot g^{-1}$ affect the sorption of pesticides, ranging from 3 to 79.4 $mg \cdot g^{-1}$ [48]. Most herbicides and insecticides are acidic. Weak acids and weak bases have little effect on the stability of pesticides. Strong bases, strong acids, and light can promote the hydrolysis of pesticides. Most pesticides are nonpolar and slightly soluble or insoluble in water (Table S1). The mechanisms of low-surface-area and high-temperature biochar for adsorbing acidic and nonpolar pesticides include the pore filling mechanism, the hydrophobic effect, the H-bond and π-bond, which are changed to π-π interaction, electrical interaction, physical adsorption, and chemical adsorption after the modification. The mechanisms of low-surface-area and low-temperature biochar for adsorbing nonpolar pesticides are the surface polarity mechanism, the pore-filling mechanism, the hydrophobic effect, and π-π interaction. After modification, the adsorption mechanisms are electrostatic interaction and physical adsorption (Tables 1 and 2). The removal of pesticides with biochar is mainly attributed to the adsorption of biochar. It indicates specific interactions such as the pore-filling mechanism and hydrophobic and π-π interaction between biochar and pesticide in the process of adsorption, which illustrates that the Freundlich isotherm model fits better for the adsorption process. Due to large SSA and sufficient surface pores, biochar possesses high adsorption capacity and can adsorb a large amount of pesticide in a short time.

Table 2. The study of pesticides removed by modified biochar under different modification methods.

Raw Material	Pyrolysis Temperature °C	pH	Modification Method	Specific Surface Area ($m^2 \cdot g^{-1}$)	Otal Pore Volum ($cm^3 \cdot g^{-1}$)	Maximum Adsorption Capacity ($mg \cdot g^{-1}$)	Maximum Removal Rate%	Contaminant	Adsorption Mechanism	Adsorption Kinetics	Adsorption Isotherm	Active Matrix	Reference
walnut shell	700	7	illite$FeCl_3$	232.77	0.29	126.72	95%	metolachlor (herbicide)	π-π electron interaction and chemical reaction	pseudo-second order	Langmuir	soil	[49]
oil palm empty fruit bunch	300	8.14	chitosan	1.19	—	increase by 75 %	—	imazapic (herbicide)	—	—	Langmuir	soil	[50]
pinus radiata shavings	450	—	Al-oxide	219	0.0681	146.054	56.72%	isoproturon (herbicide)	—	—	Freundlich	soil	[51]
Moringa oleifera Lam. seed husk	300	—	nitric acid	5.77	0.0409	10.321	33.03%	atrazine (herbicide)	electrostatic interactions and hydrogen bonds	pseudo-second order	Langmuir	water	[52]
phragmite powders	500	—	nano $CuFe_2O_4$	189.6	0.12	269.4	98.9%	glyphosate (herbicide)	physisorption, chemisorption, electrostatic interactions and coordination bonding	pseudo-second order	Freundlich	water	[53]
rice husk	700	10.12	steam activated	251.47	0.083	160.77	16.08%	carbofuran (insecticide)	electrostatic action, physisorption and chemisorption	—	Freundlich	water	[54]
corn stalk	600	10	$Ni(NO_3)_2$ $FeCl_3$ $ZnCl_2$	14.26	—	143.15	71.58%	atrazine (herbicide)	chemisorption, π-π bond interaction	pseudo-second order	Freundlich	water	[55]
corn straw	300	—	H_3PO_4	638.1	—	79.6	96%	atrazine (herbicide)	Van der Waals' forces, H-bond, electrostatic interaction and porefilling	pseudo-second order	Freundlich	water	[56]
tangerine seed	600	7	H_3PO_4	659.62	0.6203	93.46	87.52%	carbamate pesticides (insecticide)	Van der Waals' forces, H-bond	Pseudo-second order	Langmuir	water	[57]
peach stones	500	5.2	orthophosphoric acid	6.179	0.006	39.37	99%	imidacloprid (insecticide)	H-bond pi–pi physical interaction	pseudo-second order	Langmuir	water	[58]

Table 2. *Cont.*

Raw Material	Pyrolysis Temperature °C	pH	Modification Method	Specific Surface Area ($m^2 \cdot g^{-1}$)	Otal Pore Volum ($cm^3 \cdot g^{-1}$)	Maximum Adsorption Capacity ($mg \cdot g^{-1}$)	Maximum Removal Rate%	Contaminant	Adsorption Mechanism	Adsorption Kinetics	Adsorption Isotherm	Active Matrix	Reference
corn straw	500	7	KOH	59.23	0.0231	2.84	88%	atrazine (herbicide)	electrostatic interaction	pseudo-second order	Langmuir	water	[59]
rice straw	600	6.93	H_3PO_4	192.3	0.161	0.05	89.5%	imidacloprid (insecticide)	—	Elovich	Freundlich	water	[60]
corn stalk	600	2.38 ±0.01	K_2CO_3 H_2SO_4 HNO_3	691.28	0.943	22.84	38.07%	2,4-dichlorophenoxyacetic acid (2,4-D) (herbicide)	π-π interaction, chemical adsorption and H-bond	—	Langmuir	water	[61]
sludge	400	—	$FeCl_3$	—	—	1.42	92.50%	dicamba (herbicide)	chemical adsorption	pseudo-second order	—	water	[62]
cotton straw cellulose	110	—	the methacrylic acid	27.77	—	—	95%	Sulfonylurea herbicides (SUHs) (herbicide)	π-π interaction and H-bond	pseudo-second order	Freundlich	water	[63]
tea waste	500	7 ± 0.2	Chitosan $AgNO_3$	—	—	5.643	93%	imidacloprid (insecticide)	chemical adsorption	pseudo-second order Elovich	—	water	[64]
Merremia vitifolia plant	105	—	ultrasound H_2SO_4	172.8	—	66.93	94%	2,4-D (herbicide)	electrostatic interaction, physical nature	pseudo-first order	Langmuir	water	[65]
coconut fiber	600	—	HCl	402.4	0.151	90.9	90%	dichlorvos (insecticide)	the pore filling, the hydrophobic interaction, H-bond	pseudo-second order	Langmuir	water	[66]
date stones	300	—	HCl	421	—	8.6	93%	aldrin (insecticide)	intra-particle diffusion, external mass transfer and physical adsorption	pseudo-second order	Freundlich	water	[67]
corn stalk	800	—	2-methylimidazole $Co(NO_3)_2 \cdot 6H_2O$	280	—	189	97%	imidacloprid (insecticide)	the pore filling, H-bond and π-π interaction	pseudo-second order	Freundlich	water	[68]

Due to the diverse features of biochar, which vary significantly with different source materials and pyrolysis settings, it can serve as both a soil amendment and a corrective remedy for pesticide breakdown. Biochar works as a super sorbent by lowering pesticides' accessible concentrations, which results in an increase in soil microbial biomass and the potential to improve soil quality [69,70].

2.2. Modification Methods of Biochar

Biochar can be modified by gas activation, ball milling, radiation, acid, alkali, oxidant, metal ion, and other treatment methods illustrated in Figure 2. For instance, modified biochar with increased surface area, porosity, and/or functional groups of a material in order to increase its sorption capacity has garnered more attention in recent years [22]. The choice of method depends on its application field [71]. The modification of biochar can significantly improve its activity and increase its application potential in pesticide-polluted environmental remediation [72]. Modification of biochar with chemical reagents may change its physicochemical characteristics, thereby improving its sorption capability, as found in Table 2.

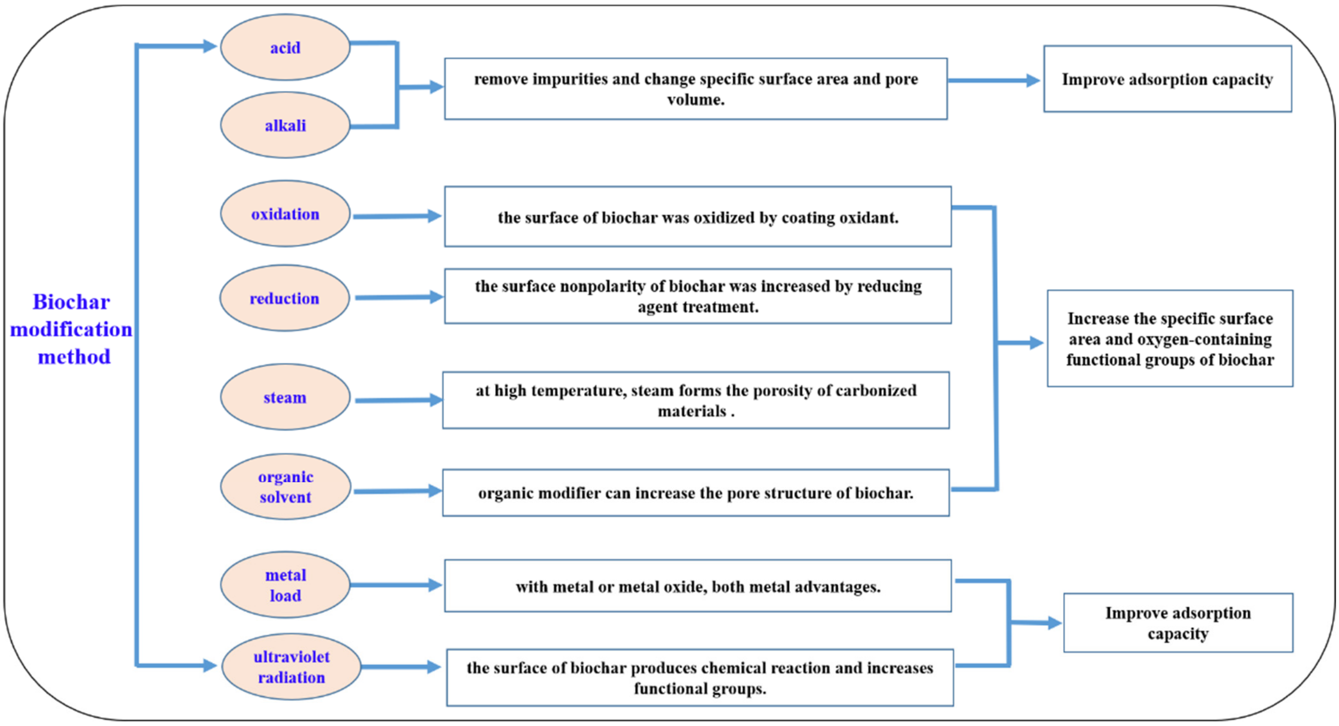

Figure 2. Common modification methods of biochar.

As shown in Table 2, the biochar modification methods include acid, alkali, oxidant, metal ion, and others. Compared with that of unmodified biochar, the maximum adsorption capacity of modified biochar ranging from 2.84 to 269.4 mg·g^{-1} was significantly improved by increasing the adsorption sites and promoting the function of biochar. The removal rates varied from 87.52% to 99%, which were mainly focused on herbicides and insecticides, while there is little research on fungicides. The sorption capacity and removal rate increased, suggesting that high pH is favorable for sorption on biochar. Pesticide adsorption kinetics can be well-represented by both the pseudo-first and pseudo-second order nonlinear kinetic models. In a word, modified biochar provides better remediation effects on pesticide-contaminated soils.

Using different biochar and modification methods had led to differences in the adsorption mechanism of pesticides. When most of the biochar is modified by chemicals, the pore filling mechanism is lower, increasing chemical adsorption. Most mechanisms are π-π interactions and hydrogen bonds. Biochar prepared from rice husk has more, also involving soil, seeds, and plants. Biochar made from rice bran, rice husk, reed powder, and corn straw has more than four adsorption mechanisms for pesticides, while cassava, slurry, and pine needle have only one adsorption mechanism for pesticides. In particular, the effect of modified biochar on the environmental behavior of maximum pesticide adsorption capacity ($mg \cdot g^{-1}$) and removal rate (%) is to be considered.

The modification methods of biochar are mainly chemical methods, and pH before and after modification is related to the added modified substances (Table S2). After the modification of the biochar with acid substances, the pH of the modified biochar decreases, and the range is about 1.45 to 1.89. Under the same modification conditions, due to different raw materials prepared, the properties after modification are generally different. By modification, biochar's environmental behavior of maximum pesticides adsorption capacity ($mg \cdot g^{-1}$) and removal rate (%) is increased (Table S2). The specific surface area ($mg^2 \cdot g^{-1}$) and total pore volume ($cm^3 \cdot g^{-1}$) of the modified biochar are mostly increased. The removal rate of pesticide pollutants from corn straw biochar modified with acid substances increases from 38% to 96%. The maximum adsorption capacity of oil palm empty fruit modified by chitosan increases from 8% to 75%.

Due to different modification methods for biochar made of the same raw materials, the maximum adsorption capacity and removal rate of the modified biochar for the same pollutant are improved. The maximum adsorption capacity of atrazine by modified corn straw biochar is about 47.22 to 48.09 $mg \cdot g^{-1}$, and the maximum removal rate is 23.61% to 58%. As shown in Table S2, experimental result is greatly related to the influence of raw materials. The same raw material, with different modified substances, will show different properties, but the influence on the removal rate of pollutants and the maximum adsorption capacity is not significant.

Pyrolysis temperature, duration time, composition, and concentration of input organic matter, as well as the inclusion of exogenous modifiers, all have a significant effect on the resulting biochar's characteristics [73]. The effect of biochar's pore geometry on adsorption is not clear [74]. Moreover, the relevant mechanisms should be adequately considered for maximizing the all-around efficiency of biochar amendments [75].

3. The Effect of Biochar on the Environmental Fate of Pesticides

3.1. The Effect of Biochar on Sorption of Pesticides

According to Sophia and Lima (2018) [76], adsorption onto inexpensive materials is a viable and promising strategy for removing both organic and inorganic pollutants [77]. Chemical sorption is less expensive, more efficient, and faster than biological methods. Adsorption occurs initially when pesticides encounter soil and is one of the most important processes for pesticide removal from soil. It has been shown to be a cost-effective and efficient pesticide removal technology [78]. Pesticide sorption and desorption in soil is the basis for understanding pesticide environmental behavior and biotoxicity [79]. Pesticide bioaccessibility and bioavailability in soil are inextricably tied to desorption processes, since the component must be released back into the soil solution to perform its intended impact [80]. Biochar can enhance pesticide sorption and lower the concentration of free pesticides in soil, which not only minimizes pesticide biotoxicity but also prevents pesticides from mitigating possible environmental dangers linked with harmful compounds and their metabolites [35,81,82]. Porosity, surface area, surface charge, pH, functional groups, carbon content, aromatic structure, and mineralogy all contribute to biochar's sorption ability [83,84]. Biochar's high organic carbon content and large surface area provide an abundance of pesticide sorption sites via hydrophobic partitioning and pore-filling [85]. The variances in biochar's sorption capacity are frequently due to changes in their properties, which vary according to the biomass source and manufacturing process used. After a long time, the efficiency of biochar's sorption capacity is likely to be reliant on the initial rate of biochar application to the soil. However, aging in biochar-amended soils likely reduces biochar's adsorption capability by altering its physicochemical characteristics [86]. Further investigation is needed to get insight into the fundamental mechanisms to clarify the specific pesticide characteristics that determine each behavior [87]. Biochar has an ability as a soil supplement to minimize pesticide contamination by boosting sorption and decreasing mobility [88]. Adsorption of pesticides by biochar impacts the processes of mobility and conversion, as well as pesticide absorption and usage in plants.

Several interactions between biochar and pesticides are depicted in Figure 3, including hydrophobic adsorption H-bonding, electrostatic, π-π electron donor–acceptor interactions, and cation–π bonding. Pesticides are removed from the environment by a variety of methods, including physical adsorption, complex formation, precipitation, ion exchange, and electrostatic interactions **[89]**. Through particular interactions and their strong aromaticity, surface functional groups and negative surface charge might enhance pesticide adsorption. The interaction between adsorbents and adsorbates is described using several adsorption isotherm models. The Langmuir and Freundlich isotherm models are the most often utilized in the adsorption system, demonstrating the presence of both physisorption and chemisorption **[90]**. On the basis of ideal monolayer adsorption, the Langmuir isotherm model was constructed, and the Freundlich isotherm model was used to calculate non-ideal adsorption on heterogeneous surfaces and multilayer adsorption. Pseudo-second-order kinetics is a third model that is also applicable to adsorption. However, it can serve as a theoretical foundation for the optimal use of biochar as a sorbent in environmental applications [91]. Adsorption is the simplest, most effective, and most widely used technology for most remediation attempts, and biochar is the most used adsorbent due to its wide applicability for pesticide removal **[92]**.

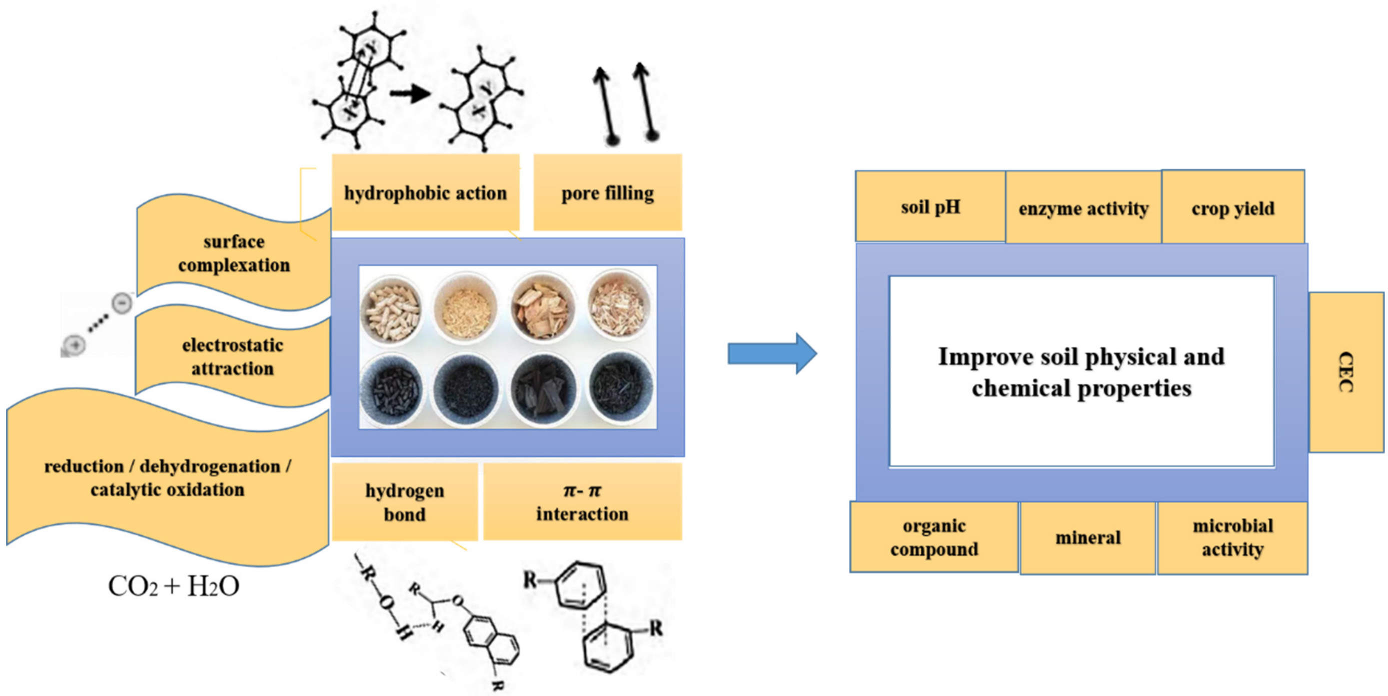

Figure 3. Mechanism of biochar remediation of soil pollution.

3.2. The Effect of Biochar on Degradation of Pesticides

Sorption and degradation are the major mechanisms that regulate pesticide effectiveness and the danger of runoff contamination [93]. Due to its high adsorption capacity, biochar has been extensively studied for its influence on pesticide sorption, desorption, and degradation in agricultural soils [94]. Dissipation study is critical because it will aid in the correct and safe application of pesticides [95]. Because of its high specific surface area and abundance of oxygen-containing functional groups, biochar is considered an effective pesticide amendment that reduces the biodegradation of pesticides in soils. This helps pesticides remain stable in the soil and is likely to play an important role in this process [96].

Pesticide dissipation is reduced in biochar-amended soil due to enhanced adsorption and decreased desorption from the biochar surface, limiting pesticide bioavailability. However, adding biochar may increase microbial stimulation and hence pesticide breakdown. Application of biochar to agricultural soils can change pesticide persistence and break down products. When applied to agriculture, biochar's sorption nature can affect pesticide absorption and breakdown. Biochar can affect pesticide environmental destiny through sorption, desorption, and degradation in soils [97]. Soil biodegradation of pesticides is altered by biochar depending on which activity is prominent. The persistence of pesticides in soil is closely related to their degradation kinetics. The influence of pesticide properties and environmental conditions plays an important role in environmental fate. Pesticide residues and half-life increase with the dose and number of applications. Its degradation grade in soil is divided according to the guidelines for an environmental safety evaluation test of chemical pesticides. Biochar has a certain degradation effect on pesticides, and the amount of biochar has a significant impact on the degradation rate of pesticides. The more biochar added to the soil, the slower the degradation rate of pesticides in the soil [27,98]. Biochar improved the soil and delays the digestion process of insecticides chlorpyrifos and fipronil [99]. After pesticide application, pesticide residues in soil gradually decrease with time, and the degradation trend is according to the first-order kinetic equation.

3.3. Factors Affecting Biochar on Environmental Fate of Pesticides

Due to the unique physicochemical features of biochar, it often has a high capacity for adsorbing pesticides prevalent in the soil environment. These properties are highly dependent on the feedstock (pinewood, wheat straw, rice husk, dairy manure, sugar beet tailings, and sewage sludge) and pyrolysis conditions (temperature, heating rate, and residence time), which are two critical factors affecting the amounts of functional groups on the surface of biochar [100]. For example, biochar produced at greater pyrolysis temperatures might provide more sorption sites for pesticides due to its increased surface area. However, high heating degrades the acidic functional groups on the surface of biochar, reducing its potential to adsorb NH_4^+–N [101,102]. In addition, it has been shown that the adsorption capacity of biochar is related to its physical and chemical properties, such as specific surface area, pore diameter size, degree of carbonization, aromaticity, etc. However, a single factor such as aromaticity is not able to explain the responding trends of sorption [103,104]. Sorption of environmental constituents, especially natural organic matter, and oxidation reactions have been established as major contributors to the aging of biochar, which might impact biochar sorption affinity for pollutants [105]. However, by lowering the amounts of functional groups on the surface, this can also result in decreased pesticide sorption. Biochar's structure and sorption capability are very variable depending on the raw materials used and the pyrolyzing conditions. The most critical element affecting the structure and sorption behavior of biochar is the pyrolyzing temperature. The yield of biochar decreases with the increase of temperature, and the pH value is mostly alkaline. The carbon content, C/N, ash content, and adsorption of pesticides basically increase with the increase of temperature, while soluble carbon content and volatile matter deficiency show the opposite trend [106]. Minerals form on the surface of the biochar after pyrolysis and clogg the pores. Ash might bind to pesticides but has a detrimental effect on sorption [107]. It may cover the reactive surfaces of biochar, masking its real pesticide sorption capability. Thus, acid washing is required to increase the specific surface area of biochar. Many factors influence pesticide sorption of biochar in soil, including biochar characteristics. Note that soil and ambient variables such as moisture, temperature, pH, and minerals impact biochar stability [108].

The solubility, pKa, molecule size, and substituent nature of aromatic biochars all influence the adsorption mechanism. Since pH affects the surface charge of biochar and the molecular form of pesticides in soils, it is one of the most critical elements controlling the adsorption process [106]. Pesticide features such as kind, molecular size, molecular polarity, and functional groups influence sorption, desorption, and degradation in soils supplemented with biochar [109]. The sorption mechanisms shift when the solute concentration change. Biochar can alter the fate and bioavailability of pesticides in soil, which affects the biodegradation of pesticides. This primarily depends on biochar properties, soil characteristics, and pesticide types. Clearly, further research is required to determine how long biochar in soil may continue to bind pesticides and hence influence their efficacy.

4. Application of Biochar for Remediation of Pesticide-Contaminated Soils

Biochar can be used in contaminated soils as an amendment and remediating agent to immobilize and reduce the bioavailability and toxicity of pesticides. Applying biochar to agricultural soils has varying impacts depending on the feedstock, pyrolysis temperature, and application rates [110]. Understanding biochar's function in various applications can help develop or choose the best biochar for a given application based on feedstock composition, production parameters, and post-treatment qualities. Addition of biochar to the soil has two roles: it drives contaminants into or adsorbs them onto the biochar, while it can also release nutrients that increase the rate of microbial degradation of the contaminants. Applying biochar to soil can play a significant role in altering nutrient dynamics, soil contaminants, and microbial functions. Biochar improves soil fertility in pesticide-contaminated soils. Certain sorption/deactivation potential (shown by high sorption and low desorption) for pesticides is retained by the biochar after nearly three years in soils. Table 3 demonstrates that biochar can effectively improve soil quality and reduce its ecological risk.

Table 3. Application of biochar in soil pollution.

Biochar Type	Pyrolysis Temperature	Contaminant (Pesticide)	Application Effects	Active Matrix	Reference
rice straw	field under natural conditions	clomazone (herbicide)	Rice straw residues burnt in an open field considerably reduced clomazone's herbicidal activity against barnyard grass.	soil	[111]
wheat straw	450 °C	atrazine (herbicide) trifluralin (herbicide)	In comparison to unamended soil, a 3.5-fold increase in atrazine application rate was necessary. The herbicides' effectiveness to suppress weeds remained insufficient even when application dosages were four times greater than the authorized rates.	soil	[112]
corn straw	500 °C	1,3-dichloropropene (fumigant)	To obtain complete nematicidal activity, the dosage of 1,3-dichloropropene fumigant has to be quadrupled at a biochar amendment level of 26 t ha-1 in soil.	soil	[113]
wheat straw	natural conditions	diuron (herbicide)	Diuron herbicide effectiveness was greatly reduced in char-amended soil.	soil	[114]
Eucalyptus spp. wood chips	850 °C	chlorpyrifos (insecticide) carbofuran (insecticide)	Pesticide absorption by plants dropped significantly as soil biochar concentration increased. It slows the rate of pesticide microbial breakdown, hence extending the duration of pesticide residues in the environment.	soil	[115]
red gum wood chip	850 °C	diuron (herbicide)	The soil treated with biochar produced by the pyrolysis of red gum chips boosted diuron sorption and increased the nonlinearity of the adsorption isotherm and the degree of sorption-desorption hysteresis. Small quantities of charcoal formed at high temperatures (e.g., the inside of wood logs during a fire) can have a significant influence on the release behavior of organic compounds in soil.	soil	[116]
sugarcane top	500 °C	atrazine (herbicide)	Biochar generated from organic matter slowed atrazine breakdown in soils to varied degrees depending on the rate of input.	soil	[117]
rice straw	550 °C	bispyribac-sodium (herbicide)	Increased microbial activity and bacterial population in soil following amendment with URS and biochars revealed the significance of amendment in preserving soil quality and function by increasing microbial parameters.	soil	[118]

Table 3. *Cont.*

Biochar Type	Pyrolysis Temperature	Contaminant (Pesticide)	Application Effects	Active Matrix	Reference
wheat straw	700 °C	tebuconazole (bactericide)	Not only did the biochar-immobilized WZ-2 speed tebuconazole breakdown, but it also restored native soil microbial enzyme activity and community composition.	soil	[119]
rice hull	600 °C	fomesafen (herbicide)	In agricultural soils, biochar additions likely change the fate of herbicides by reducing their transit via improved adsorption.	soil	[120]
corn stalk	600 °C	atrazine (herbicide)	bFeMBC protected the function and metabolic activity of beneficial bacteria susceptible to atrazine contamination during the early stage of pollution, hence preserving their relative abundance.	soil	[121]
walnut shell	900 °C	linuron diuron monuron (herbicide)	Pesticides entrapped in biochar have a restricted uptake by organisms, and as a result, their toxicity decreases, resulting in low pest control efficacy of pesticides in biochar-amended soils.	soil	[122]
Eucalyptus wood	800 °C	metolachlor (herbicide) sulfentrazone (herbicide)	It may have an effect on pest control and necessitates a greater pesticide application rate, directly increasing production costs and maybe introducing a new risk to the environment.	soil	[123]
magnolia tree woodchip	500 °C	thiacloprid (insecticide)	While biochar decreases thiacloprid's bioavailability in soil, the delayed degradation and increased earthworm concentration in old biochar-amended soil signal that the environmental hazards associated with biochar application to earthworms persist.	soil	[124]
crofton weed	500 °C	acetochlor (herbicide)	These findings show that ageing biochar in soil for an extended length of time may enhance the pesticide hazard to crops.	soil	[125]
oil palm empty fruit bunches	300 °C	imidazolinone (herbicide)	The developed EFB and RH biochars have the potential to be employed in the soil as an eco-friendly and cost-effective biosorbent to mitigate the dangers of imidazolinone herbicides and safeguard the environment from their contamination.	soil	[126]

Table 3. *Cont.*

Biochar Type	Pyrolysis Temperature	Contaminant (Pesticide)	Application Effects	Active Matrix	Reference
eucalyptus origin	400-500 °C	diuron (herbicide)	Due to the increased diuron sorption capacity and decreased diuron desorption capacity of sandy soils following biochar application, the danger of diuron leaching and pollution of subsurface water may be reduced.	soil	[127]
rice husk	550 °C	fenoxaprop-ethyl (herbicide)	The use of biochar resulted in a decrease in the toxicity of earthworms. Biochar was found to have a beneficial effect on residues and toxicity. Biochar has a high potential for soil remediation and may be a positive agricultural approach for the soil environment.	soil	[128]
wheat straw	500 °C	fomesafen (herbicide)	Biochar made from wheat straw can help to minimize the danger of fomesafen contamination in soil and improve the soil microbial ecology.	soil	[129]

Insecticides used as chemical growth inducers, increased hormone releasers, pesticides, weedicides, and synthetic fertilizers cause environmental issues. The enormous benefits of biochar in agriculture and the environment are coupled with downsides [130]. Illustrating the negative effects of improper biochar usage, using biochar in soil remediation on a large scale may expose animals, plants, microbes, and agricultural crops to harmful effects from the biochar's adsorbed hazardous chemicals. This might have deleterious impacts on the biotic environment. Certain biochars can function well in improving soil, while other biochars cannot [131]. The appropriate modification methods depend on the environmental application [132]. As biochars' properties change over time, the pesticides' application rate might need to be adjusted for different pesticides every cropping season. The variation of biochar properties can affect its stability in the environment, highlighting the need to study the impact of biochar amendments on the sorption and environmental fate of pesticides in agricultural soils under specific local conditions. The effect of other contaminants on pesticide removal by biochar in soils, the effect of pesticide properties on its behavior in biochar-amended soils, and the large-scale use of biochar in agricultural soils for multifunction have also been evaluated. Its many roles have aided future study directions. This suggests that applying biochar to soil might be a realistic way to relieve these stresses [133]. Agronomic, environmental, and economic benefits may result from applying biochar to soil strategically. Biochars may be tailored for particular environmental purposes, making them a potential option [134].

5. Challenges and Opportunities

5.1. Cost of Biochar and Modified Biochar

Biochar application is motivated by the desire to minimize the use of comparably more expensive conventional sorbents in water treatment [135]. It can be used to improve pesticide treatment in agricultural fields. As the international production, distribution, and applications of biochar continue to grow, it is important to study its environmental impacts and economic performance to assess its overall value [136]. However, relatively limited attention has assessed how biochar amendment affects plant growth in contaminated soils [137]. When contemplating modified biochar as a soil supplement, one must consider the cost of these modifications, even if they often yield better pesticide sorption effectiveness. Low-cost biochar has widespread potential in soil remediation and can help identify suitable types of biochar or develop engineered biochar with specific functions [102].

5.2. Application of Biochar Return to Field

With a growing global population and limited arable land, restoring soil quality to nonproductive soils is critical to future food production, food security, and energy supply. Biochar may help in this attempt [138]. Biochar has qualities comparable to those of activated carbons but is far less expensive. Biochar has the potential to be utilized as a renewable and sustainable sorbent to remove contaminants from the soil due to its high surface-to-volume ratio and large surface area (as shown in Figure 1). However, the processes governing the fate and behavior of organic pollutants in the environment, particularly pesticides in biochar-amended soil, are poorly known [139]. To optimize the advantages of biochar in soil settings, the methods by which biochar interacts with soil components should be further investigated [140]. This will provide insight into the effect of biochar on soil ecology and biogeochemical processes. The specific processes of contaminant-biochar retention and release over time, as well as the environmental impact of biochar additions on soil organisms, remain unknown [141]. How and to what degree biochar can alter pollutant transit and fate in the environment is uncertain. Soil pollutants, herbicides, and minerals must be stabilized and bioavailable using charcoal. This will enable the construction of biochar with specified physicochemical features and help manage the released pollutants. Biochar is not without its environmental dangers, such as pollutant release, biota toxicity, and impact on global carbon fluxes and contaminant movement [140].

While these are valid concerns, physical, chemical, and biological treatments can affect the effectiveness of biochar [142].

Biochar offers several advantages in forest soils, especially in low-fertility plantation soils [143,144]. Due to its unusual structure and remarkable physicochemical qualities, biochar has shown promise as a compost ingredient. It improves physicochemical and nutritional characteristics, reduces bioavailability, and removes resistance genes from compost. Biochar increases fertilizer utilization efficiency and water retention capacity in soil. Straw is a readily available biomass with a global production surpassing 3.97 billion tons per year [102,145]. Among all biochar types, straw biochar was shown to be the best compost supplement [102]. Crop straw direct burning in the field which will cause serious air pollution is prohibited in China. Returning crop straw without direct burning to the field may aggravate the occurrence of various crop diseases. The direct straw return to the field will be transformed into a technical chain of "collection and storage-carbonization-productization-return to the field". Based on carbonization technology, through the industrialization and large-scale application of carbon-based agricultural inputs, farmland soil carbon sequestration will be realized, greenhouse gas emission will be reduced, and full quantitative utilization of straw and the improvement of farmland quality will be promoted. Straw-derived biochar returning to the field for emission reduction and sequestration of carbon technology, as one of ten major technical projects of the Ministry of Agriculture and Rural Affairs, China in 2021, will provide a great opportunity for biochar application for remediation of pesticide-contaminated soils. With the continuous application of pesticides, the contamination of soil by pesticides will continue to occur. However, whether repeated biochar return to pesticide-contaminated fields will cause long-term adverse effects on the soil ecosystem is still unknown.

5.3. Effect of Biochar on Climate Change

Biochar has emerged as a new class of biomass-derived functional materials that can be obtained using a plethora of thermochemical conversion techniques [146]. Biochar made from diverse biomass has been widely employed to increase soil fertility, reduce harmful gas emissions, sequester carbon, and act as a catalyst in energy generation [147]. Thus, employing pyrolysis to create biochar and storing it in soil is gaining popularity as a way to combat climate change. Biomass is gaining attention as a renewable energy alternative to replace present fossil fuel resources [148]. With China already aiming to peak CO_2 emissions by 2030 and attain carbon neutrality by 2060, biochar has a bright future. Thermochemical conversion of solid waste into biochar can assist the circular economy in several ways, including climate change mitigation and carbon sequestration [149]. Because biochar is made from a variety of source materials and is recyclable, it may convert trash into treasure when used to cure the environment. Using biochar to sequester soil carbon seems to have significant adaptation/mitigation potential, if cost-effective manufacturing and inclusion methods can be established [150].

6. Conclusions

The extensive and ineffective use of pesticides over the decades has resulted in considerable soil pollution, but it has helped enhance agricultural output by lowering disease and insect pests. Aside from boosting soil quality and agricultural output, modified biochar is increasingly being used to remediate polluted soils [151,152]. Soil remediation utilizing eco-friendly additives to combat pesticides in soil appears to be one solution. Modified biochar is a more potential and beneficial soil amendment solution for pesticide-contaminated soils. It can also increase soil fertility and trap carbon produced by the thermal decomposition of organic materials in oxygen-limited environments. Modified biochar has high porosity with plentiful oxygen functional groups and aromatic surfaces to boost soil sorption capacity for pesticides. The capacity of modified biochar to remediate contaminants from environmental matrices is also addressed. At present, pesticide-polluted soil remediation with modified biochar is mostly used in laboratory tests, and field application research is less frequent. In this perspective, future study should focus on the influence of modified biochar additions with low cost and high practical application value on pesticide sorption and environmental destiny in agricultural fields. Carbon sequestration, soil fertility enhancement, pollution remediation, and agricultural byproduct/waste recycling are possible modified biochar uses [153].

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app122211544/s1, Table S1: Chemical properties of different pesticide contaminants; Table S2: Comparison of biochar and modified biochar on adsorption capacity and removal rate.

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