sustainability

MDPI

Article

The Effect of Remediation of Soil Co-Contaminated by Cu and Cd in a Semi-Arid Area with Sewage Sludge-Derived Biochar

Zhipu Wang [1,*,†], Nan Wei [2,†], Fei Yang [3], Daoren Hanikai [4], Shifeng Li [1], Yawei Zhai [1,*], Jiabin Zhou [5], Dan Liu [5], Xiaoxian Yuan [1], Shiji Bie [1] and Yixuan Tian [1]

[1] State Key Laboratory of Heavy Oil Processing, China University of Petroleum-Beijing at Karamay, Karamay 834000, China; lsfddmlh@163.com (S.L.); guyeee0612@163.com (Y.T.)
[2] Center for Soil Protection and Landscape Design, Chinese Academy of Environmental Planning, Beijing 100041, China
[3] Karamay Shuangxin Environmental Technology Co., Ltd., Karamay 834000, China
[4] Xinjiang Uygur Autonomous Region Environmental Protection Scientific Research Institute, Urumqi 830000, China
[5] School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, China; jbzhou@swpu.edu.cn (J.Z.); liuanhui93@163.com (D.L.)
* Correspondence: wzpcumt@163.com (Z.W.); zhaiyw@cupk.edu.cn (Y.Z.)
† These authors contributed equally to this work.

Abstract: In this study, biochar derived from sewage sludge was applied to remediate Cu and Cd co-polluted soil in semi-arid areas for the first time, in which the effects of biochar on the improvement of soil physicochemical and biological properties as well as the immobilization of Cu and Cd were investigated. Soil water holding capacity increased by 0.22–2.74%, soil CEC increased by 0.52–4.06 units, soil SOM content increased by 1.41–5.97 times, and urease and catalase activities increased by 0.012–0.032 mg·g^{-1}·24 h^{-1}, 0.18–2.95 mg H_2O_2·g^{-1}, but soil pH increased only slightly by 0.69 units after biochar application. In addition, although the total content of these two metals in the soil increased with the use of biochar, the content of DTPA-Cu and Cd decreased by −0.128–0.291 mg/kg, 0–0.037 mg/kg, with the increase in biochar application, and the content of acid-soluble Cu in the soil decreased from 27.42 mg/kg to 3.76 mg/kg, the mobility and bioavailability of these two metals in the soil decreased. Finally, the complexation of organic functional groups with the soil dominates the immobilization process of metals, especially Cu. These findings suggest that biochar from sewage sludge can effectively improve soil quality and remediate heavy metal-contaminated soils in semi-arid regions. Meanwhile, the use of sludge-based biochar for the remediation of contaminated soils also provides a new method for the safe disposal of sewage sludge and a new way for sustainable development. In subsequent studies, methods such as modification are recommended to improve the efficiency of sludge-based biochar for the removal of Cu and Cd.

Keywords: biochar; sewage sludge; heavy metals; soil; remediation; co-contaminate

check for updates

Citation: Wang, Z.; Wei, N.; Yang, F.; Hanikai, D.; Li, S.; Zhai, Y.; Zhou, J.; Liu, D.; Yuan, X.; Bie, S.; et al. The Effect of Remediation of Soil Co-Contaminated by Cu and Cd in a Semi-Arid Area with Sewage Sludge-Derived Biochar. *Sustainability* **2024**, *16*, 4961. https://doi.org/10.3390/su16124961

Academic Editor: Agostina Chiavola

Received: 28 March 2024
Revised: 17 May 2024
Accepted: 24 May 2024
Published: 10 June 2024

Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

With the increasing development of industry, municipal wastewater treatment plants around the world produce a large amount of sewage sludge every year [1]. China annually produces over 13 Mt DS year^{-1} (million tons dry solid per year) of sewage sludge. In the United States, annual sewage sludge production has reached almost 8 Mt DS year^{-1} [2]. Global sewage sludge production will reach 103 million tons by 2025, approximately [3]. Sludge contains organic pollutants, parasitic organisms, and toxic heavy metals such as cadmium, chromium, nickel, copper, and zinc, with potentially high environmental risks [4]. An effective method for the disposal of waste sewage sludge is a hot issue of global concern for environmental protection. A significant portion of sludge is improperly treated, leading to secondary pollution in various environmental matrices such as soil and surface water [5].

Many sludge disposal technologies have been developed, such as incineration, landfill and pyrolysis. However, sludge incineration produces dioxins, which seriously pollute the atmosphere [6]. The application of landfills in the sewage sludge treatment process is also restricted by limited land resources and possible environmental risks [7]. Most sewage sludge has a high calorific value, which could potentially provide good economic and social benefits if treated with proper energy conversion and thermal–chemical technologies [8]. Pyrolysis is a promising technology that can produce functional products such as biochar, oil and gas [9].

Biochar raw materials come from various materials that can be classified into sewage sludge, agricultural waste and wood, food waste, and marine feedstock [10]. Sewage sludge is the most common biochar raw material [11]. In many ways, converting sewage sludge to biochar can be advantageous for the environment. Some of these ways are reducing the volume of sludge abandoned, reducing the cost of disposal, controlling groundwater pollutants, increasing soil carbon sequestration, and reducing GHG emissions [2]. In addition, biochar derived from sewage sludge can kill pathogenic organisms, completely decompose organic pollutants and reduce the bioavailability of heavy metals, providing treatment for soil contaminated with heavy metals [12]. The presence of carbonates, phosphates, and silicates in biochar has the potential to cause the precipitation of heavy metals such as $CdCO_3$ [13], $Pb_5(PO_4)_3Cl$ [14], and $Pb_5(PO_4)_3OH$ [15]. The biochar's surface is loaded with many organic functional groups, including carboxyl, phenolic, hydroxyl, and imine, among others [16–20]. Through coordination and chelation, these functional groups have the potential to form stable complexes with metals found in soils, which would ultimately result in the metals being immobilized [21–24]. By converting heavy metals from chemical forms that are unstable and bioavailable to forms that are stable and non-bioavailable, biochar amendment can successfully minimize the ecotoxicity of soil heavy metals [25]. Biochar derived from sewage sludge contains abundant exchangeable K, Ca, and Mg, which can be replaced by Pb, Cd, and Zn in the soils through ion exchange [20,26–28].

Sources of heavy metals in soil include natural and anthropogenic factors. As a result of the combustion of fossil fuels, ore processing, etc., heavy metals can easily infiltrate into the air, water and soil, and then into the food chain of plants and animals [29]. Cu is a heavy metal that is relatively common in the environment, and irrigation of agricultural land with Cu-containing wastewater causes Cu to accumulate in the soil and crops, which can cause poor crop growth and contaminate food. On the other hand, excessive intake of Cu can also cause great harm to the human body when a large amount of heavy metal residue in the body will cause a burden on the body's internal organs and cause Cu toxicity [30]. As for Cd, as a toxic, non-essential heavy metal element. Cd and cadmium-containing compounds are mainly hazardous to the human body's kidneys, bones, muscles, etc., and in severe cases, they can lead to renal failure or even death [31]. Nevertheless, the remediation of soil co-contaminated with Cu and Cd is a problem because the two metals in the soil have different chemical properties. It has been proven in previous studies that biochar generated from plants can successfully immobilize Cu and Cd and simultaneously remove Cu^{2+} and Cd^{2+} from an aqueous solution [32–34]. Compared to biochar formed from plants, biochar derived from sewage sludge has a higher mineral concentration, allowing it to extract a greater quantity of heavy metals from the surrounding environment [35–37].

Arid and semi-arid areas covering over 40% of the earth's surface land are undergoing degradation due to intensive land use [38]. Reductions in the capacity of the soil to retain moisture, the fertility of the soil, and the organic matter content of the soil all contribute to a significant limitation of plant production in these regions, which has severely and severely hampered the development of agriculture [39]. As a result, the ecological balance will be aggravated, biodiversity will be destroyed, and the sustainable development of agriculture will be seriously limited. At the same time, heavy metal soil contamination is another concern when metal resources are extracted and processed in such regions [40]. Significant concentrations of heavy metals in the soil can have a detrimental impact on the structure of the soil, the physical and chemical properties of the soil, the efficiency with which water is

used, and the activity of soil microbes, which indicates that there is a significant probability that plant growth will be inhibited [41]. Furthermore, the coexistence or interaction of multiple heavy metal elements is highly susceptible to the formation of soluble complexes, which increase mobility and make it easier for pollution to spread.

Sun et al. revealed that high content of O and Na contents in sludge-derived biochar contributed to surface complexation and cation exchange, which were the main removal mechanisms for Cd(II), while the presence of coexisting metal ions inhibited the removal of Cd(II) [42]. Zhao et al. utilized biochar to simultaneously remove Cr, Cu, Zn, and Cd, discovering that the simultaneous removal of heavy metals was influenced by the interaction of the heavy metals compared with the individual removal of heavy metals [43]. Cu and Cd have different characteristics, the behaviors of these elements in soil may be different after the amendment with biochar obtained from sewage sludge. Consequently, the effect and method of biochar immobilizing the two metals can be different. It has not been investigated whether or not it is possible to use biochar made from sewage sludge to clean up soil contaminated with both Cu and Cd. The effects and possible mechanisms of the biochar on immobilizing Cu and Cd coexisting in the soil remain unknown. We hypothesized that sewage sludge-based biochar could improve soil quality and effectively immobilize Cu and Cd in soils of arid and semi-arid areas. The objectives of this research were as follows: (1) study the influences of the biochar on physicochemical properties, fertility, and microbial activities in the soil; (2) evaluate biochar's impact on soil metal immobilization; (3) investigate the distribution and transformation of Cu and Cd in different chemical forms while elucidating the possible immobilization mechanisms.

2. Materials and Methods

2.1. Soil and Biochar

A farm in Xinjiang, located at 41°52′45″ North and 95°18′15″ East, provided a sample of the top layer of soil, which was from 0 to 20 cm deep. The content of the soil is composed of 68.5% sand, 20.3% silt, and 11.2% clay. The texture of the soil is sandy loam. Table 1 displays the characteristics of the soil. Cu and Cd are both present in the soil. The quantities of copper and cadmium in the soil are higher than the threshold values recommended by the Chinese guideline for agricultural soil quality (GB15618–2018). These threshold values are 100 and 0.3 mg/kg, respectively, while the soil pH ranges from 6.5 to 7.5.

Table 1. Basic properties of the soil and the biochar.

Properties	Unit	Soil	Biochar
pH	-	7.08 ± 0.30	8.95 ± 0.66
EC	Ms/cm	200.32 ± 10.46	428.32 ± 20.26
CEC	cmol/kg	1.98 ± 0.11	33.55 ± 2.10
SOM	%	1.04 ± 0.58	-
AP	mg/kg	26.12 ± 1.98	171.76 ± 16.22
AN	mg/kg	19.56 ± 1.22	76.42 ± 5.31
AK	mg/kg	130.28 ± 6.80	1366.28 ± 30.55
WHC	%	4.43 ± 0.18	-
Total heavy metal contents			
Cd	mg/kg	0.57 ± 0.03	2.17 ± 0.18
Cu	mg/kg	155.24 ± 12.25	335.84 ± 18.20

EC: electrical conductivity; CEC: cation exchange capacity; SOM: soil organic matter; AP: available phosphorus; AN: available nitrogen; AK: available potassium; WHC: water holding capacity.

The experiment utilized sewage sludge obtained from the first municipal sewage treatment plant in Urumqi, which served as the source of information. Under the protection of nitrogen dioxide, the sludge was pyrolyzed in a furnace that remained constant. Experiments involving pyrolysis were carried out at a temperature of 600 °C for two hours to yield biochar with a better-developed pore structure. Wang et al. list the method and

apparatus for pyrolysis [44]. The essential characteristics of the sludge are summarized in Table 1.

2.2. Sample Characterization

Classification of the soil texture following the methodology developed by Bouyouco [45]. The soil pH and EC were measured using a dual pH/conductivity meter (WM-32EP, DKK, Osaka, Japan) in solutions of 1:5 and 1:10 (wt./vol.) dirt to distilled water. The results of these measurements were compared. The results of these measurements were compared. The method for measuring CEC was by NY/T 1121.5-2006 [46]. The method for measuring SOM was by NY/T 1121.6-2006 [47]. The LY/T 1228-2015 [48] was utilized to measure the soil's AN. The NY/T 1121.7-2014 [49] was utilized to measure the soil's AP (UV Spectrophotometer, 8000A, Chongqing, China). The NY/T 889-2004 [50] was utilized to measure the soil's AK (Flame Spectrophotometer, M420Cs, Sherwood Scientific, Cambridge, UK). The NY/T 1121.22-2010 [51] was utilized to measure the soil's WHC. Measured soil enzyme activities according to the methods used by Tu et al. [52]. Soil urease activity was determined using the sodium hypochlorite-sodium phenate colorimetry assay. Soil catalase activity was determined using the permanganimetric assay. Using the same meters used for the soils, the pH and EC of the biochar were determined by combining them with deionized water in a ratio of 1:10 (weight/volume) biochar. The CEC, AP, AN, and AK of the biochar were then measured per the procedures specified for the soil.

The samples' Cu and Cd concentrations were measured with an atomic adsorption spectrometer (Analytik Jena, AAS6 Vario, Jena, Germany) following digestion with $HClO_4$-HNO_3 [53]. The metal content of soils treated with biochar was evaluated using a modified version of the BCR technique [54]. Following the methodology outlined by Lindsay and Sabey for DTPA extraction, the concentrations of Cu and Cd in their bioavailable forms were determined [55].

2.3. Incubation Experiments

Polythene cups with a capacity of 500 milliliters were used for the incubation studies. The soil (150 g) was amended with biochar at five different rates of 0%, 2%, 4%, 6%, and 10% (wt./wt.) and labeled S0, S2, S4, S6, and S10, respectively. Following the incubation period of 60 days, all of the soil samples were placed in an oscillating incubator, where they were vibrated at a rate of two hundred revolutions per minute for 3 h. It was observed that the water content of the soil contained within each polythene cup stayed at around 60% of the overall capacity of the field to store water during the incubation period. The soil contained within each polyethylene cup was collected and analyzed throughout the experiment.

2.4. Statistical Analyses

All treatments were performed in triplicate. To analyze the soil properties and the bioavailability of Cu and Cd in the three treatments, SPSS version 19.0 was utilized. Analyzing statistically significant variations in the soil characteristics indicated above, a one-way analysis of variance (ANOVA) was undertaken. The significance level for Duncan's test to compare the effects of the three treatments was set at $p < 0.05$. The graphs were drawn using Origin version 9.1.

3. Results and Discussion

3.1. Physicochemical Properties

As a result of the incorporation of biochar, the soil's WHC, pH, CEC, and EC all exhibited alterations, as shown in Figure 1. Compared with control soil, biochar amendment improved soil WHC (Figure 1a). According to the results of the experiment, the majority of the soil was composed of coarse particles, which exhibited high permeability and low soil water-holding capacity. Because of its highly porous structure, biochar can reduce the amount of water lost through evaporation and infiltration from semi-arid sandy soils while simultaneously increasing its capacity to hold water [56]. In coarse-grained, sandy

soils, biochar particles occupy the pore space of the soil, which slows down the infiltration rate [57]. Moreover, the numerous pores that are present in biochar help to both retain water and increase the water-holding capacity of soil that has been treated with biochar [58]. According to the findings of this research, soil WHC increased dramatically with rising biochar application rates, indicating that the addition of the sewage sludge-derived biochar facilitated the improvement in available moisture for sandy soils in semi-arid areas.

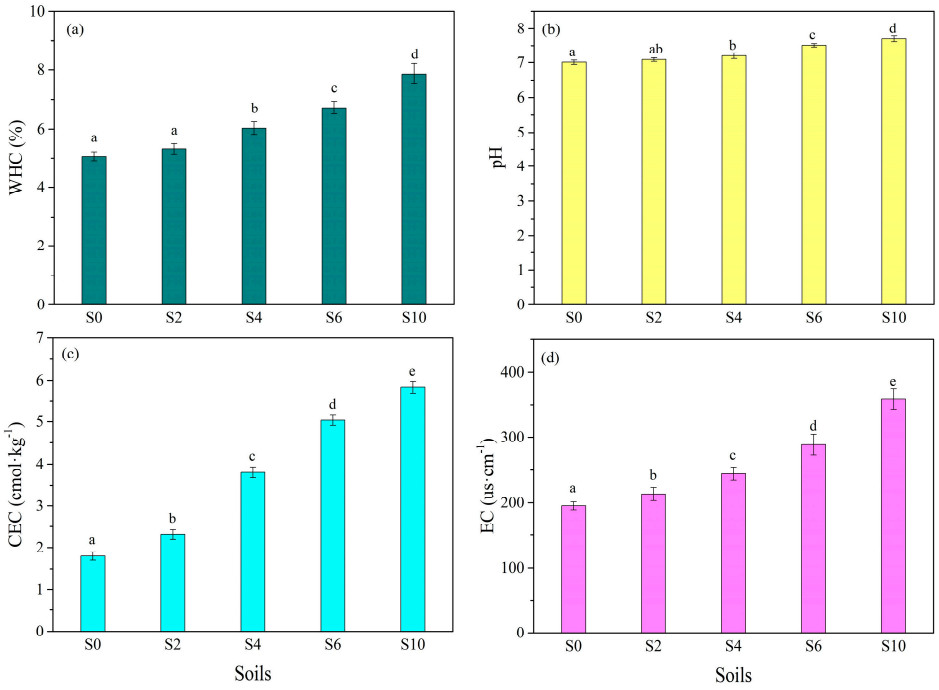

Figure 1. Effects of the biochar on soil physicochemical properties. (**a**) WHC; (**b**) pH; (**c**) CEC; (**d**) EC. WHC: water holding capacity; CEC: cation exchange capacity; EC: electrical conductivity.

The biochar produced from sewage sludge can potentially increase the soil's pH, which may provide challenges when applied to semi-arid alkaline soils. A small increase in soil pH of 0.69 units was observed during this investigation. This was accompanied by an increase in the application rate of biochar from 0 to 10% (Figure 1b), which suggested that the incorporation of biochar into the soil had a marginal impact on the pH of the soil. Yue et al. also observed a slight increase in the pH value of alkaline soil after applying sewage sludge-derived biochar [59]. Chen et al. applied biochar to Pb, Cu, and Cd co-contaminated soils and revealed that varied biochar properties and the increased soil pH resulted in a lower risk of metals released from soils over time [60].

After applying biochar at a rate of 2%, there was a discernible increase of 0.51 units in the CEC of the soil compared to the CEC of the control soil. An increase in the amount of biochar applied resulted in a significant rise in the CEC of the soil (Figure 1c). Negatively charged surface functional groups are typically responsible for increased soil CEC due to biochar amendment [61]. Additionally, the rise in soil CEC contributes to the enhancement of nutrient retention in semiarid soil, promoting the reduction in the amount of fertilizer required for agricultural production [62]. Moreover, soil EC notably increased after biochar amendment (Figure 1d), which solubilizing soluble salts may cause in biochar [63]. When biochar generated from sewage sludge was used to remediate sandy soil co-contaminated by multiple heavy metals in a semi-arid area, comparable observations were reported in prior work [64].

3.2. Soil Fertility

Figure 2 illustrates the changes in the soils' SOM, AP, AN, and AK contents due to adding biochar. Most soils in semi-arid regions are characterized by low soil fertility

and nutrient retention capacity [65]. Any activity that improves these qualities could assist in improving the quality of the soil. Lin et al. discovered that Cu^{2+} and Cd^{2+} were removed mainly via surface complexion, precipitation, and ion exchange. After biochar remediation, the CEC and SOM concentrations in the soil increased, which was beneficial for the immobilization of heavy metals in the soil [66]. In this study, biochar amendment effectively increased SOM content in the soils, resulting in a 1.41–5.97-fold rise in the biochar-treated soils compared to the results obtained from the control soil (Figure 2a). The high organic carbon content of biochar contributes directly to increased SOM [67]. It does this by promoting the activities of microorganisms and the decomposition of biological stumps in soils, which indirectly increases the amount of SOM [68].

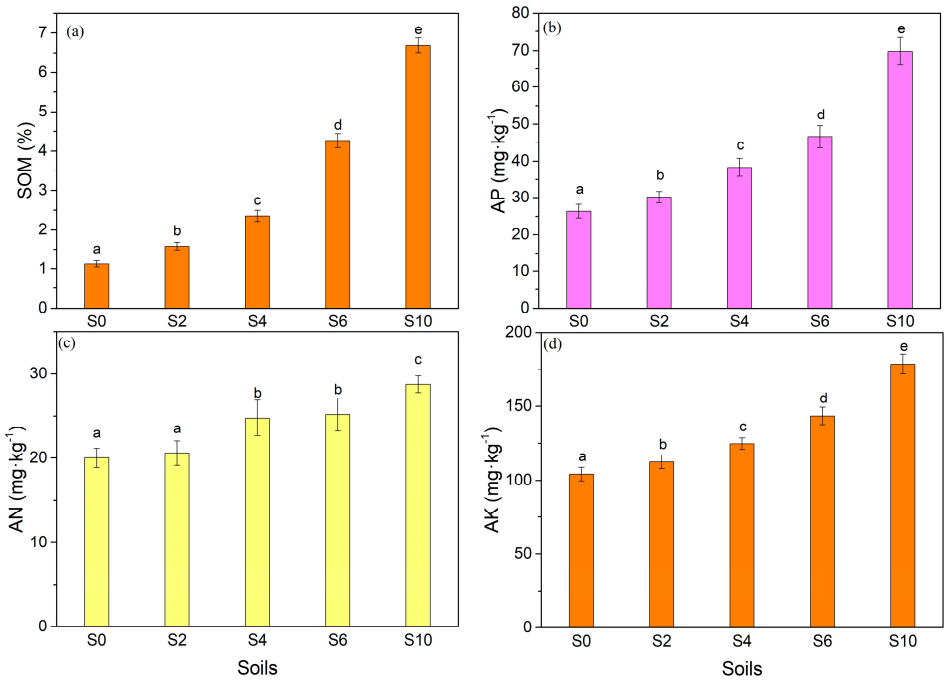

Figure 2. Effects of the biochar on soil fertility. (**a**) SOM; (**b**) AP; (**c**) AN; (**d**) AK. SOM: soil organic matter; AP: available phosphorus; AN: available nitrogen; AK: available potassium.

Moreover, compared to biochar obtained from plants, biochar derived from sewage sludge has more mineral elements, such as K, P, N, Ca, and Mg. It can potentially contribute nutrients that are more easily accessible for plant growth [28]. Using biochar also improves the availability of K and P due to the improved retention of nutrients in the soil [42,62]. Results demonstrated that compared to the control soil, soil AP, AN, and AK in the biochar-treated soils increased by 2.65, 1.44, and 1.72-fold, respectively, when biochar application rates increased from 2 to 10%. Based on these findings, it is evident that the incorporation of biochar formed from sewage sludge into semi-arid soil will result in an increase in soil fertility, which will be beneficial.

3.3. Enzyme Activities

The changes that occurred in the enzyme activity of the soil after amending it with biochar are depicted in Figure 3. Enzymes discovered in the soil, such as urease and catalase, are always utilized as bio-indicators to assess microorganisms' activities in the soil [69]. Due to its porous structure, high nutrient content, and high sorption capacity, biochar has the potential to positively impact the enzyme activities of soil after it has been applied to soils [70]. In this particular investigation, adding biochar increased the activities of urease and catalase in the soil. This finding suggests that biochar can promote microbial activities in semi-arid soil.

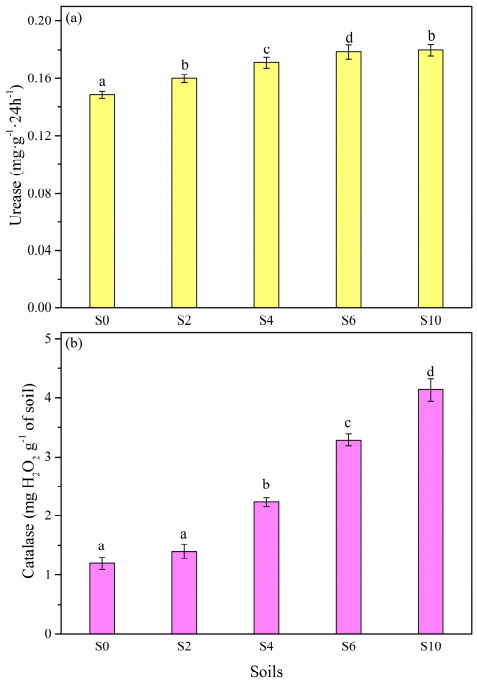

Figure 3. Effects of the biochar on soil enzyme activities. (**a**) Urease; (**b**) Catalase.

3.4. Immobilization of Heavy Metals

3.4.1. Total Contents and Bioavailability of the Metals

The total Cu and Cd content of the soils rose after biochar amendment (Figure 4a) due to the higher contents of Cu and Cd in the biochar than that in the selected soil (Table 1). Specifically, the total Cu and Cd content of the soils increased from 155.48 and 0.57 mg/kg to 175.30 and 0.97 mg/kg, respectively, when the application rate of biochar was increased from 0 to 10%. In contrast, DTPA-Cu and Cd declined with rising biochar application rates (Figure 4b). According to this evidence, the two metals' bioavailability decreased when biochar was added to the soil.

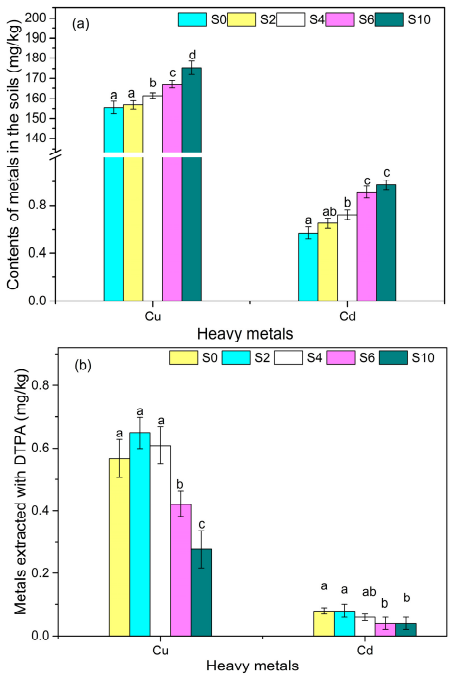

Figure 4. Heavy metals in the soil after amendment with the biochar. (**a**) Total contents of heavy metals; (**b**) metals extracted with DTPA. DTPA: diethylenetriaminepentaacetic acid.

3.4.2. Fractions of the Metals

Figure 5 shows the contents of Cu and Cd extracted by the modified BCR method in the biochar-treated soils. Metals in soils can be divided into four fractions: (1) Acid soluble fraction (F1), (2) reducible fraction (F2), (3) oxidizable fraction (F3), and (4) residual fraction (F4) [71,72]. Heavy metal mobility and bioavailability in soils are determined mainly by their chemical forms rather than their amounts, and the mobility and bioavailability decrease in the following sequence: F1 > F2 > F3 > F4 [73]. This research has discovered that the incorporation of biochar into soils results in a change in the chemical forms of Cu and Cd.

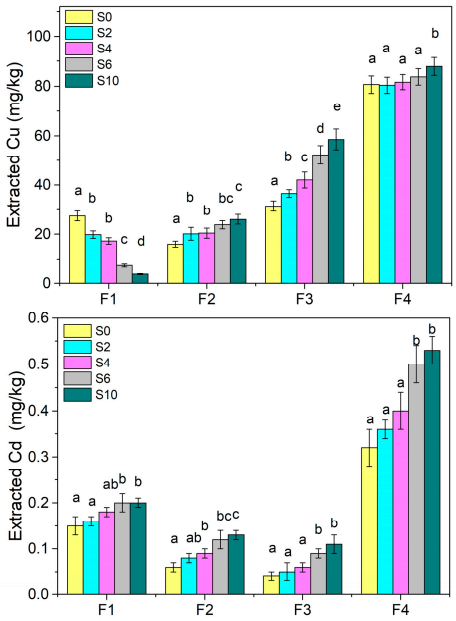

Figure 5. Contents of Cu and Cd in the soil extracted by modified BCR method. BCR: Bureau Communautaire de Référence.

Heavy metals in an acid-soluble fraction are mobile and easily absorbed by plants growing in soils [54]. As a result of this research, it was discovered that using biochar resulted in a reduction in acid-soluble Cu. Increasing the application rates of biochar from 0% to 10% decreased the amount of acid-soluble Cu found in soils, which went from 27.42 mg/kg to 3.76 mg/kg. A comparable pattern was observed in the amount of acid-soluble Cd found in soils. Based on the findings presented above, it was concluded that the biochar amendment decreased the mobility and bioavailability of the two metals within the soil.

In the meantime, the amount of Cu found in the reducible fraction increased from 15.97 to 26.06 mg/kg when the biochar application rate increased from 0% to 10%. Following the addition of biochar, there was an increase in the amount of reducible Cd in the soils. This was most likely caused by the adsorption of Cd in the soils by the ferromanganese oxides in the biochar [74]. Jiang et al. and Yue et al. observed that reducible Zn, Cu, Cd, Pb, and Cr increased after biochar amendment [59,75].

A substantial rise in the amount of Cu and Cd found in an oxidizable fraction was seen in this investigation after the addition of biochar. In particular, for Cu, the oxidizable Cu significantly increased from 31.44 to 58.54 mg/kg when the biochar application rate went from 0% to 10% because of the enhanced affinity of organic matter in the soil for Cu [76]. Metals as a residual fraction are stable and non-bioavailable in the environment [77]. Generally, Pb, Cr, Cu, Cd, and Zn are higher in the residual percentage of biochar made from sewage sludge than in soils [76]. Thus, the contents of residual Cu and Cd in the soils increased slightly following biochar amendment in this study.

3.4.3. Percentage of Four Fractions of Heavy Metals

Changes in the distributions of Cu and Cd fractions in the soils that were treated with biochar are depicted in Figure 6. The changes in the distributions of heavy metal fractions were used to assess the transformation of four different fractions in the soil after the addition of biochar [78]. In this study, biochar amendment transformed Cu from the acid-soluble fraction to the oxidizable fraction (Figure 6a), which dominated the immobilization process of Cu in biochar-treated soils. The percentage of oxidizable Cu significantly increased from 20.23 to 33.40% when biochar application rates increased from 0 to 10%, while that of acid-soluble Cu visibly decreased from 17.62 to 1.57%. Compared with Cd, Cu had a higher affinity for organic functional groups such as -COOH, phenolic -OH, and C=N on the biochar surface [76].

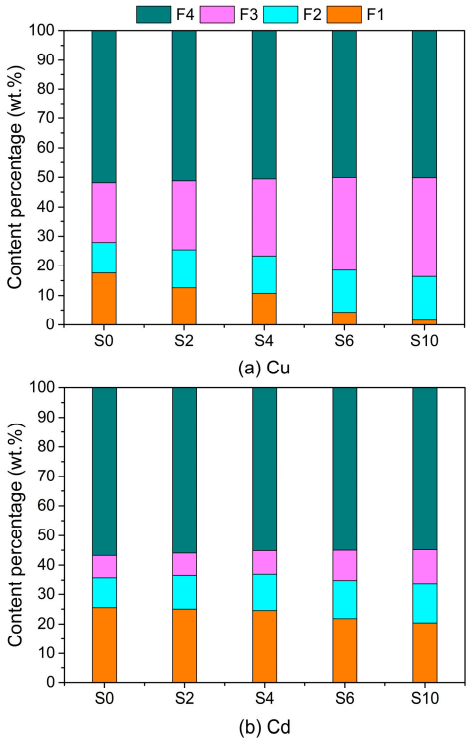

Figure 6. Chemical form distributions of Cu and Cd in the soil after amendment with the biochar.

Complexes formed between Cu and organic functional groups have been found to have higher stability constants than those formed between Cd and organic functional groups, according to research that was conducted in the past [79]. The organic functional biochar groups formed a complex with Cu and immobilized it while this experiment was conducted [75]. Several modification methods such as chemical treatment, steaming, gaseous activation, natural aging, and ball milling can improve biochar. Compared to pristine biochar, applying freeze–thaw and dry–wet processes to biochar for aging considerably increased its surface area, pure volume, and oxygen functional groups [80]. The porosity structure of biochar, together with its capacity to take in soluble organic carbon, makes it an ideal home and food supply for the bacteria that live in the soil. Consequently, the fact that this occurs leads to an increase in the quantity of organic matter as well as an improvement in the activity of soil microorganisms, which in turn leads to an increase in the soil's capacity to immobilize copper [81]. When it comes to immobilizing copper in soils, complexation is the major mechanism that biochar provides [59].

In the meantime, the incorporation of biochar made it possible to transform Cd from the mobile fraction, which is the soluble acid fraction, to comparatively stable fractions, which are the reducible and oxidizable fractions. Park et al. reported a similar observation, wherein the biochar amendment decreased the amount of acid-soluble Cd but increased

oxidizable and reducible Cd in the soil [76]. The specific adsorption of ferromanganese oxides in biochar is probably responsible for the increase in reducible Cd found in the soil [73]. Biochar amendment increased soil organic matter and consequently increased the Cd combined with organic functional groups [82]. In contrast, following the increase in soil organic matter, the reducing conditions created by the decomposition of organic matter appear to have accelerated the formation of Cd precipitation in the soils [83], contributing to the increase in oxidizable Cd in the biochar-treated soils. Meng et al. observed that the treatment of Cd and Cu-contaminated soils with biochar should focus on the coexistence types and concentration ranges of heavy metals, which can significantly affect the remediation effects of biochar. For Cd, nonmineral mechanisms preferentially adsorbed and immobilized heavy metals over mineral mechanisms, but the adsorption capacities attributed to mineral mechanisms were larger than those attributed to nonmineral mechanisms; for Cu, nonmineral mechanisms always dominated and gradually increased with increasing concentrations [84].

4. Conclusions

Utilizing waste sewage sludge to prepare biochar is a current research hotspot, "use waste to cure waste, turn waste into treasure", which can comprehensively exploit resources. This research is the first to use biochar extracted from sewage sludge to remediate Cu and Cd co-contaminated soils in semi-arid areas. Compared to previous research on biochar remediation for single heavy metals in soil, multi-metal co-pollution remediation efficiency was greatly enhanced. The findings show that applying biochar derived from sewage sludge in semi-arid areas improves soil water holding capacity, increases available P, N, K, and soil organic matter contents, and enhances soil microbial activity. Although the addition of biochar did not result in a significant increase in soil pH, decreasing DTPA-Cu and Cd levels and metal bioavailability in the soil as the amount of biochar added increased. The content of DTPA-Cu and Cd decreased by −0.128–0.291 mg/kg, 0–0.037 mg/kg, with the increase in biochar application, and the content of acid-soluble Cu in the soil decreased from 27.42 mg/kg to 3.76 mg/kg, the mobility and bioavailability of these two metals in the soil decreased. Moreover, Cu and Cd were efficiently immobilized in the soil by facilitating their change from mobile acid-soluble fractions to relatively stable fractions (reducible and oxidizable fractions). To summarize, preparing biochar is a promising approach for sludge reuse, which can minimize the volume of sludge, as well as remediate heavy metal-contaminated soils to promote the sustainable development of agriculture in semi-arid areas.

Author Contributions: Conceptualization, Z.W. and N.W.; methodology, Z.W. and Y.Z.; data curation, F.Y. and D.H.; writing—original draft, Z.W. and S.L.; investigation, J.Z. and D.L.; software, Y.Z. and X.Y.; writing—review and editing, Z.W. and Y.Z.; project administration, S.B. and Y.T. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Natural Science Foundation of Xinjiang Uygur Autonomous Region (No. 2021D01F37), the Sichuan Science and Technology Program (24QYCX0252), and the Karamay Innovative Environment Construction Plan Project (2024hjcxrc0110).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The datasets are available from the corresponding author upon reasonable request.

Acknowledgments: The authors are grateful for the reviewers' valuable comments.

Conflicts of Interest: Author Fei Yang was employed by the company Karamay Shuangxin Environmental Technology Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Zhang, Y.; Qin, J.; Yi, Y. Biochar and hydrochar derived from freshwater sludge: Characterization and possible applications. *Sci. Total Environ.* **2021**, *763*, 144550. [CrossRef] [PubMed]
2. Ghorbani, M.; Konvalina, P.; Walkiewicz, A.; Neugschwandtner, R.W.; Kopecky, M.; Zamanian, K.; Chen, W.H.; Bucur, D. Feasibility of Biochar Derived from Sewage Sludge to Promote Sustainable Agriculture and Mitigate GHG Emissions—A Review. *Int. J. Environ. Res. Public Health* **2022**, *19*, 12983. [CrossRef] [PubMed]
3. Wang, Y.; Zhang, Z.; Wang, X.; Guo, H.; Zhu, T.; Zhao, Y.; Lu, X.; Zhang, Y.; Ni, B.-J.; Liu, Y. Medium-chain fatty acids production from sewage sludge through anaerobic fermentation: A critical review. *Chem. Eng. J.* **2023**, *477*, 147138. [CrossRef]
4. Zhen, K.; Zhu, Q.; Zhai, S.; Gao, Y.; Cao, H.; Tang, X.; Wang, C.; Li, J.; Tian, L.; Sun, H. PPCPs and heavy metals from hydrothermal sewage sludge-derived biochar: Migration in wheat and physiological response. *Environ. Sci. Pollut. Res. Int.* **2022**, *29*, 83234–83246. [CrossRef] [PubMed]
5. Xiang, T.; Shi, C.; Guo, Y.; Zhang, J.; Min, W.; Sun, J.; Liu, J.; Yan, X.; Liu, Y.; Yao, L.; et al. Effect-directed analysis of androgenic compounds from sewage sludges in China. *Water Res.* **2024**, *256*, 121652. [CrossRef]
6. Yang, Y.Q.; Cui, M.H.; Guo, J.C.; Du, J.J.; Zheng, Z.Y.; Liu, H. Effects of co-pyrolysis of rice husk and sewage sludge on the bioavailability and environmental risks of Pb and Cd. *Environ. Technol.* **2021**, *42*, 2304–2312. [CrossRef] [PubMed]
7. Li, X.; Chen, Y.; Tan, W.; Chen, P.; Yang, H.; Chen, H. Prediction of char yield and nitrogen fixation rate from pyrolysis of sewage sludge based on machine learning. *J. Anal. Appl. Pyrolysis* **2023**, *171*, 105948.
8. Yang, G.; Hu, Y.; Chen, D.; Zhou, N.; Jiao, L.; Guo, Q. Quantification of the formed environmentally persistent free radicals (EPFRs) in the pyrolyzed sewage sludges from municipal and industrial wastewater treatment. *J. Anal. Appl. Pyrolysis* **2024**, *177*, 106371. [CrossRef]
9. Yin, X.; Xi, M.; Li, Y.; Kong, F.; Jiang, Z. Improvements in physicochemical and nutrient properties of sewage sludge biochar by the co-pyrolysis with organic additives. *Sci. Total Environ.* **2021**, *779*, 146565. [CrossRef]
10. Łapiński, D.; Wiater, J.; Szatyłowicz, E. The Content of Heavy Metals in Waste as an Indicator Determining the Possibilities of their Agricultural Use. *J. Ecol. Eng.* **2019**, *20*, 225–230. [CrossRef]
11. Domingues, R.R.; Trugilho, P.F.; Silva, C.A.; Melo, I.; Melo, L.C.A.; Magriotis, Z.M.; Sanchez-Monedero, M.A. Properties of biochar derived from wood and high-nutrient biomasses with the aim of agronomic and environmental benefits. *PLoS ONE* **2017**, *12*, e0176884. [CrossRef] [PubMed]
12. Da Silva Mendes, J.; Fernandes, J.D.; Chaves, L.H.G.; Guerra, H.O.C.; Tito, G.A.; de Brito Chaves, I. Chemical and Physical Changes of Soil Amended with Biochar. *Water Air Soil Pollut.* **2021**, *232*, 338. [CrossRef]
13. Yang, X.; Lu, K.; McGrouther, K.; Che, L.; Hu, G.; Wang, Q.; Liu, X.; Shen, L.; Huang, H.; Ye, Z.; et al. Bioavailability of Cd and Zn in soils treated with biochars derived from tobacco stalk and dead pigs. *J. Soils Sediments* **2015**, *17*, 751–762. [CrossRef]
14. Kopittke, P.M.; Asher, C.J.; Menzies, N.W. Prediction of Pb speciation in concentrated and dilute nutrient solutions. *Environ. Pollut.* **2008**, *153*, 548–554. [CrossRef] [PubMed]
15. Cao, X.; Ma, L.; Liang, Y.; Gao, B.; Harris, W. Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. *Environ. Sci. Technol.* **2011**, *45*, 4884–4889. [CrossRef] [PubMed]
16. Odinga, E.S.; Waigi, M.G.; Gudda, F.O.; Wang, J.; Yang, B.; Hu, X.; Li, S.; Gao, Y. Occurrence, formation, environmental fate and risks of environmentally persistent free radicals in biochars. *Environ. Int.* **2020**, *134*, 105172. [CrossRef]
17. Gao, J.; Zhao, T.; Tsang, D.C.W.; Zhao, N.; Wei, H.; Feng, M.; Liu, K.; Zhang, W.; Qiu, R. Effects of Zn in sludge-derived biochar on Cd immobilization and biological uptake by lettuce. *Sci. Total Environ.* **2020**, *714*, 136721. [CrossRef] [PubMed]
18. Zhang, G.; Zhao, Z.; Zhu, Y. Changes in abiotic dissipation rates and bound fractions of antibiotics in biochar-amended soil. *J. Clean. Prod.* **2020**, *256*, 120314. [CrossRef]
19. Rinklebe, J.; Shaheen, S.M.; El-Naggar, A.; Wang, H.; Du Laing, G.; Alessi, D.S.; Sik Ok, Y. Redox-induced mobilization of Ag, Sb, Sn, and Tl in the dissolved, colloidal and solid phase of a biochar-treated and un-treated mining soil. *Environ. Int.* **2020**, *140*, 105754. [CrossRef]
20. Zeeshan, M.; Ahmad, W.; Hussain, F.; Ahamd, W.; Numan, M.; Shah, M.; Ahmad, I. Phytostabalization of the heavy metals in the soil with biochar applications, the impact on chlorophyll, carotene, soil fertility and tomato crop yield. *J. Clean. Prod.* **2020**, *255*, 120318. [CrossRef]
21. Hou, R.; Li, T.; Fu, Q.; Liu, D.; Li, M.; Zhou, Z.; Li, Q.; Zhao, H.; Yu, P.; Yan, J. The effect on soil nitrogen mineralization resulting from biochar and straw regulation in seasonally frozen agricultural ecosystem. *J. Clean. Prod.* **2020**, *255*, 120302. [CrossRef]
22. Long, X.X.; Yu, Z.N.; Liu, S.W.; Gao, T.; Qiu, R.L. A systematic review of biochar aging and the potential eco-environmental risk in heavy metal contaminated soil. *J. Hazard. Mater.* **2024**, *472*, 134345. [CrossRef] [PubMed]
23. Wu, P.; Wang, Z.; Wang, H.; Bolan, N.S.; Wang, Y.; Chen, W. Visualizing the emerging trends of biochar research and applications in 2019: A scientometric analysis and review. *Biochar* **2020**, *2*, 135–150. [CrossRef]
24. Pathy, A.; Ray, J.; Paramasivan, B. Biochar amendments and its impact on soil biota for sustainable agriculture. *Biochar* **2020**, *2*, 287–305. [CrossRef]
25. Zhang, L.; Xiang, Y.; Jing, Y.; Zhang, R. Biochar amendment effects on the activities of soil carbon, nitrogen, and phosphorus hydrolytic enzymes: A meta-analysis. *Environ. Sci. Pollut. Res. Int.* **2019**, *26*, 22990–23001. [CrossRef] [PubMed]
26. Yuan, J.H.; Xu, R.K.; Zhang, H. The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresour. Technol.* **2011**, *102*, 3488–3497. [CrossRef] [PubMed]

27. Birer, A.M.; Gozmen, B.; Sonmez, O.; Kalderis, D. Evaluation of sewage sludge biochar and modified derivatives as novel SPE adsorbents for monitoring of bisphenol A. *Chemosphere* **2021**, *268*, 128866. [CrossRef] [PubMed]
28. Hazrati, S.; Farahbakhsh, M.; Cerda, A.; Heydarpoor, G. Functionalization of ultrasound enhanced sewage sludge-derived biochar: Physicochemical improvement and its effects on soil enzyme activities and heavy metals availability. *Chemosphere* **2021**, *269*, 128767. [CrossRef]
29. Shao, H.; Wei, Y.; Zhang, F.; Li, F. Effects of Biochars Produced from Coconut Shell and Sewage Sludge on Reducing the Uptake of Cesium by Plant from Contaminated Soil. *Water Air Soil Pollut.* **2020**, *231*, 550. [CrossRef]
30. Wu, Y.; Yang, J.; Tang, J.; Kerr, P.; Wong, P.K. The remediation of extremely acidic and moderate pH soil leachates containing Cu (II) and Cd (II) by native periphytic biofilm. *J. Clean. Prod.* **2017**, *162*, 846–855. [CrossRef]
31. Chen, G.; Ma, Y.; Xu, W.; Chen, Z.; Li, Z.; Zhou, J.; Yu, W. Remediation of cadmium-contaminated soil by micro-nano nitrogen-doped biochar and its mechanisms. *Environ. Sci. Pollut. Res. Int.* **2023**, *30*, 48078–48087. [CrossRef] [PubMed]
32. Ahmad, Z.; Gao, B.; Mosa, A.; Yu, H.; Yin, X.; Bashir, A.; Ghoveisi, H.; Wang, S. Removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solutions by biochars derived from potassium-rich biomass. *J. Clean. Prod.* **2018**, *180*, 437–449. [CrossRef]
33. Gao, R.; Hu, H.; Fu, Q.; Li, Z.; Xing, Z.; Ali, U.; Zhu, J.; Liu, Y. Remediation of Pb, Cd, and Cu contaminated soil by co-pyrolysis biochar derived from rape straw and orthophosphate: Speciation transformation, risk evaluation and mechanism inquiry. *Sci. Total Environ.* **2020**, *730*, 139119. [CrossRef] [PubMed]
34. Qiu, M.; Liu, L.; Ling, Q.; Cai, Y.; Yu, S.; Wang, S.; Fu, D.; Hu, B.; Wang, X. Biochar for the removal of contaminants from soil and water: A review. *Biochar* **2022**, *4*, 19. [CrossRef]
35. Bogusz, A.; Oleszczuk, P. Sequential extraction of nickel and zinc in sewage sludge- or biochar/sewage sludge-amended soil. *Sci. Total Environ.* **2018**, *636*, 927–935. [CrossRef] [PubMed]
36. Liu, L.; Liu, X.; Wang, D.; Lin, H.; Huang, L. Removal and reduction of Cr(VI) in simulated wastewater using magnetic biochar prepared by co-pyrolysis of nano-zero-valent iron and sewage sludge. *J. Clean. Prod.* **2020**, *257*, 120562. [CrossRef]
37. Rodriguez-Franco, C.; Page-Dumroese, D.S. Woody biochar potential for abandoned mine land restoration in the U.S.: A review. *Biochar* **2021**, *3*, 7–22. [CrossRef]
38. Kneller, T.; Harris, R.J.; Bateman, A.; Munoz-Rojas, M. Native-plant amendments and topsoil addition enhance soil function in post-mining arid grasslands. *Sci. Total Environ.* **2018**, *621*, 744–752. [CrossRef]
39. Syed, A.; Sarwar, G.; Shah, S.H.; Muhammad, S. Soil Salinity Research in 21st Century in Pakistan: Its Impact on Availability of Plant Nutrients, Growth and Yield of Crops. *Commun. Soil Sci. Plant Anal.* **2020**, *52*, 183–200. [CrossRef]
40. Feng, W.; Gao, J.; Cen, R.; Yang, F.; He, Z.; Wu, J.; Miao, Q.; Liao, H. Effects of Polyacrylamide-Based Super Absorbent Polymer and Corn Straw Biochar on the Arid and Semi-Arid Salinized Soil. *Agriculture* **2020**, *10*, 519. [CrossRef]
41. Mukherjee, I.; Singh, U.K.; Singh, R.P.; Anshumali; Kumari, D.; Jha, P.K.; Mehta, P. Characterization of heavy metal pollution in an anthropogenically and geologically influenced semi-arid region of east India and assessment of ecological and human health risks. *Sci. Total Environ.* **2020**, *705*, 135801. [CrossRef] [PubMed]
42. Sun, Y.; Liu, C.; Gao, Y.; Zhang, T.; Jia, Y.; Wang, S. All-in-one strategy to prepare molded biochar with magnetism from sewage sludge for high-efficiency removal of Cd(II). *J. Hazard. Mater.* **2023**, *454*, 131488. [CrossRef] [PubMed]
43. Zhao, S.; Li, Q.; Tang, Z.; Yang, Y.; Wu, J.; Gao, P.; Qian, Y.; Chen, J.; Xue, G. Simultaneous removal of Cr, Cu, Zn, and Cd by nano zero-valent iron modified sludge biochar in high salinity wastewater. *Sep. Purif. Technol.* **2024**, *347*, 127560. [CrossRef]
44. Wang, Z.; Shu, X.; Zhu, H.; Xie, L.; Cheng, S.; Zhang, Y. Characteristics of biochars prepared by co-pyrolysis of sewage sludge and cotton stalk intended for use as soil amendments. *Environ. Technol.* **2020**, *41*, 1347–1357. [CrossRef]
45. Bouyoucos, G.J. Hydrometer Method Improved for Making Particle Size Analyses of Soils. *Agron. J.* **1962**, *54*, 464–465. [CrossRef]
46. *NY/T 1121.5-2006*; Soil Testing—Part 5: Method for Determination of Soil Cation Exchange Capacity in Calcareous Soil. Ministry of Agriculture: Beijing, China, 2006.
47. *NY/T 1121.6-2006*; Soil Testing—Part 6: Method for Determination of Soil Organic Matter. Ministry of Agriculture: Beijing, China, 2006.
48. *LY/T 1228-2015*; Nitrogen Determination Methods of Forest Soils. State Forestry Administration: Beijing, China, 2015.
49. *NY/T 1121.7-2014*; Soil Testing—Part 7: Method for Determination of Available Phosphorus in Soil. Ministry of Agriculture: Beijing, China, 2014.
50. *NY/T 889-2004*; Determination of Exchangeable Potassium and Non-Exchangeable Potassium Content in Soil. Ministry of Agriculture: Beijing, China, 2004.
51. *NY/T 1121.22-2010*; Soil Testing—Part 22: Cutting Ring Method for Determination of Field Water—Holding Capacity in Soil. Ministry of Agriculture: Beijing, China, 2014.
52. Tu, C.; Wei, J.; Guan, F.; Liu, Y.; Sun, Y.; Luo, Y. Biochar and bacteria inoculated biochar enhanced Cd and Cu immobilization and enzymatic activity in a polluted soil. *Environ. Int.* **2020**, *137*, 105576. [CrossRef]
53. Hossain, M.K.; Strezov, V.; Chan, K.Y.; Nelson, P.F. Agronomic properties of wastewater sludge biochar and bioavailability of metals in production of cherry tomato (*Lycopersicon esculentum*). *Chemosphere* **2010**, *78*, 1167–1171. [CrossRef] [PubMed]
54. Rauret, G.; López-Sánchez, J.F.; Sahuquillo, A.; Rubio, R.; Davidson, C.; Ure, A.; Quevauviller, P. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monit.* **1998**, *1*, 57–61. [CrossRef]

55. Lindsay, W.; Sabey, B. Solubility and plant uptake of cadmium in soils amended with cadmium and sewage sludge. *Environ. Qual.* **1977**, *6*, 72–77.
56. Wang, Y.; Liu, Y.; Liu, R.; Zhang, A.; Yang, S.; Liu, H.; Zhou, Y.; Yang, Z. Biochar amendment reduces paddy soil nitrogen leaching but increases net global warming potential in Ningxia irrigation, China. *Sci. Rep.* **2017**, *7*, 1592. [CrossRef]
57. Liu, Z.; Dugan, B.; Masiello, C.A.; Gonnermann, H.M. Biochar particle size, shape, and porosity act together to influence soil water properties. *PLoS ONE* **2017**, *12*, e0179079. [CrossRef] [PubMed]
58. Laghari, M.; Mirjat, M.S.; Hu, Z.; Fazal, S.; Xiao, B.; Hu, M.; Chen, Z.; Guo, D. Effects of biochar application rate on sandy desert soil properties and sorghum growth. *Catena* **2015**, *135*, 313–320. [CrossRef]
59. Yue, Y.; Cui, L.; Lin, Q.; Li, G.; Zhao, X. Efficiency of sewage sludge biochar in improving urban soil properties and promoting grass growth. *Chemosphere* **2017**, *173*, 551–556. [CrossRef] [PubMed]
60. Chen, X.; Jiang, S.; Wu, J.; Yi, X.; Dai, G.; Shu, Y. Three-year field experiments revealed the immobilization effect of natural aging biochar on typical heavy metals (Pb, Cu, Cd). *Sci. Total Environ.* **2024**, *912*, 169384. [CrossRef] [PubMed]
61. Purakayastha, T.J.; Bera, T.; Bhaduri, D.; Sarkar, B.; Mandal, S.; Wade, P.; Kumari, S.; Biswas, S.; Menon, M.; Pathak, H.; et al. A review on biochar modulated soil condition improvements and nutrient dynamics concerning crop yields: Pathways to climate change mitigation and global food security. *Chemosphere* **2019**, *227*, 345–365. [CrossRef]
62. Arif, M.; Ilyas, M.; Riaz, M.; Ali, K.; Shah, K.; Ul Haq, I.; Fahad, S. Biochar improves phosphorus use efficiency of organic-inorganic fertilizers, maize-wheat productivity and soil quality in a low fertility alkaline soil. *Field Crops Res.* **2017**, *214*, 25–37. [CrossRef]
63. Lehmann, J.; Rillig, M.C.; Thies, J.; Masiello, C.A.; Hockaday, W.C.; Crowley, D. Biochar effects on soil biota—A review. *Soil Biol. Biochem.* **2011**, *43*, 1812–1836. [CrossRef]
64. Mendez, A.; Gomez, A.; Paz-Ferreiro, J.; Gasco, G. Effects of sewage sludge biochar on plant metal availability after application to a Mediterranean soil. *Chemosphere* **2012**, *89*, 1354–1359. [CrossRef] [PubMed]
65. Xu, S.; Pan, D.; Hu, F.; Wu, Y.; Wang, H.; Chen, Y.; Yuan, H.; Gao, L.; Xiao, G. Highly efficient Cr/β zeolite catalyst for conversion of carbohydrates into 5-hydroxymethylfurfural: Characterization and performance. *Fuel Process. Technol.* **2019**, *190*, 38–46. [CrossRef]
66. Lin, P.; Liu, H.; Yin, H.; Zhu, M.; Luo, H.; Dang, Z. Remediation performance and mechanisms of Cu and Cd contaminated water and soil using Mn/Al-layered double oxide-loaded biochar. *J. Environ. Sci.* **2023**, *125*, 593–602. [CrossRef]
67. Sarma, B.; Farooq, M.; Gogoi, N.; Borkotoki, B.; Kataki, R.; Garg, A. Soil organic carbon dynamics in wheat—Green gram crop rotation amended with vermicompost and biochar in combination with inorganic fertilizers: A comparative study. *J. Clean. Prod.* **2018**, *201*, 471–480. [CrossRef]
68. Bordoloi, S.; Gopal, P.; Boddu, R.; Wang, Q.; Cheng, Y.-F.; Garg, A.; Sreedeep, S. Soil-biochar-water interactions: Role of biochar from Eichhornia crassipes in influencing crack propagation and suction in unsaturated soils. *J. Clean. Prod.* **2019**, *210*, 847–859. [CrossRef]
69. Hu, X.-F.; Jiang, Y.; Shu, Y.; Hu, X.; Liu, L.; Luo, F. Effects of mining wastewater discharges on heavy metal pollution and soil enzyme activity of the paddy fields. *J. Geochem. Explor.* **2014**, *147*, 139–150. [CrossRef]
70. Diatta, A.A.; Fike, J.H.; Battaglia, M.L.; Galbraith, J.M.; Baig, M.B. Effects of biochar on soil fertility and crop productivity in arid regions: A review. *Arab. J. Geosci.* **2020**, *13*, 595. [CrossRef]
71. Saracoglu, S.; Soylak, M.; Eli, L. Extractable Trace Metals Content of Dust from Vehicle Air Filters as Determined by Sequential Extraction and Flame Atomic Absorption Spectrometry. *J. AOAC Int.* **2009**, *92*, 1196–1202. [CrossRef] [PubMed]
72. Wang, Z.; Wang, J.; Xie, L.; Zhu, H.; Shu, X. Influence of the Addition of Cotton Stalk during Co-pyrolysis with Sewage Sludge on the Properties, Surface Characteristics, and Ecological Risks of Biochars. *J. Therm. Sci.* **2019**, *28*, 755–762. [CrossRef]
73. Liu, S.; Liu, J.; Zhao, J.; Xia, D.; Pan, F.; Liu, C.; Kyzas, G.Z.; Fu, J. Palygorskite changes heavy metal bioavailability and microbial functional diversity in sewage sludge composting. *Environ. Technol.* **2015**, *36*, 2855–2862. [CrossRef] [PubMed]
74. Lu, K.; Yang, X.; Gielen, G.; Bolan, N.; Ok, Y.S.; Niazi, N.K.; Xu, S.; Yuan, G.; Chen, X.; Zhang, X.; et al. Effect of bamboo and rice straw biochars on the mobility and redistribution of heavy metals (Cd, Cu, Pb and Zn) in contaminated soil. *J. Environ. Manag.* **2017**, *186 Pt 2*, 285–292. [CrossRef] [PubMed]
75. Jiang, J.; Xu, R.K.; Jiang, T.Y.; Li, Z. Immobilization of Cu(II), Pb(II) and Cd(II) by the addition of rice straw derived biochar to a simulated polluted Ultisol. *J. Hazard. Mater.* **2012**, *229–230*, 145–150. [CrossRef] [PubMed]
76. Park, J.H.; Choppala, G.K.; Bolan, N.S.; Chung, J.W.; Chuasavathi, T. Biochar reduces the bioavailability and phytotoxicity of heavy metals. *Plant Soil* **2011**, *348*, 439–451. [CrossRef]
77. Jin, J.; Wang, M.; Cao, Y.; Wu, S.; Liang, P.; Li, Y.; Zhang, J.; Zhang, J.; Wong, M.H.; Shan, S.; et al. Cumulative effects of bamboo sawdust addition on pyrolysis of sewage sludge: Biochar properties and environmental risk from metals. *Bioresour. Technol.* **2017**, *228*, 218–226. [CrossRef]
78. Cui, L.; Pan, G.; Li, L.; Bian, R.; Liu, X.; Yan, J.; Quan, G.; Ding, C.; Chen, T.; Liu, Y.; et al. Continuous immobilization of cadmium and lead in biochar amended contaminated paddy soil: A five-year field experiment. *Ecol. Eng.* **2016**, *93*, 1–8. [CrossRef]
79. Pandey, A.K.; Pandey, S.D.; Misra, V. Stability constants of metal-humic acid complexes and its role in environmental detoxification. *Ecotoxicol. Environ. Saf.* **2000**, *47*, 195–200. [CrossRef] [PubMed]
80. Ghorbani, M.; Konvalina, P.; Neugschwandtner, R.W.; Soja, G.; Bárta, J.; Chen, W.-H.; Amirahmadi, E. How do different feedstocks and pyrolysis conditions effectively change biochar modification scenarios? A critical analysis of engineered biochars under H_2O_2 oxidation. *Energy Convers. Manag.* **2024**, *300*, 117924. [CrossRef]

81. Beesley, L.; Moreno-Jiménez, E.; Gomez-Eyles, J.L.; Harris, E.; Robinson, B.; Sizmur, T. A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. *Environ. Pollut.* **2011**, *159*, 3269–3282. [CrossRef]
82. Zhu, X.; Chen, B.; Zhu, L.; Xing, B. Effects and mechanisms of biochar-microbe interactions in soil improvement and pollution remediation: A review. *Environ. Pollut.* **2017**, *227*, 98–115. [CrossRef] [PubMed]
83. Covelo, E.F.; Vega, F.A.; Andrade, M.L. Competitive sorption and desorption of heavy metals by individual soil components. *J. Hazard. Mater.* **2007**, *140*, 308–315. [CrossRef] [PubMed]
84. Meng, Z.; Huang, S.; Wu, J.; Lin, Z. Competitive adsorption and immobilization of Cd, Ni, and Cu by biochar in unsaturated soils under single-, binary-, and ternary-metal systems. *J. Hazard. Mater.* **2023**, *451*, 131106. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.