agriculture

MDPI

Article

Effects of Ageing on Surface Properties of Biochar and Bioavailability of Heavy Metals in Soil

Zhengwu Cui [1], Yang Wang [1,*], Nan Wang [1,2], Fangfang Ma [1] and Yuyu Yuan [1,2]

[1] Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, Changchun 130102, China; cuizhengwu@iga.ac.cn (Z.C.); wangnan@iga.ac.cn (N.W.); mafangfang0101@126.com (F.M.); yuanyuyu@iga.ac.cn (Y.Y.)
[2] University of Chinese Academy of Sciences, Beijing 100049, China
* Correspondence: wangyangw@iga.ac.cn

Abstract: This study aims to explore the effects of biochar ageing on its surface properties and the bioavailability of heavy metals in soil. The biochar was subjected to chemical oxidation/dry–wet cycles (CDWs), chemical oxidation/freeze–thaw cycles (CFTs), and natural ageing (NT) to analyze changes in the elemental composition, pH, specific surface area, pore volume, and surface functional groups. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were applied to characterize the functional groups and microstructure, and the BCR sequential extraction method was employed to demonstrate the fractionation distribution of Cu, Cd, and Pb. The results showed that the CDWs and CFTs treatments significantly reduced the carbon content of the biochar (with a maximum reduction to 47.70%), increased the oxygen content (up to 49.17%), and notably increased the specific surface area and pore volume. The pH decreased significantly from 9.91 to 4.92 and 4.99 for the CDWs and the CFTs, respectively. The FTIR analysis indicated notable changes in hydroxyl and carboxyl functional groups, and the SEM revealed severe microstructural damage in biochar after the CDWs and CFTs treatments. The heavy metal fractionation analysis indicated that exchangeable Cu, Cd, and Pb significantly increased after the CDWs treatment, reaching 31.40%, 5.25%, and 6.79%, respectively. In conclusion, biochar ageing significantly affects its physicochemical properties and increases the bioavailability of heavy metals, raising concerns about its long-term remediation effectiveness.

Keywords: biochar; ageing; surface properties; heavy metals; bioavailability

Citation: Cui, Z.; Wang, Y.; Wang, N.; Ma, F.; Yuan, Y. Effects of Ageing on Surface Properties of Biochar and Bioavailability of Heavy Metals in Soil. *Agriculture* **2024**, *14*, 1631. https://doi.org/10.3390/agriculture14091631

Academic Editor: Nguyen V. Hue

Received: 20 August 2024
Revised: 14 September 2024
Accepted: 15 September 2024
Published: 18 September 2024

1. Introduction

Biochar, a carbon-rich material produced through the anaerobic or partially anaerobic pyrolysis of organic sources, has gained recognition in agriculture and environmental sciences as a promising solution to multiple environmental challenges [1,2]. It exhibits a broad pH range (5.9–12.3), a high cation exchange capacity, a specific surface area, and a well-defined micro-pore structure [3]. Biochar is rich in functional groups and nutrients like nitrogen, phosphorus, silicon, iron, and magnesium [4]. These properties make biochar an attractive soil amendment, as its application has been shown to improve various soil properties by reducing bulk density, enhancing structure, mitigating acidity, minimizing nutrient loss, and boosting soil fertility, crop yield, and microbial activity [5]. Additionally, biochar plays a crucial role in environmental remediation by immobilizing metal ions and other contaminants, thus helping in pollution control [6]. Biochar has been selected as the main technology for the removal of heavy metals from soils due to its porous structure and its high selectivity for metal adsorption by functional groups on its surface [7]. The sensitivity of biochar to environmental factors such as pH enhances its adsorption efficiency, making it an effective solution [8]. Furthermore, biochar offers a cost-effective solution, especially when produced from abundant agricultural residues, making it economically

viable for large-scale applications [9]. Its contribution to the ecological balance in soils makes it an important tool for sustainable agriculture and pollution remediation efforts. The novelty of biochar lies in its potential to offer a multifunctional approach to soil enhancement, pollutant immobilization, and carbon sequestration, contributing to climate change mitigation efforts [10]. The versatility of biochar applications stems from its ability to function under different soil conditions, making it a widely applicable solution across various soil types and climates [11]. Despite these benefits, researchers have raised concerns about the long-term stability of biochar in soil. Physical and chemical properties of biochar may not remain stable [12,13] due to factors like soil moisture, temperature, organic matter, and microorganisms, which can alter its surface characteristics and potentially impact its effectiveness during soil amendments. This evolving phenomenon of biochar properties over time is known as "biochar ageing" [13–15]. Over time, ageing processes alter biochar's surface characteristics, potentially diminishing its capacity for pollutant adsorption, carbon sequestration, and nutrient retention [16,17]. This raises important questions about the long-term efficacy and sustainability of biochar use in soil.

Currently, systematic research on the formation of aged biochar and its effects on pollutant behavior is limited. Most studies have employed artificial simulation methods to investigate the impacts of ageing on biochar's surface properties. These simulations accelerate ageing by exposing biochar to various conditions, revealing changes in its physical and chemical properties [18–20]. Various artificial ageing techniques, such as physical, chemical, and microbial ageing, have been developed for short-term laboratory simulations to explore the biochar ageing processes [21]. Chemical ageing involves exposing biochar to oxidizing agents like H_2O_2, H_2SO_4, HNO_3, and other oxidizing mixtures in a controlled environment [22]. Physical ageing methods, like freeze–thaw cycles and dry–wet alternations, are commonly used to manipulate temperature and humidity conditions to simulate ageing [23]. Microbial ageing involves mixing biochar with microbial cultures and cultivating the mixture under specific conditions. These artificial ageing methods offer valuable insights into the transformations of biochar properties, enhancing our understanding of its stability and behavior in natural environments. During ageing, biochar undergoes significant changes in its surface and structural properties, with soil particles clogging the fine pores of the biochar and reducing the specific surface area [24]. Furthermore, prolonged ageing decreases the carbon content, increases the oxygen content, and forms oxygen-containing functional groups [14]. Additionally, ageing also releases various organic compounds that enhance the surface charge. In general, changes in surface properties can affect biochar's capability in adsorption, carbon sequestration, and heavy metal immobilization, which are critical for optimizing its application in various environmental issues [13,21].

At present, research on biochar ageing is concentrated on the pre-application ageing of biochar, which involves modifying the material prior to its addition to contaminated soil. By comparing the surface structure and chemical composition of biochar before and after ageing, the differences in the pollutant adsorption capacity between initial and aged biochar were identified [25]. When applied to soil, biochar can effectively adsorb and immobilise heavy metals and organic pollutants through a variety of physical and chemical mechanisms, making it an effective tool for soil improvement and pollution remediation. However, the long-term behavior of biochar in soil and its impact on the environment remain unknown. In particular, it is unclear whether the processes of physical, chemical, and biological ageing result in the re-release of pollutants adsorbed by biochar into the soil, or the release of other new pollutants. Furthermore, it is uncertain whether ageing enhances biochar's pollutant adsorption capability or affects the bioavailability of pollutants. Further research is needed to address these uncertainties and to better understand the implications of biochar ageing in practical environmental applications. Therefore, a thorough investigation is essential to evaluate the feasibility of using biochar as a long-term solution for addressing contemporary environmental concerns. The aim of this study was to elucidate the key mechanisms by which biochar ageing influences the bioavailability of

heavy metals in biochar-amended soils. To achieve this, the following research tasks were performed: (1) Simulate various artificial ageing processes (e.g., chemical oxidation, freeze–thaw cycles, and dry–wet cycles) to investigate the changes in the elemental composition, specific surface area, surface functional groups, and surface morphology of ageing biochar. (2) Use sequential extraction methods to quantify fractional changes and assess the impact of biochar ageing on the bioavailability of heavy metals such as Cu, Cd, and Pb. (3) Analyze and theoretically describe the mechanisms by which different ageing processes alter the surface properties of biochar, thereby affecting the bioavailability of heavy metals in soil. (4) Compare the effects of different ageing treatments to determine which processes most significantly influence biochar's ability to immobilize or release heavy metals over time. The findings provide valuable insights into the long-term feasibility of biochar as a soil amendment and offer scientific support for its effective use in the sustainable remediation of heavy metal-contaminated soils.

2. Materials and Methods

2.1. Soil and Biochar

The experimental soil was collected in April 2022 from the surface layer of a maize field in Mishazi Town, Changchun City, Northeast China (125.42 E, 44.14 N). The soil type was mollisols, which is characterized by a high fertility level and cultivability. The samples were naturally dried and sieved through a 1 mm mesh. The physical and chemical properties of the soil are presented in Table 1.

Table 1. Basic physicochemical properties of the experimental soil.

Soil Type	Organic Matter g/kg	pH	Cation Exchange Capacity cmol/kg	Composition of Soil Particle Size %		
				2~0.02 mm	0.02~0.002 mm	<0.002 mm
mollisols	27.65	6.26	29.56	36.74	25.96	34.28

Corn is one of the most important crops in Northeast China, and corn straw is abundantly available, making it a sustainable and readily accessible feedstock for biochar production. Compared to rice straw biochar, corn straw biochar has a higher lignin content and a more porous structure, which enhances its adsorption capacity and effectiveness in immobilizing pollutants such as heavy metals. The biochar was obtained from Nanjing Qinfeng Straw Technology Co., Ltd., Nanjing, China. We used corn straw as the primary raw material, pyrolyzed at 550 °C and maintained for 2 h under anoxic conditions. The average pyrolysis yield of the biochar was 33.67% by mass. The fundamental physicochemical properties of the biochar are presented in Table 2.

Table 2. Basic physicochemical properties of the biochar.

Elements	Nitrogen (N)%	Carbon (C)%	Hydrogen (H)%	Oxygen (O)%	H/C	O/C	(N+O)/C	pH	Specific Surface Area m^2/g
Biochar	1.28	56.39	2.26	40.07	0.040	0.71	0.73	9.91	11.05

2.2. Biochar Ageing

A specific amount of biochar with a particle size < 1 mm was thoroughly mixed with the air-dried experimental soil to achieve a 2% biochar-amended soil. A standard solution (dilute to 2000 mL) of heavy metals was prepared by using $Cu(NO_3)_2$, $Cd(NO_3)_2$, and $Pb(NO_3)_2$, and the initial concentrations were set to 0.82 g/L, 0.0058 g/L, and 0.89 g/L, respectively. Ten kilograms of 2% biochar-amended soil was accurately weighed, and 1800 mL of heavy metal standard solution was uniformly mixed, resulting in a moisture content of 60% field capacity and spiked concentrations of Cu^{2+}, Cd^{2+}, and Pb^{2+} of 50,

0.5, and 100 mg/kg, respectively. Keeping the moisture content unchanged during pre-cultivation and ageing was carried out for two weeks. After this period, the soil was air-dried and sieved through a 1 mm mesh.

The ageing experiments were conducted over a period of more than one month in May and June 2022, and three distinct ageing treatments were performed: natural ageing (NT), chemical oxidation/freeze–thaw cycles (CFTs), and chemical oxidation/dry–wet alternations (CDWs). These ageing processes were selected because they mimic real-world environmental factors such as temperature fluctuations, moisture changes, and chemical interactions, which are critical for understanding biochar's long-term behavior in soil environments. For the CFTs treatment, a specific volume of 15% hydrogen peroxide (H_2O_2: Biochar, 20:1 *w/v*) was added to 1 kg of 2% biochar-amended soil. The mixture was oxidized in a water bath at 80 °C for 6 h, then dried at 105 °C to evaporate the excess H_2O_2 and moisture. After drying, the biochar-amended soil was kept at 60% field capacity and subjected to 10 d of freeze–thaw cycles (freezing at −10 °C for 12 h, thawing at 5 °C for 12 h) in a temperature-controlled incubator. This procedure defined the CFT alteration, and a total of three ageing cycles were carried out. The chemical oxidation process for the CDWs treatment was the same as described earlier. After oxidation, the biochar-amended soil samples were saturated with distilled water for 16 h to reach 100% field capacity and then dried at 60 °C in an oven for 8 h. This process defined the chemical oxidation/dry–wet alternation, and a total of three ageing cycles were carried out. Natural ageing served as a control to compare biochar changes in a more gradual, real-world scenario. The NT treatment involved incubating the biochar-amended soil at room temperature (25–28 °C) with an initial moisture content set at 60% of the field capacity. The initial moisture content was restored every three days using the weighing method. The duration of the NT treatment was consistent with the other two ageing methods. Each ageing treatment included three replicates.

2.3. Biochar Characterization

A characterization of the biochar was conducted to assess its physicochemical properties before and after ageing, providing insights into how environmental factors affect biochar's functionality.

2.3.1. The Separation of Biochar

The biochar was separated from the soil matrix using a water-based method, where density differences facilitated separation. Approximately 100 g of the biochar-amended soil from the different ageing treatments was collected and placed into a 250 mL beaker. About 150 mL of deionized water was added and stirred with a glass rod for 2 min. After allowing it to settle for 24 h, the biochar and soil were separated by density. The supernatant was poured through a 100-mesh nylon sieve to collect the suspended biochar from water's surface. The obtained biochar was rinsed several times with deionized water to remove residual soil and plant debris and then dried in an oven at 60 °C for subsequent analysis.

2.3.2. pH

To determine the pH of the biochar samples, 1 g of each sample was mixed with 20.0 mL of deionised water in a rotary shaker for 1 h. This suspension was further allowed to settle for one more hour at 25 °C, and then the pH was measured using a pH meter (Leici, Shanghai, China).

2.3.3. Elemental Analysis

The C, H, N, and sulphur (S) content of the biochar was determined using a Vario MACRO Cube elemental analyzer to monitor how biochar composition changes over time and under different ageing conditions. The O content was calculated by subtraction using the following formula: O (%) = 100% − C (%) − N (%) − H (%) − S (%). Since

the proportion of S is very low, it was considered negligible and therefore excluded from the calculation.

2.3.4. Specific Surface Area

The specific surface area of the biochar, critical for understanding adsorption capacity, was measured using the Brunauer–Emmett–Teller (BET) method, with nitrogen adsorption as the adsorbate.

2.3.5. Surface Functional Groups

Fourier transform infrared spectroscopy (FTIR) was used to identify changes in surface functional groups by the KBr tableting method (Thermo Fisher, Nicolet In10, Waltham, MA, USA). The presence and alterations in the functional groups, such as -OH, -C=O, and -C-O, are crucial for understanding biochar's chemical interactions with heavy metals in soil. The samples were scanned in the spectral region with a resolution of 2 cm^{-1} and a scanning range of 4000–400 cm^{-1}.

2.3.6. Surface Morphology

Scanning electron microscopy (SEM) was employed to visualize the microstructural changes in biochar due to ageing. SEM images help confirm physical damage or changes in the porosity and structure of biochar that can impact its efficacy in contaminant immobilization. A suitable amount of the biochar was adhered to a sample table using tape, followed by a gold spray technique for sample coating. The gold-coated samples were analysed by scanning electron microscopy (SEM), and the energy spectrum was determined using corresponding software.

2.4. Heavy Metal Fractionation and Quality Control

To assess how biochar ageing affects the bioavailability of heavy metals, biochar-amended soil from each treatment was subjected to the Community Bureau of Reference (BCR) sequential extraction method. This method categorizes metals into exchangeable, reducible, oxidizable, and residual fractions, providing insights into how much of each metal remains bioavailable after biochar ageing. The extraction of the different fractionations of Cu, Cd, and Pb from the biochar-amended soil before and after ageing was performed as described by Xiao et al. (2017) [26].

The quality control of the analysis was ensured by using blank samples, replicates, and the standard reference material (GSS-16 for soils) provided by the CRM/RM Information Centre of China. The recovery rate (sum of species/total metal) ranged between 90% and 110%, indicating the satisfactory extraction of the metals from the soil through aqua regia digestion and BCR sequential extraction. The detection limits for cadmium, copper, and lead were 0.001, 0.1, and 0.01 mg/kg, respectively.

3. Results

3.1. Variations in the pH Value, Elemental Composition, and Specific Surface Area of Biochar

Table 3 presents a comprehensive analysis of the elemental composition and pH values of biochar before and after different ageing treatments. The content of the N and H elements remained unchanged in the three aged biochar samples compared to the initial biochar (CK), indicating a minimal impact on these elements, while the ageing process significantly affected the content of C and O within the biochar. This suggested that the ageing process primarily affects the C and O elements, which play key roles in biochar's adsorption capabilities. The CDWs treatment exhibited the most pronounced alterations, with a notable decline in the C content from 56.39% to 47.70% and an accompanying increase in the O content from 40.07% to 49.17%. These findings indicate that strong oxidative processes occurred during the CDWs treatment, which led to the decomposition of the biochar's carbon framework and the formation of oxygen-containing functional groups. Similarly, the CFTs treatment also showed significant changes, with a reduction in the C

content to 48.74% and an increase in the O content to 47.72%, albeit slightly less dramatic than the CDWs treatment. In contrast, the NT treatment exhibited a milder reduction in the C content (to 53.75%) and an increase in the O content (to 42.46%). The O/C ratio, a critical indicator of biochar oxidation, significantly increased for all treatments, reaching 1.03 for the CDWs, 0.98 for the CFTs, and 0.79 for the NT. This reflects the degree of oxidation biochar undergoes during the ageing process, with the CDWs treatment showing the highest level of oxidation. Similarly, the (N+O)/C ratio increased across all the treatments, emphasizing the role of oxygen in altering biochar's chemical structure. The H/C ratio exhibited slight increases across all the treatments, reaching 0.045 for the CFTs, 0.043 for the NT, and 0.042 for the CDWs, suggesting that the hydrogen-related changes were minimal compared to those involving oxygen.

Table 3. The effects of ageing on the elemental composition and the pH value of biochar.

Treatments	N%	C%	H%	O%	H/C	O/C	(N+O)/C	pH
CK	1.28	56.39	2.26	40.07	0.040	0.71	0.73	9.91
CDWs	1.12	47.70	2.01	49.17	0.042	1.03	1.05	4.92
CFTs	1.37	48.74	2.17	47.72	0.045	0.98	1.01	4.99
NT	1.46	53.75	2.33	42.46	0.043	0.79	0.82	9.13

In terms of pH, the CDWs and CFTs treatments led to substantial decreases, from 9.91 to 4.92 and 4.99, respectively, indicating that both the ageing processes increase the acidity of biochar. The increased acidity can be linked to the formation of acidic functional groups like carboxyl, which arise due to oxidation. In contrast, the NT treatment showed a smaller decrease in pH, reaching 9.13, which suggests that natural ageing results in milder changes to biochar's chemical properties. Overall, the ranking of the ageing effects on the pH and the elemental composition was CDWs > CFTs > NT.

A comparative analysis of the effects of the NT, CFTs, and CDWs treatments on the biochar's physical properties revealed substantial differences (Table 4). The CFTs treatment demonstrated the greatest enhancement in specific surface area, increasing by 6.440 m^2/g, followed by the CDWs with a 5.614 m^2/g increase, while the NT exhibited only a modest increase of 0.890 m^2/g. This substantial increase in the surface area for the CFTs and the CDWs can be attributed to the loss of unstable carbon and the exposure of previously occluded pores, as these treatments promote the breakdown of biochar's structure. With regard to pore volume, the CFTs and the CDWs exhibited a notable increase of 0.013 cm^3/g and 0.012 cm^3/g, respectively, which was significantly higher than the increase of 0.006 cm^3/g observed in the NT. This expansion in pore volume suggests that the harsh environmental conditions simulated during the CDWs and the CFTs ageing processes (e.g., temperature and moisture fluctuations) contribute to the degradation of biochar's structure and the formation of new pore spaces. As for pore size, both the CFTs and the CDWs resulted in a reduction of approximately 0.200 nm to 1.653 nm and 1.654 nm, respectively, while the pore size remained unchanged following the NT treatment at 1.854 nm. The reduction in pore size for the CDWs and CFTs treatments indicates that hydrothermal variation during ageing leads to the collapse of larger macropores into micropores, thus reducing the average pore size, but potentially increasing the density of smaller pores.

Table 4. Variations in the specific surface area of biochar before and after ageing.

Treatments	Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
CK	11.101	0.024	1.854
CDWs	16.715	0.036	1.654
CFTs	17.541	0.037	1.653
NT	11.991	0.030	1.854

Overall, the experimental findings underscore the differential effects of ageing methods on biochar's physicochemical properties. The CFTs treatment was the most impactful, causing significant changes in surface area, pore volume, and pore size, followed by CDWs. In contrast, the NT treatment had a lesser effect, reflecting the slower natural ageing process. These results have important implications for the use of biochar in long-term environmental applications, as they demonstrate how ageing processes can significantly influence its ability to adsorb heavy metals and other contaminants.

3.2. Variations in the Surface Functional Groups of Biochar

Figure 1 presents the FTIR results for the initial biochar (CK) and the three aged biochar samples (CDWs, CFTs, and NT). The FTIR analysis revealed that both the initial and the aged biochar exhibited absorption peaks corresponding to approximately 6–7 functional groups, indicating the presence of similar chemical structures, although their intensities and positions varied due to ageing. The absorption peak around 3432 cm^{-1} corresponds to the stretching vibration of hydroxyl (-OH) groups, which mainly originate from the carbohydrates in the biochar and, to a lesser extent, from the water absorbed by the samples [27]. The presence of this peak in both the aged and the initial biochar reflects the persistence of the hydroxyl groups throughout the ageing process. However, distinct shifts in the -OH peak were observed across the treatments, with the CDWs, CFTs, and NT biochar showing shifts to 3435.30 cm^{-1}, 3431.66 cm^{-1}, and 3429.52 cm^{-1}, respectively. The shifts indicate subtle changes in the hydrogen-bonding environment of the biochar due to ageing, particularly with the CDWs showing the most pronounced alteration. The peak at 2927 cm^{-1}, attributed to the stretching vibration of aliphatic -CHx (-CH_2- or -CH_3-) groups, was significantly reduced or completely eliminated after the ageing process, especially in the CDWs treatment [28]. This suggests that the aliphatic hydrocarbons or cycloalkane groups, which are less stable, degrade during ageing. The disappearance of these groups may indicate the oxidation and breakdown of biochar's organic matrix, leading to reduced structural stability and affecting its adsorption capabilities.

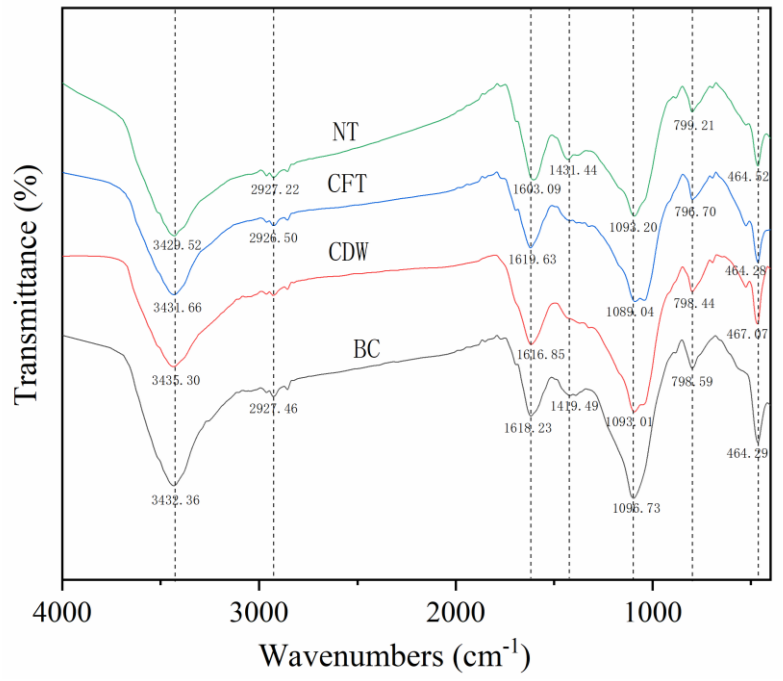

Figure 1. FTIR spectra of initial and aged biochar.

The absorption peak at 1618 cm^{-1}, corresponding to the stretching vibrations of -C=O and -C=C groups in the aromatic ring, showed shifts in its intensity and position after ageing [29,30]. In particular, the peak shifted to 1616.85 cm^{-1} in the CDWs, 1619.63 cm^{-1} in the CFTs, and 1603.09 cm^{-1} in the NT treatments. These shifts reflect changes in the chemical environment of aromatic and carbonyl groups, signifying an increase in oxidation processes within the biochar, particularly for the CDWs and the CFTs treatments. This enhanced oxidation aligns with the observed increase in oxygen content, as noted in the elemental composition analysis. The -COO stretching vibration peak at 1420 cm^{-1} was absent in the biochar treated with the CDWs and the CFTs, suggesting a significant loss of carboxyl groups due to the harsher ageing conditions [27]. Carboxyl groups play a key role in heavy metal complexation and adsorption. Their disappearance implies a reduced capacity for biochar to immobilize heavy metals through surface complexation, which is a critical function for soil remediation. The peak at 1096 cm^{-1}, representing the stretching vibrations of -C-O, -C-C, or -C-O-C groups in esters, showed notable increases across all the aged biochar samples, particularly exhibiting double peaks [31]. This increase reflects the formation of oxygen-containing functional groups, indicating biochar oxidation during ageing. These functional groups can interact with metal ions, affecting biochar's adsorption properties, but excessive oxidation may reduce biochar's long-term stability. Additionally, the peak at 464 cm^{-1}, corresponding to Si-O-Si stretching vibrations, exhibited a lower intensity in the aged biochar compared to the CK, particularly in the CDWs and the CFTs treatments [32]. This reduction may indicate the structural degradation of silicate compounds within biochar, further contributing to its decreased adsorption capacity and physical integrity after ageing.

3.3. Variations in the Surface Morphology of Biochar

Figure 2 displayed SEM images that illustrated the surface morphology of the biochar before and after the different ageing treatments. The images revealed the significant impact of the three ageing methods (CDWs, CFTs, and NT) on the structural integrity and surface characteristics of the biochar. The surface of the initial biochar exhibited a distinct, densely and regularly arranged tubular pore structure with smooth and undamaged surface pores (Figure 2a). This intact microstructure is indicative of biochar's high stability and adsorption potential in its untreated form, which is essential for the effective immobilization of heavy metals. The microstructure of the aged biochar treated with the CDWs exhibited notable alterations, such as surface fractures, the destruction of the tubular pore structure, local fragmentation, and the collapse of pore walls. These alterations led to the blockage of adsorption sites on the biochar's surface and a reduction in pore size (Figure 2b). This structural degradation significantly compromises biochar's adsorption capacity, as the loss of available pores directly reduces the surface area for heavy metal binding. The pore structure of the aged biochar treated with the CFTs was also significantly damaged, resulting in thinner pore walls, with an increase in the number of micropores on the biochar surface, and reduced pore size (Figure 2c). Although this increase in micropores could suggest an improved adsorption capacity, the simultaneous reduction in pore size and the weakening of the pore walls diminish the structural integrity of the biochar. In contrast, the surface of the biochar treated with the NT showed only partial damage, with the pore structure remaining largely intact and exhibiting minimal damage (Figure 2d).

3.4. The Effect of Biochar Ageing on the Stability of Heavy Metals in Soil

Figure 3 illustrated the changes in the fractionation of Cu, Cd, and Pb in the biochar-amended soil after cultivation, highlighting the effects of the different biochar ageing processes on the stability of these heavy metals. The distribution of the heavy metals across various fractions provides insights into their mobility and the potential environmental risk, as the more bioavailable and exchangeable forms were more likely to leach into the soil and pose contamination risks.

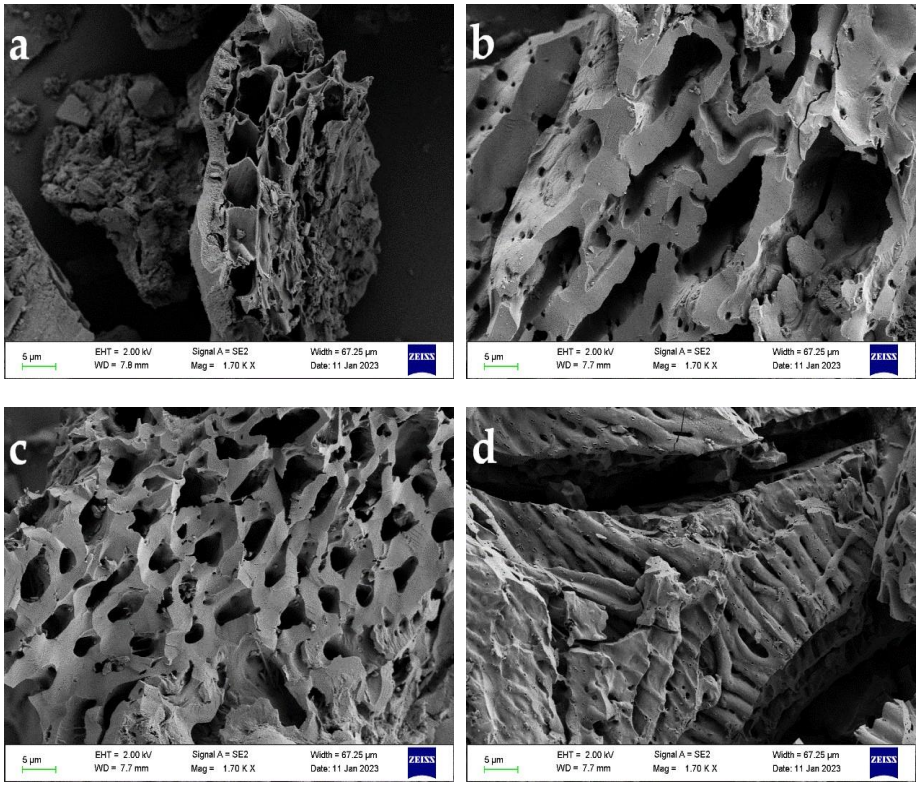

Figure 2. Scanning electron microscope analyses of initial and aged biochar at 5 µm resolution ((**a**) unaged biochar; (**b**) chemical oxidation/dry–wet alternations ageing biochar; (**c**) chemical oxidation/freeze–thaw cycles ageing biochar; (**d**) natural ageing biochar).

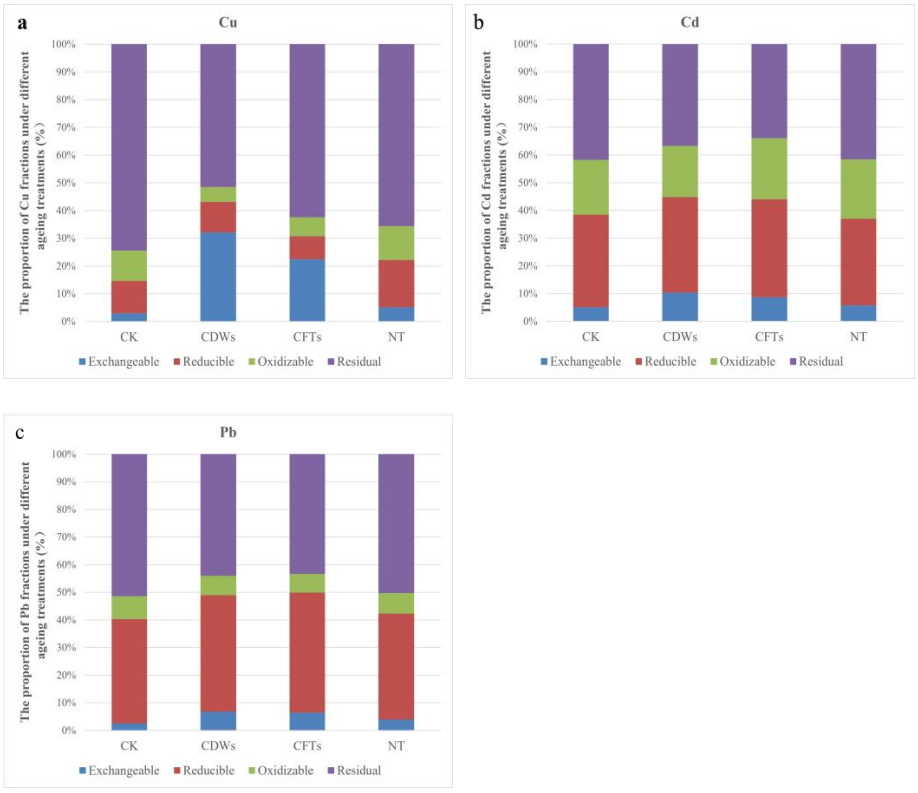

Figure 3. Distribution of heavy metal fractions in biochar-amended soil under different ageing treatments ((**a**) proportion of Cu fractions; (**b**) proportion of Cd fractions; (**c**) proportion of Pb fractions).

Copper was initially present predominantly in the residual fraction (74.36%), which is considered the most stable and least bioavailable form. The remaining Cu was distributed between the oxidizable fraction (11.72%), reducible fraction (10.95%), and only a small proportion (2.97%) was found in the exchangeable form, which represents the most mobile and bioavailable fraction (Figure 3a). After ageing, the concentration of residual Cu decreased significantly, particularly in the CDWs and CFTs treatments, leading to a substantial increase in the exchangeable fraction. The CDWs treatment resulted in a notable rise in exchangeable Cu to 31.40%, while the CFTs increased it to 21.93%. In comparison, the natural ageing (NT) treatment had a much smaller effect, with exchangeable Cu increasing by only 5.24%. Cadmium in the initial biochar-amended soil was predominantly present in the residual (41.80%) and the reducible (33.43%) fractions, with smaller amounts in the oxidizable (19.69%) and exchangeable (5.08%) fractions (Figure 3b). After ageing, Cd showed a shift from more stable forms to more mobile and bioavailable forms, particularly in the CDWs and CFTs treatments. Exchangeable Cd increased by 5.25% in the CDWs-treated biochar-amended soil and by 3.61% in the CFTs-treated biochar-amended soil, indicating a significant rise in its mobility. In contrast, the NT treatment had a much smaller effect, with the reducible fraction increasing by only 0.66%. Lead, like Cu and Cd, showed a similar trend in its distribution across the different fractions. Initially, Pb was primarily present in the residual (51.44%) and reducible (37.76%) fractions, with smaller amounts in the oxidizable (8.29%) and exchangeable (2.51%) fractions (Figure 3c). After ageing, the residual and oxidizable fractions of Pb decreased across all three treatments, while the exchangeable and reducible fractions increased. In particular, the CDWs and CFTs treatments led to a rise in exchangeable Pb, reaching 6.79% and 5.67%, respectively, while the NT treatment caused a smaller increase to 3.89%. The reducible fraction of Pb also increased significantly, ranging from 38.36% to 43.46% after ageing. The results above suggest that the CDWs and CFTs treatments significantly enhance the mobility and bioavailability of Cu, Cd, and Pb, likely due to the increased degradation of biochar's structural integrity and changes in surface functional groups, which reduce biochar's capacity to stabilize heavy metals.

4. Discussion

The results of the BCR sequential extraction indicated that the biochar ageing processes significantly enhanced the transformation of heavy metals (Cu, Cd, Pb) in soil from stable residual and oxidisable fractionation to more active exchangeable fractionation. Specifically, the CDWs and CFTs treatments increased the proportion of exchangeable Cu fractionation from an initial 2.97% to 31.40% and 21.93%, respectively, with comparable increases observed for Cd and Pb. The changes in biochar's surface functional groups and physical structure are crucial factors influencing the activation and stabilization of heavy metals [33].

4.1. Changes in Surface Functional Groups during the Ageing of Biochar and the Effects on Heavy Metal Bioavailability

The ageing process induced significant changes in the pH value and the elemental composition (C, O, H, N) of biochar, closely related to the formation and evolution of surface functional groups. The CDWs and CFTs treatments caused a notable decrease in the pH, from 9.91 to 4.92 and 4.99, respectively, consistent with other studies that attribute the increased acidity to the formation of functional groups such as carboxyl and hydroxyl [34–37]. The FTIR spectra analysis (Figure 1) showed that the biochar treated with the CDWs and the CFTs exhibited increased relative contents of C=O (1618 cm^{-1}) and C-O (1096 cm^{-1}) oxygen-containing functional groups, indicating the enhanced oxidation of biochar during ageing. The elemental analysis further confirmed a decrease in the C content and a corresponding increase in the O content after the CDWs and CFTs treatments, driven by the dissolution of unstable carbon on biochar surfaces [15,35,36]. The reduction in -CHx stretching vibration peaks (2927 cm^{-1}) signified the breakdown of organic compounds, which is a key factor in the decline of biochar's adsorption capacity [14]. As the ageing process progressed, the biochar was exposed to oxygen, moisture, and microbial activity in

the soil, which could trigger oxidation reactions. The reactions led to the formation of more oxygen-containing functional groups, thereby increasing the content of O and the O/C ratios [37]. The rise in C-O bonds in the aged biochar, particularly in the CDWs and CFTs treatments, reflected the oxidation process and the transformation of biochar's chemical composition [29,35].

Changes in surface functional groups had a direct impact on the bioavailability of heavy metals in the soil. The ability of biochar to adsorb heavy metals depends on processes such as electrostatic adsorption, ion exchange, and complexation [38,39]. Increased aromaticity enhances biochar's electron-donating capacity, thereby strengthening the electrostatic adsorption of heavy metals [9]. However, the biochar aged by the CDWs and CFTs treatments showed a 5% and 12.5% increase in the H/C ratio, respectively, indicating reduced aromaticity, which weakened the adsorption capacity for heavy metals and increased their mobility and bioavailability [40,41]. Previous research by Derakhshan et al. (2018) [42] and Yuan et al. (2021) [43] has demonstrated that negatively charged functional groups, such as -OH, -COOH, and -C=O, play a crucial role in coordinating with heavy metals and reducing their activity. However, as biochar ages, the transformation and depletion of these functional groups diminish its ability to complex with heavy metals, resulting in higher concentrations of free metals in the soil. The reduction in the intensity of the hydroxyl (-OH) (3432 cm^{-1}) stretching vibration peak on the aged biochar's surfaces also indicated a decline in complexation, thereby rendering heavy metals more susceptible to desorption and increasing their activity [44]. Carboxyl groups have been demonstrated to effectively adsorb and immobilize heavy metal ions through surface complexation [45]. As illustrated in Figure 1, the disappearance of the -COO (1420 cm^{-1}) stretching vibration peak in the biochar treated with the CDWs and the CFTs confirmed the reduced complexation ability and a subsequent increase in free heavy metal ions in soil.

4.2. The Effects of Ageing on the Physical Structure of Biochar and Its Heavy Metal Adsorption Capacity

Biochar's physical structure, including its specific surface area, pore size, and pore volume, was significantly altered by ageing. The SEM images (Figure 2) demonstrated that the biochar subjected to the NT treatment retained its structural integrity, while the CDWs- and CFTs-treated biochar exhibited considerable damage, including cracks, pore wall ruptures, and pore collapses. These structural changes directly impacted the biochar's stability and adsorption performance [35].

Following the CDWs and CFTs ageing treatments, the biochar's specific surface area increased significantly to 5.614 m^2/g and 6.440 m^2/g, respectively, compared to only 0.890 m^2/g for the NT. Previous studies have attributed this increase to the loss of unstable carbon and the exposure of initially covered or filled pores [46–48]. The CFTs-treated biochar, in particular, exhibited a larger increase in the specific surface area, likely due to the freeze–thaw effects, which create more pore space as expanding ice crystals damage the pore walls [49]. Furthermore, the pore volume of the biochar exhibited an increase of 0.013 cm^3/g and 0.012 cm^3/g following the CFTs and CDWs treatments, respectively. This increase can be attributed to the decomposition of organic materials due to oxidation during the ageing process and the proliferation of pores caused by temperature and moisture changes [50]. However, the pore size decreased by approximately 0.200 nm for both the CFTs and CDWs treatments, consistent with other studies that report the collapse of macropores into micropores during ageing [35,51]. While an increased specific surface area and pore volume typically enhance biochar's adsorption capacity for heavy metals, the simultaneous collapse of pore structures and the reduction in pore size limit the number of available adsorption sites. This structural deterioration reduces biochar's capacity to adsorb heavy metals and increases their mobility and bioavailability in soil. The decrease in pore size, combined with the loss of functional groups, further weakens the electrostatic adsorption and complexation mechanisms, which are critical for immobilizing heavy metals [43,52].

The adsorption of heavy metals onto biochar is governed by surface interactions such as electrostatic attraction, ion exchange, and complexation with functional groups like -OH, -COOH, and -C=O [39]. While these functional groups are effective at binding metal ions, the ageing process leads to their depletion, reducing biochar's adsorption capacity. The increased pore volume and surface area resulting from ageing initially support metal adsorption; however, the concurrent reduction in pore size and the collapse of pore structures limit the overall number of active sites available for adsorption. As a result, heavy metals shift from stable residual forms to more bioavailable exchangeable fractions, as seen in the increased proportions of Cu, Cd, and Pb in the CDWs- and CFTs-treated biochar. This increase in metal mobility raises concerns about the long-term environmental risks associated with biochar amendments. Despite its initial effectiveness, biochar's declining performance over time, particularly under accelerated ageing conditions, highlights the need for the careful consideration of biochar's long-term stability when used for soil remediation. In summary, this study demonstrates that biochar ageing significantly impacts both its structural and chemical properties, reducing its effectiveness in immobilizing heavy metals. These findings emphasize the need for further research to optimize biochar's properties and develop strategies to mitigate the effects of ageing, ensuring biochar's long-term efficacy in contaminated soil environments

5. Conclusions

This study introduced a novel approach to understanding the long-term effects of biochar ageing on its physicochemical properties and its ability to immobilize heavy metals in contaminated soils. By simulating different ageing processes, including chemical oxidation/freeze–thaw cycles (CFTs), chemical oxidation/dry–wet cycles (CDWs), and natural ageing (NT), this research provided valuable insights into how biochar's adsorption capacity and structural integrity evolve over time.

The ageing treatments, especially the CDWs and the CFTs, resulted in significant reductions in pH, carbon content, and pore size, alongside increases in oxygen content, specific surface area, and pore volume. These changes indicate that biochar becomes more oxidized and porous, directly affecting its ability to adsorb and immobilize heavy metals. The FTIR analysis revealed an increase in oxygen-containing functional groups (e.g., ketones, esters, and aromatic carbons) after ageing, reducing the biochar's chemical stability and organic carbon content, thus diminishing its effectiveness for long-term environmental applications like carbon sequestration. The SEM analysis confirmed that the CDWs and CFTs treatments caused considerable damage to the biochar's pore structure, while the NT led to minimal structural degradation, highlighting how artificial ageing accelerates deterioration compared to natural processes. The BCR sequential extraction method showed that ageing increased the exchangeable fractionations of Cu, Cd, and Pb, especially under the CDWs and CFTs treatments, raising concerns about the long-term environmental effectiveness of biochar.

These results align with previous studies on biochar degradation over time but uniquely emphasize the severe impact of artificial ageing processes like the CDWs and the CFTs. In conclusion, biochar ageing significantly alters its structural and chemical properties, affecting its capacity to immobilize heavy metals. This study underscores the importance of considering biochar ageing in long-term soil remediation and calls for further research to enhance its durability and effectiveness in mitigating environmental risks.

Author Contributions: Conceptualization, Z.C. and Y.W.; methodology, Z.C.; software, N.W. and F.M.; validation, Z.C.; investigation, Y.Y.; data curation, Z.C. and N.W.; writing—original draft preparation, Z.C.; writing—review and editing, Y.W.; supervision, Y.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key R&D Program of China Program, Grant No. 2023YFD1501003; the Strategic Priority Research Program of the Chinese Academy of Sciences, Grant No. XDA28020102; and the National Basic Science and Technology Resources Survey Project, Grant No. 2021FY100402.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Sakhiya, A.K.; Anand, A.; Kaushal, P. Production, activation, and applications of biochar in recent times. *Biochar* **2020**, *2*, 253–285. [CrossRef]
2. Supraja, K.V.; Kachroo, H.; Viswanathan, G.; Verma, V.K.; Behera, B.; Doddapaneni, T.R.K.C.; Kaushal, P.; Ahammad, S.Z.; Singh, V.; Awasthi, M.K.; et al. Biochar production and its environmental applications: Recent developments and machine learning insights. *Bioresour. Technol.* **2023**, *387*, 129634. [CrossRef] [PubMed]
3. Tsolis, V. and Barouchas. P. Biochar as soil amendment: The effect of biochar on soil properties using VIS-NIR diffuse reflectance spectroscopy, biochar aging and soil microbiology—A review. *Land* **2023**, *12*, 1580. [CrossRef]
4. Cao, X.; Xu, X.; Yang, F. The Interfacial Behavior between Biochar and Soil Minerals and Its Effect on the Char Stability. In Proceedings of the ASA, CSSA and SSSA International Annual Meetings, Tampa, FL, USA, 22–25 October 2017.
5. Lian, F.; Xing, B. Black carbon (biochar) in water/soil environments: Molecular structure, sorption, stability, and potential risk. *Environ. Sci. Technol.* **2017**, *51*, 13517–13532. [CrossRef]
6. Sachdeva, S.; Kumar, R.; Sahoo, P.K.; Nadda, A.K. Recent advances in biochar amendments for immobilization of heavy metals in an agricultural ecosystem: A systematic review. *Environ. Pollut.* **2023**, *319*, 120937. [CrossRef] [PubMed]
7. Kumar, P.; Singhania, R.R.; Sumathi, Y.; Kurrey, N.K.; Chen, C.W.; Patel, A.K.; Dong, C.D. Investigating innovative techniques for biochar modification to enhance the removal of heavy metals from aqueous environments: A comprehensive review. *Clean Technol. Environ. Policy* **2024**, 1–23. [CrossRef]
8. Wang, Y.; Chen, L.; Zhu, Y.; Fang, W.; Tan, Y.; He, Z.; Liao, H. Research status, trends, and mechanisms of biochar adsorption for wastewater treatment: A scientometric review. *Environ. Sci. Eur.* **2024**, *36*, 25. [CrossRef]
9. Shi, X.; Yang, W.; Li, J.; Yao, Z. The Application of Biochar as Heavy Metals Adsorbent: The Preparation, Mechanism, and Perspectives. *Int. J. Environ. Res.* **2024**, *18*, 41. [CrossRef]
10. Zhang, X.; Zhang, Q.; Zhan, L.; Xu, X.; Bi, R.; Xiong, Z. Biochar addition stabilized soil carbon sequestration by reducing temperature sensitivity of mineralization and altering the microbial community in a greenhouse vegetable field. *J. Environ. Manag.* **2022**, *313*, 114972. [CrossRef]
11. Singh, H.; Northup, B.K.; Rice, C.W.; Prasad, P.V. Biochar applications influence soil physical and chemical properties, microbial diversity, and crop productivity: A meta-analysis. *Biochar* **2022**, *4*, 8. [CrossRef]
12. Zhang, R.; Xie, Y.; Zhou, G.; Li, Z.; Ye, A.; Huang, X.; Xie, Y.; Shi, L.; Cao, X.; Zhang, J.; et al. The effects of short-term, long-term, and reapplication of biochar on the remediation of heavy metal-contaminated soil. *Ecotoxicol. Environ. Saf.* **2022**, *248*, 114316. [CrossRef] [PubMed]
13. Cheng, H.; Xing, D.; Twagirayezu, G.; Lin, S.; Gu, S.; Tu, C.; Hill, P.; Chadwick, D.; Jones, D. Effects of field-aging on the impact of biochar on herbicide fate and microbial community structure in the soil environment. *Chemosphere* **2024**, *348*, 140682. [CrossRef] [PubMed]
14. Ghaffar, A.; Ghosh, S.; Li, F.; Dong, X.; Zhang, D.; Wu, M.; Li, H.; Pan, B. Effect of biochar aging on surface characteristics and adsorption behavior of dialkyl phthalates. *Environ. Pollut.* **2015**, *206*, 502–509. [CrossRef]
15. Ren, X.; Sun, H.; Wang, F.; Zhang, P.; Zhu, H. Effect of aging in field soil on biochar's properties and its sorption capacity. *Environ. Pollut.* **2018**, *242*, 1880–1886. [CrossRef] [PubMed]
16. Qu, J.; Zhang, X.; Guan, Q.; Kong, L.; Yang, R.; Ma, X. Effects of biochar underwent different aging processes on soil properties and Cd passivation. *Environ. Sci. Pollut. Res.* **2022**, *29*, 57885–57895. [CrossRef]
17. Wang, Z.; Bian, Y.; Xu, Y.; Zheng, C.; Jiang, Q.; An, C. Artificial aging induced changes in biochar, s properties and Cd^{2+} adsorption behaviors. *Environ. Sci. Pollut. Res.* **2023**, *30*, 20133–20146. [CrossRef]
18. Ren, X.; Sun, H.; Wang, F.; Cao, F. The changes in biochar properties and sorption capacities after being cultured with wheat for 3 months. *Chemosphere* **2016**, *144*, 2257–2263. [CrossRef]
19. Chang, R.; Sohi, S.P.; Jing, F.; Liu, Y.; Chen, J. A comparative study on biochar properties and Cd adsorption behavior under effects of ageing processes of leaching, acidification and oxidation. *Environ. Pollut.* **2019**, *254*, 113123. [CrossRef] [PubMed]
20. Tan, L.; Ma, Z.; Yang, K.; Cui, Q.; Wang, K.; Wang, T.; Wu, G.; Zheng, J. Effect of three artificial aging techniques on physicochemical properties and Pb adsorption capacities of different biochars. *Sci. Total Environ.* **2020**, *699*, 134223. [CrossRef]
21. Mia, S.; Dijkstra, F.A.; Singh, B. Aging induced changes in biochar's functionality and adsorption behavior for phosphate and ammonium. *Environ. Sci. Technol.* **2017**, *51*, 8359–8367. [CrossRef]

22. Fan, Q.; Sun, J.; Chu, L.; Cui, L.; Quan, G.; Yan, J.; Hussain, Q.; Iqbal, M. Effects of chemical oxidation on surface oxygen-containing functional groups and adsorption behavior of biochar. *Chemosphere* **2018**, *207*, 33–40. [CrossRef] [PubMed]
23. Liu, Z.; Demisie, W.; Zhang, M. Simulated degradation of biochar and its potential environmental implications. *Environ. Pollut.* **2013**, *179*, 146–152. [CrossRef] [PubMed]
24. Qian, L.; Chen, M.; Chen, B. Competitive adsorption of cadmium and aluminum onto fresh and oxidized biochars during aging processes. *J. Soils Sediments* **2015**, *15*, 1130–1138. [CrossRef]
25. Xu, Z.; Xu, X.; Tsang, D.C.; Cao, X. Contrasting impacts of pre-and post-application aging of biochar on the immobilization of Cd in contaminated soils. *Environ. Pollut.* **2018**, *242*, 1362–1370. [CrossRef]
26. Xiao, L.; Guan, D.; Peart, M.R.; Chen, Y.; Li, Q. The respective effects of soil heavy metal fractions by sequential extraction procedure and soil properties on the accumulation of heavy metals in rice grains and brassicas. *Environ. Sci. Pollut. Res.* **2017**, *24*, 2558–2571. [CrossRef]
27. Dong, X.; Li, G.; Lin, Q.; Zhao, X. Quantity and quality changes of biochar aged for 5 years in soil under field conditions. *Catena* **2017**, *159*, 136–143. [CrossRef]
28. Nie, T.; Hao, P.; Zhao, Z.; Zhou, W.; Zhu, L. Effect of oxidation-induced aging on the adsorption and co-adsorption of tetracycline and Cu^{2+} onto biochar. *Sci. Total Environ.* **2019**, *673*, 522–532. [CrossRef]
29. Wang, H.; Feng, M.; Zhou, F.; Huang, X.; Tsang, D.C.; Zhang, W. Effects of atmospheric ageing under different temperatures on surface properties of sludge-derived biochar and metal/metalloid stabilization. *Chemosphere* **2017**, *184*, 176–184. [CrossRef]
30. Wang, X.; Li, C.; Li, Z.; Yu, G.; Wang, Y. Effect of pyrolysis temperature on characteristics, chemical speciation and risk evaluation of heavy metals in biochar derived from textile dyeing sludge. *Ecotoxicol. Environ. Saf.* **2019**, *168*, 45–52. [CrossRef]
31. Yi, Q.; Liang, B.; Nan, Q.; Wang, H.; Zhang, W.; Wu, W. Temporal physicochemical changes and transformation of biochar in a rice paddy: Insights from a 9-year field experiment. *Sci. Total Environ.* **2020**, *721*, 137670. [CrossRef]
32. Qian, T.; Wu, P.; Qin, Q.; Huang, Y.; Wang, Y.; Zhou, D. Screening of wheat straw biochars for the remediation of soils polluted with Zn (II) and Cd (II). *J. Hazard. Mater.* **2019**, *362*, 311–317. [CrossRef] [PubMed]
33. Gong, H.; Zhao, L.; Rui, X.; Hu, J.; Zhu, N. A review of pristine and modified biochar immobilizing typical heavy metals in soil: Applications and challenges. *J. Hazard. Mater.* **2022**, *432*, 128668. [CrossRef] [PubMed]
34. Cui, H.; Li, D.; Liu, X.; Fan, Y.; Zhang, X.; Zhang, S.; Zhou, J.; Fang, G.; Zhou, J. Dry-wet and freeze-thaw aging activate endogenous copper and cadmium in biochar. *J. Clean. Prod.* **2021**, *288*, 125605. [CrossRef]
35. Wang, L.; O'Connor, D.; Rinklebe, J.; Ok, Y.S.; Tsang, D.C.; Shen, Z.; Hou, D. Biochar aging: Mechanisms, physicochemical changes, assessment, and implications for field applications. *Environ. Sci. Technol.* **2020**, *54*, 14797–14814. [CrossRef]
36. Wang, L.; Gao, C.; Yang, K.; Sheng, Y.; Xu, J.; Zhao, Y.; Lou, J.; Sun, R.; Zhu, L. Effects of biochar aging in the soil on its mechanical property and performance for soil CO_2 and N_2O emissions. *Sci. Total Environ.* **2021**, *782*, 146824. [CrossRef]
37. Chen, X.; Lewis, S.; Heal, K.V.; Lin, Q.; Sohi, S.P. Biochar engineering and ageing influence the spatiotemporal dynamics of soil pH in the charosphere. *Geoderma* **2021**, *386*, 114919. [CrossRef]
38. Su, J.; Guo, Z.; Zhang, M.; Xie, Y.; Shi, R.; Huang, X.; Tuo, Y.; He, X.; Xiang, P. Mn-modified bamboo biochar improves soil quality and immobilizes heavy metals in contaminated soils. *Environ. Technol. Innov.* **2024**, *34*, 103630. [CrossRef]
39. Islam, M.S.; Kwak, J.H.; Nzediegwu, C.; Wang, S.; Palansuriya, K.; Kwon, E.E.; Naeth, M.A.; El-Din, M.G.; Ok, Y.S.; Chang, S.X. Biochar heavy metal removal in aqueous solution depends on feedstock type and pyrolysis purging gas. *Environ. Pollut.* **2021**, *281*, 117094. [CrossRef]
40. Liang, M.; Lu, L.; He, H.; Li, J.; Zhu, Z.; Zhu, Y. Applications of biochar and modified biochar in heavy metal contaminated soil: A descriptive review. *Sustainability* **2021**, *13*, 14041. [CrossRef]
41. Ravindiran, G.; Rajamanickam, S.; Janardhan, G.; Hayder, G.; Alagumalai, A.; Mahian, O.; Lam, S.; Sonne, C. Production and modifications of biochar to engineered materials and its application for environmental sustainability: A review. *Biochar* **2024**, *6*, 62. [CrossRef]
42. Derakhshan Nejad, Z.; Jung, M.C.; Kim, K.H. Remediation of soils contaminated with heavy metals with an emphasis on immobilization technology. *Environ. Geochem. Health* **2018**, *40*, 927–953. [CrossRef] [PubMed]
43. Yuan, C.; Gao, B.; Peng, Y.; Gao, X.; Fan, B.; Chen, Q. A meta-analysis of heavy metal bioavailability response to biochar aging: Importance of soil and biochar properties. *Sci. Total Environ.* **2021**, *756*, 144058. [CrossRef]
44. Xia, D.; Tan, F.; Zhang, C.; Jiang, X.; Chen, Z.; Li, H.; Zheng, Y.; Li, Q.; Wang, Y. $ZnCl_2$-activated biochar from biogas residue facilitates aqueous As (III) removal. *Appl. Surf. Sci.* **2016**, *377*, 361–369. [CrossRef]
45. Khare, P.; Dilshad, U.; Rout, P.K.; Yadav, V.; Jain, S. Plant refuses driven biochar: Application as metal adsorbent from acidic solutions. *Arab. J. Chem.* **2017**, *10*, S3054–S3063. [CrossRef]
46. Trigo, C.; Spokas, K.A.; Hall, K.E.; Cox, L.; Koskinen, W.C. Metolachlor sorption and degradation in soil amended with fresh and aged biochars. *J. Agric. Food Chem.* **2016**, *64*, 3141–3149. [CrossRef]
47. Liu, Y.; Sohi, S.P.; Jing, F.; Chen, J. Oxidative ageing induces change in the functionality of biochar and hydrochar: Mechanistic insights from sorption of atrazine. *Environ. Pollut.* **2019**, *249*, 1002–1010. [CrossRef] [PubMed]
48. Tan, L.; Sun, C.; Wang, Y.; Wang, T.; Wu, G.; He, H.; Zheng, J. Changes in biochar properties in typical loess soil under a 5-year field experiment. *J. Soils Sediments* **2020**, *20*, 340–351. [CrossRef]
49. Li, H.; Lu, X.; Xu, Y.; Liu, H. How close is artificial biochar aging to natural biochar aging in fields? A meta-analysis. *Geoderma* **2019**, *352*, 96–103. [CrossRef]

50. Enders, A.; Hanley, K.; Whitman, T.; Joseph, S.; Lehmann, J. Characterization of biochars to evaluate recalcitrance and agronomic performance. *Bioresour. Technol.* **2012**, *114*, 644–653. [CrossRef]
51. Hua, Y.; Zheng, X.; Xue, L.; Han, L.; He, S.; Mishra, T.; Feng, Y.; Yang, L.; Xing, B. Microbial aging of hydrochar as a way to increase cadmium ion adsorption capacity: Process and mechanism. *Bioresour. Technol.* **2020**, *300*, 122708. [CrossRef]
52. Hao, H.; Ju, W.L.; Shen, L.; Cao, Y. Different types of biochar: Effect of aging on the Cu (II) adsorption behavior. *Desalination Water Treat.* **2017**, *95*, 227–233. [CrossRef]