

Article

Effects of Carbon-Based Modified Materials on Soil Water and Fertilizer Retention and Pollution Control in Rice Root Zone

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Abstract: To seek an appropriate stabilization and remediation scheme for cadmium (Cd) and arsenic (As) pollution in farmland, a typical polluted soil sample was selected from a mining area in Southwest China for a soil box simulation experiment. Biochar (BC), a modified type of biochar made from rice husk with different mass ratios of ferric chloride and rice husk, was set up (the mass ratio of ferric chloride to rice husk was 1:9 (defined as LFB), 3:7 (defined as MFB), and 5:5 (defined as HFB) and the control group (BL)) to explore the effects of soil water and fertilizer loss, the bioavailability of Cd and As, and the bioenrichment effects of plant organs during the growth period of rice. The results showed that the porous structure and large specific surface area of biochar effectively regulated soil aggregate composition and improved soil water holding capacity. Compared to the BL treatment, soil water storage under the four carbon-based material control modes increased from 8.98% to 14.52%. Biochar has a strong ion exchangeability and can absorb soil ammonium, nitrogen, and phosphoric acid groups, effectively inhibiting the loss of soil fertilizer. Biochar improves soil pH and reduces the specific gravity of exchangeable Cd. In addition, the oxygen-containing functional groups in biochar can react with metals in a complex manner. The diethylenetriaminepentaacetic acid (DTPA) concentrations of Cd in soils treated with BC, LFB, MFB, and HFB were 79.69%, 72.92%, 64.58%, and 69.27% lower, respectively, than those treated with BL. In contrast, the Fe³⁺ in ferric chloride combines with As after hydrolysis and oxidation to form amorphous ferric arsenate precipitates or insoluble secondary minerals. Therefore, the curing effect of the modified biochar on As was more potent than that of applied biochar alone. In conclusion, ferric chloride-modified biochar can effectively inhibit the effects of water and fertilizer loss in farmland soil and realize cross-medium long-term inhibition and control of combined Cd and As pollution.

Keywords: composite pollution; stabilization; water and fertilizer retention; bioavailability; long-term resistance control



Citation: Huang, W.; Jia, Y.; Niu, C.; Zhang, H.; Wang, Y.; Feng, C. Effects of Carbon-Based Modified Materials on Soil Water and Fertilizer Retention and Pollution Control in Rice Root Zone. *Sustainability* **2024**, *16*, 6750. <https://doi.org/10.3390/su16166750>

Academic Editor: Luca Di Palma

Received: 19 June 2024

Revised: 16 July 2024

Accepted: 27 July 2024

Published: 7 August 2024



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1. Introduction

Agricultural soil and water environments, as the basic carriers of plant growth materials and energy uptake, provide an essential guarantee for the healthy and sustainable development of agriculture [1]. With the accelerated development of global industrialization, typical key industries, such as smelting and mining plants, electroplating plants, and chemical plants, pollute farmland water and the soil environment to varying degrees [2]. Among all types of pollution, heavy metal pollution is the most prominent; heavy metal erosion causes hydrological environmental pollution, soil ecological deterioration, crop yield, and quality reduction, and eventually poses a threat to human health, usually through direct contact with the food chain and other ways [3]. Most notably, in the case of arsenic–cadmium combined pollution, arsenic and cadmium have different migration characteristics and bioavailability under the influence of soil pH-Eh due to their different

elemental properties and occurrence forms [4,5]. Therefore, combined arsenic and cadmium pollution increases the uncertainty of soil environmental evolution and the difficulty of soil joint remediation.

Rice, a major food crop, supports approximately half of the global population, and nearly 90% is grown in East and South Asia [6]. However, rice has a strong physiological tolerance mechanism and strong adsorption capacity for Cd, especially in acid-polluted soil, and the enhancement of Cd bioavailability increases the risk to the soil's environmental quality [7]. According to statistics, the Cd content in up to 7% of the agricultural land in China exceeds relevant national standards, and pollutants are enriched in rice through the roots and stems [8]. Consumption of Cd-contaminated food by humans can lead to emphysema, lung disease, and kidney disease [9]. As a common environmental poison and human carcinogen, As has a potent toxic effect on animals and plants, and excessive As seriously hinders the growth and development of plants [10]. In recent years, sewage irrigation, mining, and pesticide use have led to frequent As pollution in paddy fields. The International Agency for Research on Cancer (IARC) has classified As and Cd as Class I carcinogens [11]. Therefore, it is urgent to seek green and sustainable remediation technologies to gain long-term control over soil heavy metal contamination.

Not all soils contaminated with Cd and As pose a significant risk to the environment or sustainable agriculture; the risk posed by heavy metals to soils depends mainly on pollutant bioavailability [12]. Previous studies have proposed the use of in situ passivating technology to reduce the activity of heavy metals and confirmed that materials such as sepiolite and diatomite can significantly promote the conversion of the exchange state Cd to the residue state in soil, reduce the bioavailability and migration ability of metals, and thus inhibit the accumulation of Cd in the aboveground parts of plants [13,14]. For the remediation of AS-contaminated soil, oxidants are usually used to convert As(III) into As(V). In an alkaline environment, As(V) is combined with complexing agents, thus achieving the effect of stabilizing As [15,16]. Ko et al. [17] showed that iron oxide effectively promotes arsenic transformation, reduces the diffusion ability of pollutants, and thus inhibits the enrichment of arsenic in particles. However, the construction of a technical method that considers the fixation of the heavy metals Cd and As in soil and the effective supply of water and fertilizer is an urgent problem to be solved.

Biochar is a carbon-rich material obtained by burning various raw biomass materials under oxygen-limited conditions (i.e., pyrolysis). Due to its good pore structure, surface properties, and alkaline mineral content [18], biochar can fix heavy metals in the soil through various mechanisms. Such mechanisms include cation- π interaction, physical adsorption, and surface precipitation [19]. Biochar also regulates soil particle composition and pore structure, enhancing soil water and fertilizer retention performance [20]. To improve the effects of biochar on farmland soil and water environments, researchers are committed to the research and development of modified biochar. Some scholars have improved the targeting of materials for immobilizing specific heavy metals by modifying biochar with phosphorus and sulfur [21,22]. Meanwhile, the research and development ideas for modified materials guide us to boldly attempt to composite functional materials with the goal of achieving synergistic remediation of multiple heavy metals. Based on this, we assumed that the ferric chloride-modified biochar could effectively realize the co-passivation of As and Cd and effectively improve the water and fertilizer environment of the farmland.

In this study, As and Cd composite-contaminated soil was collected from the field, and a paddy soil box culture experiment was used as the research carrier to explore the following: (1) The migration and transformation characteristics of soil water and fertilizer, (2) the inhibition and control effect of the soil As-Cd pollution migration path, and (3) the improvement mechanism of modified biochar on farmland soil and water environments. The results of this study are expected to provide a theoretical reference for the construction of a sustainable model of soil health in farmlands with As-Cd pollution.

2. Materials and Methods

2.1. Test Materials

The soil samples were taken from a typical mining area in Guizhou Province (E 108°44'25", N 27°12'26"), and the soil pollution type was combined As and Cd pollution. The concentrations of Cd and As in the soil sample were 3.38 mg/kg and 28.45 mg/kg, respectively. According to the World Standard for Classification of Soil Resources (WRB), the tested soil type was red soil [23] (USDA, 1999). The soil in the 0–20 cm soil layer in the sampling area was obtained, and impurities, such as roots and stones, were removed from the soil, which was air-dried under natural conditions. The dried soil was crushed and screened with a 2 mm diameter soil screen to facilitate uniform mixing of the soil repair materials. The experiment was conducted at the Irrigation Experiment Central Station of the Guizhou Academy of Water Resources Science. The rice variety tested was Guihong 1. Rice plants were cultivated in soil boxes, the box size was set to 1000 mm × 600 mm × 550 mm; the material was transparent glass fiber-reinforced plastic, the bottom of the box had a seepage layer of 5 cm (to calculate the soil seepage flow), and the soil height was 40 cm [24]. The soil moisture sensors were buried in layers of 5, 15, 25, and 35 cm in depth and used for real-time monitoring of soil water distribution during the growth period. The row spacing of the rice plants was set at 16 cm, and the plant spacing was set at 23 cm.

The raw material of biochar used in the experiment was rice husk, which was made using a high-temperature and anaerobic environment set in a muffle furnace (calcination temperature of 500 and 800 °C, heating rate of 15 °C·min^{−1}, and duration of 2 h) [1]. Ferric chloride is a black-brown crystal (AR) soluble in water obtained from Maclean Biochemical Technology Co., Ltd., Shanghai, China. Modified biochar was prepared according to the method proposed by Zhang et al. [25]. First, rice husks were placed in a FeCl₃ solution with a concentration of 2 mol/L. The mixture was heated in a water bath, and magnetic stirring was performed at 80 °C for 6 h. The biochar was then treated under high-temperature anaerobic conditions according to the aforementioned biochar manufacturing scheme.

2.2. Design of the Test Scheme

The rice growth cycle was from 3 June 2020 to 27 September 2020. Five treatments were set up: ① involved biochar alone (BC), ② represented the modified biochar made from ferric chloride and rice husk with the mass ratios of 1:9 (defined as LFB), ③ and ④ referred to the mass ratios of ferric chloride to rice husk as 3:7 and 5:5 (defined as MFB and HFB, respectively), and ⑤ served as the control group (BL). Considering the concentration of soil pollutants and the need for rice production, the application amount of various treatment restorants was 3% (by weight), and the restorants and soil were mixed evenly. During the first week of rice cultivation, NPK compound fertilizer (N:P₂O₅:K₂O = 11:6:8) was applied to the soil at a ratio of 500 kg/ha, followed by 200 kg/ha tillering fertilizer 15 days after completion of transplanting, and soil physical and chemical properties were analyzed by sampling before transplanting (Table 1).

Table 1. Soil physical and chemical characteristics.

Treatment	Soil Texture			pH	EC (ms·cm ^{−1})	Soil Total Porosity/ cm ³ ·cm ^{−3}	Total Carbon/ g·kg ^{−1}
	<0.005 mm	0.005~0.02 mm	>0.02 mm				
BL	36.82 ± 1.18 a	33.74 ± 1.39 c	29.44 ± 1.24 a	6.86 ± 0.05 b	1.57 ± 0.11	0.47 ± 0.03 b	22.59 ± 1.23 c
BC	29.38 ± 1.12 b	41.83 ± 1.47 a	28.79 ± 1.27 ab	7.36 ± 0.04 a	1.66 ± 0.09 c	0.54 ± 0.04 a	33.44 ± 1.56 a
LFB	32.38 ± 1.07 b	39.83 ± 1.33 ab	27.79 ± 1.16 b	7.25 ± 0.03 a	1.72 ± 0.07 b	0.53 ± 0.04 a	31.37 ± 1.87 a
MFB	33.11 ± 0.95 ab	38.21 ± 1.21 ab	28.68 ± 1.29 ab	7.33 ± 0.06 a	1.78 ± 0.12 a	0.51 ± 0.03 a	28.63 ± 1.69 b
HFB	34.57 ± 1.33 ab	36.68 ± 1.12 b	28.75 ± 1.08 ab	7.21 ± 0.04 a	1.81 ± 0.13 a	0.49 ± 0.06 ab	27.12 ± 1.93 b

Note: All data in the table are expressed as mean ± standard deviation, and a, b, ab and c indicate that the parameters are significantly different under the same treatment ($p < 0.05$). BL, BC, LFB, MFB and HFB represent the treatments set up in the research.

The sampling interval between the soil and the plants was 24 d in combination with the growth period of the crops, and the sampling depth of the soil corresponded to the embedded soil layer of the water sensor; each sampling was repeated thrice. The obtained plant samples were separated into roots, buds, leaves, rice, and other organs, which were cleaned and dried at 65 °C for 96 h for the analysis of the heavy metal enrichment effect. Based on the water demand of the crops, artificial irrigation was performed seven times during the rice growth process, and the cumulative irrigation amount was 446.3 mm. According to the monitoring data of the automatic weather station in the experimental area, the accumulated rice precipitation after transplanting was 778.6 mm. Simultaneously, water leakage from the soil at the bottom of the box was measured every four days, and the content of available nitrogen and phosphorus in the leakage was analyzed.

2.3. Indicator Measurement

As and Cd in the soil and dried plant organs were digested with a mixture of HNO₃ and HClO₄ (2:1, v/v), and their concentrations were analyzed using ICP-OES (iCAP 7000, Thermo Fisher Scientific Co., Ltd., Waltham, MA, USA). Available As and Cd in the soil were extracted using diethylenetriamine pentaacetic acid (DTPA) at a constant temperature for 2 h by shaking [26]; the bioavailability of As and Cd was then measured. The inorganic nitrogen content (NO₃⁻-N+NH₄⁺-N) in the soil was determined using an Autoanalyzer III (Bran Luebbe Co., Ltd., Hamburg, Germany) [27]. The available phosphorus concentrations were extracted with a NaHCO₃ solution at 24 ± 1 °C and determined by molybdenum-antimony-ascorbic acid colorimetry [28]. The soil cation exchange capacity (CEC) was measured using the ammonium acetate method [29], and electrical conductivity was measured using a conductivity meter (DDS-307A, INESA Scientific Instrument Co., Ltd., Shanghai, China). The total soil porosity was calculated by measuring the soil dry density and particle density [30], and the soil mechanical composition was analyzed using a laser particle size analyzer (Winner 2308, Winner Particle Co., Ltd., Jinan, China). In addition, soil total organic carbon was measured and analyzed using a carbon analyzer (TOC-VWP, Shimadzu Co., Ltd., Kyoto, Japan).

2.4. Data Analysis Method

① Analysis of soil water holding capacity

The soil-moisture characteristic curve was obtained via centrifugation. Unsaturated soil samples were immersed in distilled water for 12 h, and 12 matric suctions (0, −0.01, −0.03, −0.05, −0.1, −0.33, −0.5, −1, −3, −5, −10, and −15 bar) were then set. After reaching the set equilibrium time, the soil was weighed and dried in the oven at 105 °C for 24 h, and the volume of water content corresponding to each suction value was then calculated. Based on the van Genuchten model, soil characteristic parameters were explored using the following model expressions [31]:

$$\theta(h) = f(x) = \begin{cases} \theta_r + \frac{\theta_s - \theta_r}{[1 + |\alpha \cdot h|^n]^m}, & h < 0 \\ \theta_s, & h \geq 0 \end{cases}, \quad (1)$$

where h is the soil negative pressure measured by H₂O, cm; $\theta(h)$ is soil volumetric water content, cm³·cm⁻³; θ_r is the residual water content, cm³·cm⁻³; θ_s is the unsaturated water content, cm³·cm⁻³; α is the inverse of the intake, cm⁻¹; n and m are empirical fitting parameters, $m = 1 - 1/n$.

② Heavy metal enrichment characteristics

Based on the above analysis of heavy metal enrichment in various plant organs, the transfer (TF), distribution (DF), and bioenrichment (BCF) coefficients of As and Cd were calculated using the following formula [32]:

$$TF_{organA-organB} = C_{organB} / C_{organA}, \quad (2)$$

$$DF_{organA} = T_{organA} / T_{total}, \quad (3)$$

$$BCF_{organA} = C_{organA} / C_{soil}, \quad (4)$$

where C_{organA} and C_{organB} represent the concentration of heavy metals in plant roots (A, B, C... represents root, stalk, leaf, and grain), mg/kg; C_{soil} represents the heavy metal concentration in the soil, mg/kg; T_{organA} represents the cumulative in ts of plants, mg; and T_{total} represents the total amount of heavy metal in a plant, mg.

③ Adsorption/desorption properties of materials

The adsorption characteristics of modified carbon-based materials were evaluated by adsorption experiments for As and Cd. In this case, Cd (NO₃)₂·4H₂O and NaH₂AsO₄ were dissolved in 0.01 mol·L⁻¹ NaNO₃ (background solution) and diluted to a concentration of 1000 mg·L⁻¹, respectively, to serve as a reserve solution for the adsorption experiments. Furthermore, the heavy metal ion solution was adjusted to pH = 6.0 and then transferred to a conical flask and set aside.

Two portions of 0.15 g modified biochar were accurately weighed and placed in a 50 mL centrifuge tube, and 30 mL of 10 mg·L⁻¹ As and Cd reserve solutions were added, respectively. The reserve solution was placed in a thermostatic water bath oscillator (25 ± 0.5 °C, 180 r·min⁻¹), and then the samples were collected at 1, 5, 10, 30, 60, 120, 240, 480, 720, and 1440 min. The supernatant was passed through a 0.45 µm filter membrane, and the concentration of heavy metal ions in the filtered solution was determined using ICP-OES (iCAP 7000, Thermo Fisher Scientific Co., Ltd., Waltham, MA, USA). The adsorption capacity of heavy metals was calculated using the following formula:

$$q = (C_i - C_e) \frac{V}{m}, \quad (5)$$

where C_i is the initial heavy metal concentration in the solution, mg/L; C_e is the solution concentration at adsorption equilibrium, mg/L; V is the volume of the solution, L; and m is the material mass, g.

The Langmuir and Freundlich equations were used to fit the adsorption process of heavy metals onto the modified biochar.

$$q_e = \frac{Q_m K_l C_e}{1 + K_l C_e}, \quad (6)$$

where q_e is the equilibrium adsorption capacity, mg/kg; Q_m is the saturated adsorption capacity, mg/kg; and K_l is the Langmuir adsorption constant, L/mg.

$$q_e = K_f C_e^{\frac{1}{n}}, \quad (7)$$

where K_f is the Freundlich adsorption constant, L/mg, and n is the empirical constant of the adsorption process.

SPSS 19.0, developed by IBM (International Business Machines Corporation, Armonk, NY, USA), was used for statistical analysis, and Sigmaplot 12.5 was used for data visualization. In addition, Fisher LSD tests were used to identify differences in soil and plant indices between treatments (significance level, $p < 0.05$).

3. Results

3.1. Retention Characteristics of Soil Water and Fertilizer

3.1.1. Characteristics of Soil Water Migration

During crop growth, carbon-based materials effectively regulate the water-storage capacity of the soil layer (Figure 1). For example, at the crop seedling stage, soil water storage in the 0–10 cm layer under BL treatment was 570.8 mm but increased to 632.6 mm under BC treatment. In addition, soil water storage under the LFB, MFB, and HFB treatments was 8.11%, 6.64%, and 4.83% higher, respectively, than that under the BL treatment. This may be because biochar, as a carbon-rich and highly aromatic organic material, has a rich pore structure and large specific surface area, which contribute to the formation of

stable soil aggregates and improve soil water retention performance [33]. As proposed by Fu et al. [34], biochar can effectively improve soil structure and significantly increase soil micropore size ($\geq 0.3\text{--}0.5\text{ }\mu\text{m}$), soil porosity ($>100\text{ }\mu\text{m}$), and total porosity, thus improving the infiltration rate and water holding capacity of soil snowmelt water. Comparing the soil water storage under the conditions of applying biochar alone and modified biochar, we found that the water-holding capacity of the soil was weakened, which may be because the specific proportion of biochar in the modified materials decreased and its regulatory effect on soil bulk density and porosity decreased. With increasing soil depth, soil water storage showed a downward trend to varying degrees, and the application of carbon-based materials improved soil water storage performance and increased soil water content.

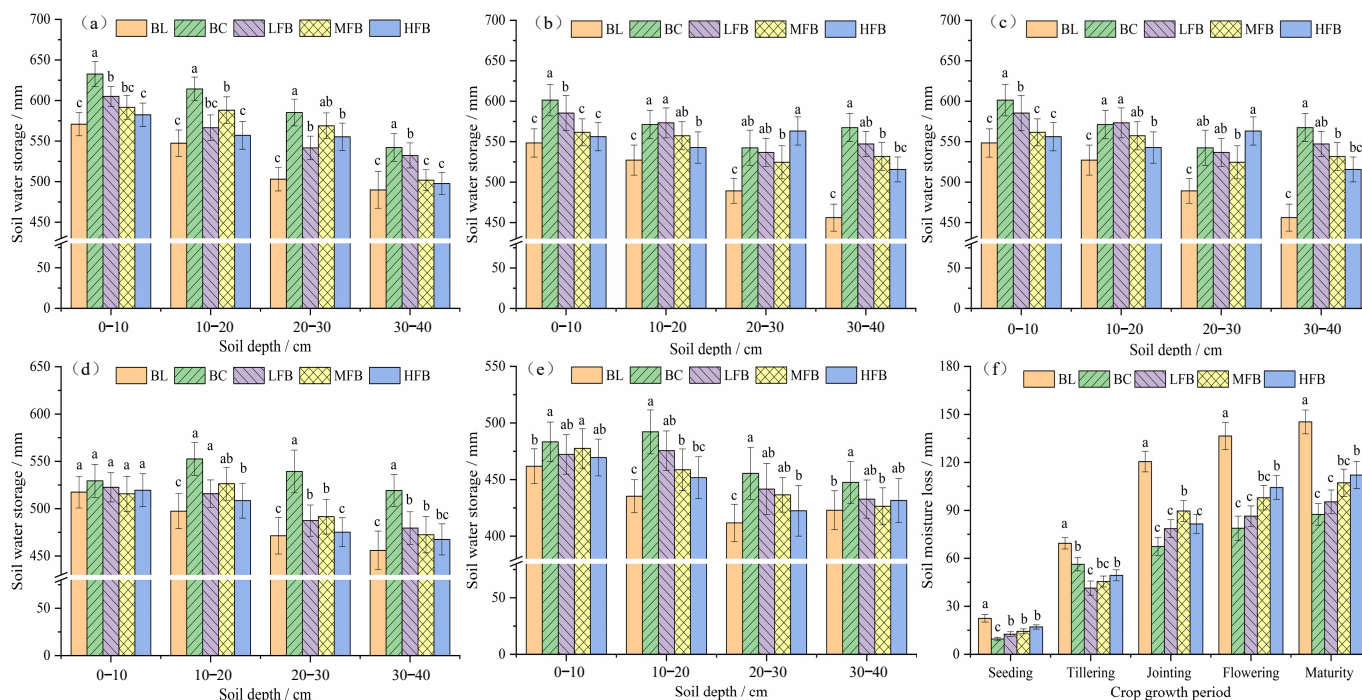


Figure 1. Characteristics of soil water migration and diffusion. (a) Water storage at the seedling stage, (b) tillering water storage, (c) water storage at the jointing stage, (d) water storage during the pumping period, (e) water storage at maturity, and (f) soil water loss at different growth stages. In addition, a, b, ab, bc and c indicate that the parameters are significantly different under the same treatment ($p < 0.05$). BL, BC, LFB, MFB and HFB represent the treatments set up in the research.

In addition, with the passage of the crop-growth period, soil water storage gradually decreased under the comprehensive action of crop transpiration, soil evaporation, and water leakage. Soil water storage decreased by 4.92–7.89% at the tillering stage and 6.67–10.26% at the jointing stage compared with the seedling stage under the BL treatment. At the same time, soil water storage under the BC, LFB, MFB, and HFB treatments showed a certain weakening trend in the tiller, jointing, flowering, and ripening stages compared with the seedling stage. This also verified that the biochar colloids discovered by Amoakwah et al. [35] could promote the aggregation of small particles of soil to form medium-sized aggregates, improve the pore size and porosity of the soil, and enhance the water-holding capacity of the soil.

Statistical analysis of soil water loss during the crop growth period showed that the application of carbon-based materials inhibited the seepage of soil water into deep soil to varying degrees (Figure 1f). At the crop seedling stage, the soil tank water loss under the BL treatment was 20.5 mm, while the soil tank water loss under the BC, LFB, MFB, and HFB treatments was reduced by 48.29%, 38.53%, 29.76%, and 26.34%, respectively, compared with the BL group. Additionally, there was a significant increase in soil water loss during

the tillering and jointing stages. The addition of biochar also inhibited soil water loss, with biochar alone being the most effective. As proposed by Hussain and Ravi [36], when biochar is applied to soil, its loose and porous nature absorbs free soil water and inhibits its diffusion and loss of water. Fischer et al. [37] found that biochar, a large skeleton polymer, has a hydrophilic adsorption effect and can delay the release of soil water and nutrients.

3.1.2. Diffusion Effect of Soil Nitrogen and Phosphorus

The effects of carbon-based functionalized materials on the spatial distribution of soil inorganic nitrogen are shown in Figure 2. At the crop growth stage, the soil inorganic nitrogen content in the 0–10 cm soil layer under the BL treatment was $95.23 \text{ mg} \cdot \text{kg}^{-1}$, while the soil inorganic nitrogen content under the BC, LFB, MFB, and HFB treatments increased by 25.31%, 17.96%, 14.81%, and 10.82%, respectively, compared with the BL treatment. Upon reaching the crop maturity stage, the soil inorganic nitrogen content decreased to different degrees under the synergistic action of crop root uptake and water transport. The average concentration of soil inorganic nitrogen under BL treatment was $77.85 \text{ mg} \cdot \text{kg}^{-1}$, and the soil inorganic nitrogen under BL treatment and modified biochar increased to different degrees. First, the increase in soil inorganic nitrogen reserves is due to the improvement in soil aeration caused by the use of biochar, which reduces the formation and emission of NO_x by inhibiting the denitrification of nitrogenous microorganisms [38]. In addition, biochar contains nitrogen, which has a replenishing effect on soil inorganic nitrogen.

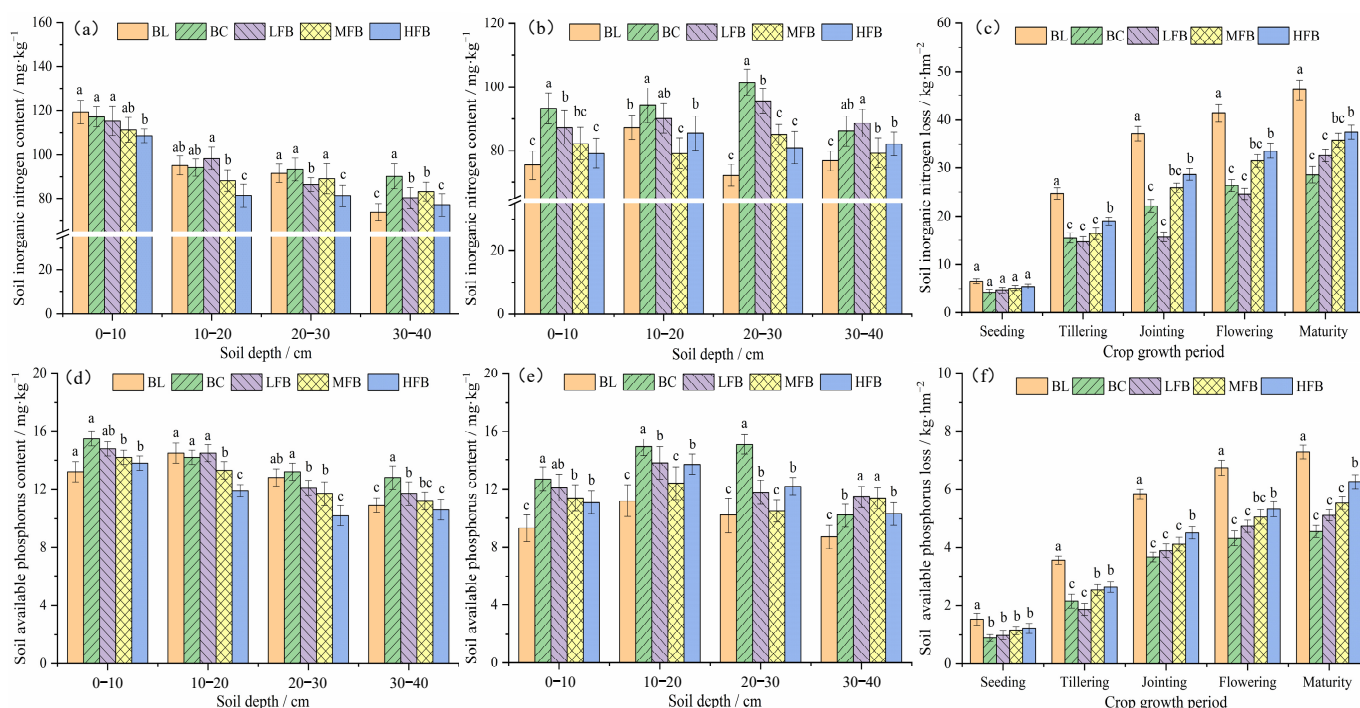


Figure 2. Migration characteristics of nitrogen and phosphorus in soil. (a) Soil inorganic nitrogen at the seedling stage, (b) soil inorganic nitrogen at maturity, (c) soil inorganic nitrogen loss, (d) available soil phosphorus at the seedling stage, (e) available soil phosphorus at maturity, and (f) available soil phosphorus loss. In addition, a, b, ab, bc and c indicate that the parameters are significantly different under the same treatment ($p < 0.05$). BL, BC, LFB, MFB and HFB represent the treatments set up in the research.

Similarly, the application of carbon-based materials increased the available soil P content. In the BL treatment, the available soil P content in the 0–10 cm soil layer was $13.25 \text{ mg} \cdot \text{kg}^{-1}$ while in the BC treatment, it was 17.42% higher than that in the BL group, which also confirmed that biochar could adsorb a large number of phosphoric acid groups on its surface. This leads to an improvement in the retention of available soil phosphorus.

Parvage et al. [39] found that the phosphorus absorbed by plants was mainly $\text{Ca}_2\text{-P}$; the application of biochar effectively improved the available soil phosphorus and promoted the accumulation and formation of crop fruits.

Based on the differences in soil inorganic nitrogen and available phosphorus content, soil nutrient loss was calculated, as shown in Figure 2c,f. By the crop maturity stage, soil inorganic nitrogen loss under the BL treatment was $46.17 \text{ kg} \cdot \text{hm}^{-1}$, while soil inorganic nitrogen loss under the BC, LFB, MFB, and HFB treatments was 38.14%, 29.33%, 22.51%, and 18.91% lower, respectively, than that under the BL treatment. This confirms that biochar has a large specific surface area, strong ion exchange capacity, and high charge density, which can reduce nitrogen leaching [40]. At the same time, carbon-based materials also reduced the amount of available soil P loss to varying degrees. Weiler et al. [41] found that the leaching amount of phosphorus was only 15.91% of that of the control group when biochar and phosphorus were applied to the soil, and biochar significantly increased the total P and available P contents. It also promoted the absorption of phosphorus and reduced phosphorus loss.

3.1.3. Response Relationship of Soil Water and Fertilizer Loss

There was a significant correlation between the soil water and nutrient loss processes (Figure 3). In the BL treatment, the slope of the fitting line for soil water loss and inorganic nitrogen loss was 3.57, whereas in the BC treatment, the slope of the scatter point fitting curve was lower than that in the BL treatment, indicating that soil inorganic nitrogen content decreased under the driving effect of soil water loss per unit. In addition, the slopes of the fitting curves of soil water and nutrient loss under the LFB, MFB, and HFB treatments showed varying degrees of decline compared with the BL treatment. The findings of this study are consistent with the views proposed by Zheng et al. [42] that biochar can improve soil field water capacity and microbial nitrogen fixation and contribute to reducing nitrogen loss.

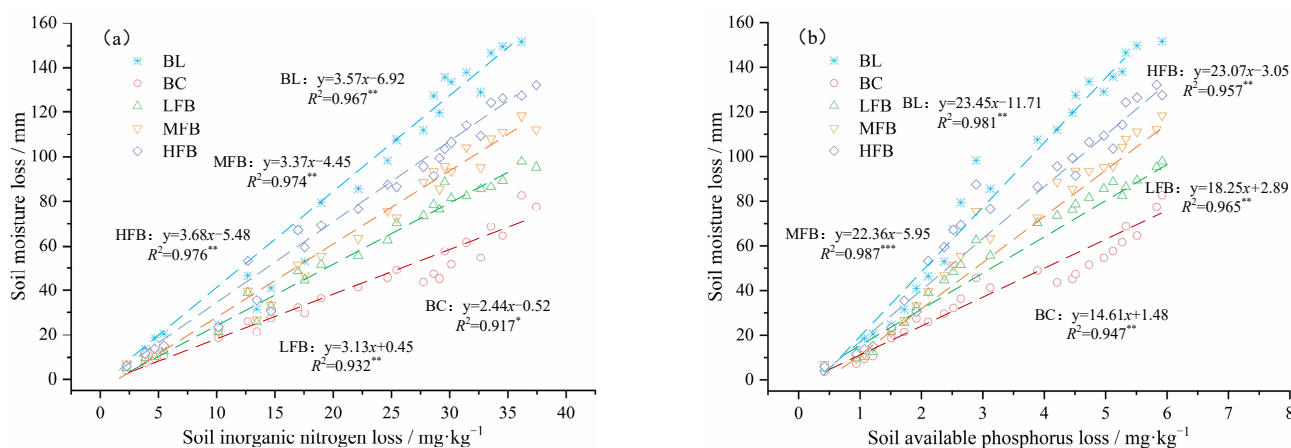


Figure 3. Response relationship between soil water and fertilizer loss. (a) Response relationship between soil inorganic nitrogen and water loss and (b) response of available soil phosphorus to water loss. Note: Asterisks denote a significant difference between different treatments: * $p < 0.05$, ** $p < 0.01$ and *** $p < 0.001$.

Further exploring the response relationship between available soil P loss and water migration and diffusion, we also found that the application of biochar alone and modified biochar treatments reduced the slope of the fitting line, indicating that carbon-based materials reduced the soil water transport capacity for available P to varying degrees. This fully confirmed that the structural groups of biochar had excellent properties of complexity, exchange, and adsorption of ions. The ability of soil particles to retain phosphate groups and reduce the loss of soil available for phosphorus leaching was also enhanced [43,44].

3.2. Prevention and Control Effects of Soil Pollution

3.2.1. Bioavailability of Soil As and Cd

The amounts of extractable Cd and As from DTPA in the soil (used as an approximation of its bioavailability) were significantly reduced by the addition of the modifier (Figure 4). A one-way analysis of variance was used ($p < 0.05$) to analyze the significant differences in metals extracted by DTPA under different treatments at different periods. During the jointing period, the DTPA extraction concentration of Cd in soil under the BL treatment was $1.52 \text{ mg} \cdot \text{kg}^{-1}$, while that under the BC, LFB, MFB, and HFB treatments was reduced by 79.68%, 72.92%, 64.58%, and 69.27%, respectively, compared with the BL treatment. This is because biochar contains a variety of functional groups, such as hydroxyl, carboxyl, and carbonyl groups, which directly immobilize Cd through surface complexation and immobilization [45]. In addition, the alkalinity of biochar indirectly reduces metal dissociation through electrostatic attraction because more negative charges are attached to the surface of the soil particles [19,46,47].

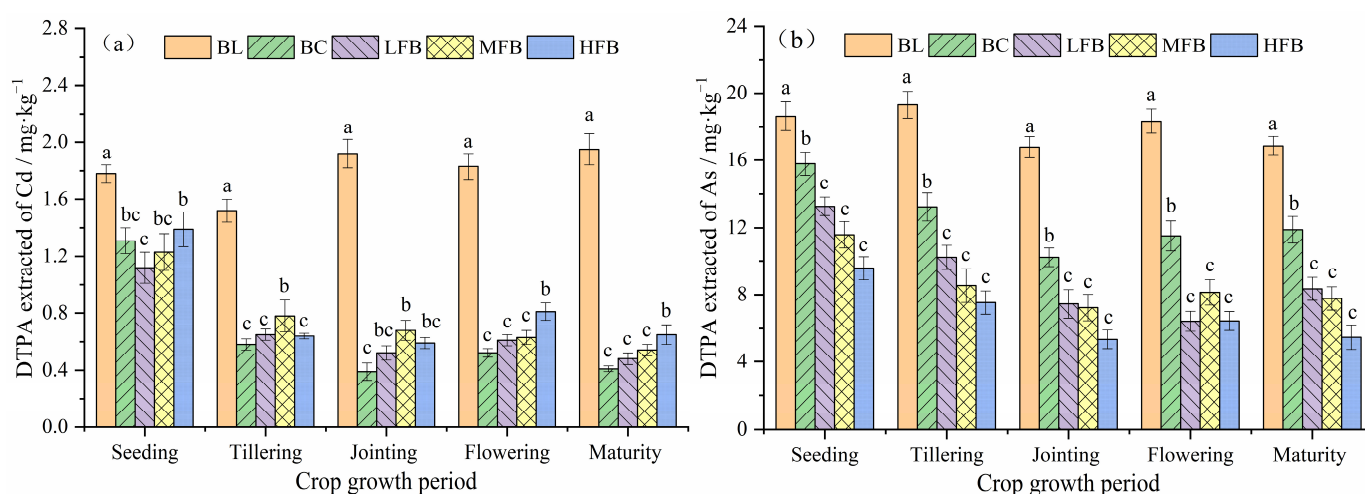


Figure 4. Bioavailability characteristics of heavy metals in soil. (a) DTPA extraction concentration of Cd and (b) DTPA extraction concentration of As. In addition, a, b, bc and c indicate that the parameters are significantly different under the same treatment ($p < 0.05$). BL, BC, LFB, MFB and HFB represent the treatments set up in the research.

At the jointing stage of crops, the DTPA extraction concentration of As in soil under the BL treatment was $16.78 \text{ mg} \cdot \text{kg}^{-1}$, while that of As in the BC treatment was 39.04% lower than in the BL treatment. Surprisingly, the passivation effect of biochar on As was weaker than on Cd. This proves once again that the organic functional groups and phosphates present on the surface of biochar are conducive to the complexation and precipitation of the heavy metal Cd [48]. In contrast, the P element rich in biochar has a competitive adsorption relationship with As, and its higher pH value promotes the desorption of As [25]. However, for the modified biochar treatment, DTPA extraction concentrations of soil As decreased to $7.46 \text{ mg} \cdot \text{kg}^{-1}$, $7.24 \text{ mg} \cdot \text{kg}^{-1}$, and $5.34 \text{ mg} \cdot \text{kg}^{-1}$ under the LFB, MFB, and HFB treatments, respectively, indicating that the modified biochar had a better stabilization effect on As than Cd. Arsenic in the soil may directly react with free iron ions to form insoluble iron–arsenic compounds, and with an increase in iron content, the contents of water-soluble arsenic and adsorbed arsenic in the soil gradually decrease [49]. After the addition of iron-containing materials to the soil, iron oxides or hydroxides are generated under the action of the soil environment, which adsorb arsenic in the soil and precipitate amorphous iron arsenate or insoluble secondary minerals [50].

3.2.2. Effect of Heavy Metal Enrichment on Plant Organs

Based on the enrichment characteristics of Cd and As, the TF, DF, and BCF of each crop organ were calculated, as shown in Table 2. The transfer coefficient of Cd in the stems of the BL group was 0.637, whereas those of the BC, LFB, MFB, and HFB groups were reduced by 32.97%, 27.32%, 22.76%, and 19.78%, respectively. In addition, the transfer coefficients of the grain organs showed a decreasing trend under the regulation of carbon-based materials. Biochar reduced the accumulation of Cd in the grains, and the DF of Cd in the grains under the four carbon-based material treatments was between 0.045 and 0.061, showing a significant decreasing trend compared with the BL treatment. This is mainly because biochar contains various functional groups, including hydroxyl, carboxyl, and carbonyl groups, which fix Cd through surface complexation and other mechanisms [45]. In addition, biochar reduces Cd ionization through electrostatic attraction owing to its negative charge, which inhibits the transdielectric transfer of Cd at the soil–root interface [19].

Table 2. Heavy metal enrichment effect in plant organs.

Indexes	Treatments	Cd			As		
		Shoot	Leaf	Grain	Shoot	Leaf	Grain
Transfer Factor (TF)	BL	0.637 ± 0.034 a	0.239 ± 0.014 ab	0.063 ± 0.004 a	0.615 ± 0.024 a	0.247 ± 0.012 b	0.052 ± 0.003 a
	BC	0.427 ± 0.022 c	0.207 ± 0.008 c	0.036 ± 0.003 c	0.542 ± 0.018 b	0.254 ± 0.009 ab	0.043 ± 0.002 b
	LFB	0.463 ± 0.019 c	0.249 ± 0.011 a	0.041 ± 0.002 c	0.575 ± 0.023 ab	0.263 ± 0.013 a	0.049 ± 0.003 a
	MFB	0.492 ± 0.018 c	0.226 ± 0.009 b	0.044 ± 0.003 c	0.531 ± 0.027 b	0.227 ± 0.011 c	0.042 ± 0.002 b
	HFB	0.511 ± 0.023 b	0.217 ± 0.011 c	0.048 ± 0.002 b	0.497 ± 0.021 c	0.249 ± 0.010 ab	0.038 ± 0.002 c
Distribution Factor (DF)	BL	0.683 ± 0.031 ab	0.242 ± 0.012 c	0.075 ± 0.005 a	0.631 ± 0.019 c	0.305 ± 0.013 a	0.065 ± 0.004 a
	BC	0.646 ± 0.028 c	0.309 ± 0.009 a	0.045 ± 0.003 c	0.675 ± 0.021 b	0.267 ± 0.014 c	0.058 ± 0.003 b
	LFB	0.691 ± 0.034 a	0.256 ± 0.014 c	0.053 ± 0.003 c	0.664 ± 0.033 b	0.287 ± 0.011 b	0.049 ± 0.003 c
	MFB	0.637 ± 0.029 c	0.306 ± 0.015 a	0.057 ± 0.004 b	0.643 ± 0.028 c	0.312 ± 0.012 a	0.045 ± 0.002 c
	HFB	0.654 ± 0.024 b	0.285 ± 0.011 b	0.061 ± 0.002 b	0.702 ± 0.035 a	0.257 ± 0.016 c	0.041 ± 0.003 c
Bio-concentration Factor (BCF)	BL	1.596 ± 0.089 a	0.609 ± 0.023 a	0.162 ± 0.012 a	1.498 ± 0.058 a	0.573 ± 0.024 a	0.125 ± 0.008 a
	BC	1.247 ± 0.054 c	0.545 ± 0.019 b	0.089 ± 0.004 c	1.354 ± 0.061 b	0.552 ± 0.028 ab	0.106 ± 0.005 b
	LFB	1.474 ± 0.048 ab	0.496 ± 0.028 c	0.098 ± 0.005 c	1.297 ± 0.049 b	0.516 ± 0.031 c	0.093 ± 0.006 c
	MFB	1.368 ± 0.052 b	0.575 ± 0.023 ab	0.112 ± 0.005 b	1.176 ± 0.067 c	0.489 ± 0.021 c	0.082 ± 0.004 c
	HFB	1.438 ± 0.041 ab	0.521 ± 0.022 c	0.127 ± 0.008 b	1.223 ± 0.052 b	0.525 ± 0.018 b	0.079 ± 0.006 c

Note: lowercase letters indicate significant differences in the translocation and bioconcentration of Cd and As in various organs ($p < 0.05$).

The coupling effect of ferric chloride with biochar effectively reduced the transfer coefficient of As in plant organs. In the BL treatment, the transfer coefficient of As in the stems was 0.615, and in the BC, LFB, MFB, and HFB treatments, the transfer coefficient decreased by 11.87%, 6.51%, 13.66%, and 19.19%, respectively. With an increase in the ferric chloride proportion, the HFB treatment had the most apparent inhibitory effect on the As transfer process. Simultaneously, the modified biochar treatment significantly reduced the bioenrichment coefficient of As in cereals. Compared to the BL treatment, the bioenrichment coefficient of As in cereals under the LFB, MFB, and HFB treatments decreased by 25.60%, 34.40%, and 36.80%, respectively. As proposed by Cutler et al. [51], microorganisms in the soil can promote the reduction of iron in an anaerobic environment. When Fe(III) is reduced to Fe(II), As(III) is oxidized to As(V), thereby reducing the activity of AS in the soil. Doherty et al. [52] proposed that ferric chloride could reduce soil pH, increase the adsorption capacity of As in soil, reduce the exchange of As in soil, and slow down the enrichment effect of plants on As.

4. Discussion

4.1. Soil Water Retention Characteristics

The van Genuchten model was used to fit the soil–water characteristic curves under various treatment conditions. The fitting parameters of the crop seedlings and maturity stages are shown in Figure 5 and Table 3, respectively. In order to more intuitively reflect the change in soil water storage performance, we divided the soil water absorption stage

into two (i.e., the high suction stage, $2.52 < \text{Log}|\Psi_{\text{H}_2\text{O}} \text{ cm}| < 4.18$ ($300 < h < 15,000 \text{ cm H}_2\text{O}$) and low suction, $\text{Log}|\Psi_{\text{H}_2\text{O}} \text{ cm}| \leq 2.52$ ($h \leq 300 \text{ cm H}_2\text{O}$) or less). In general, soil drainage occurs mainly in the macropores of the low-suction section. Although the change in suction was small, it was sufficient to cause a significant change in the water content of the macroporous soil. However, only small pores in the soil can retain water in the high-suction section; therefore, the soil water content does not change significantly with suction [53,54].

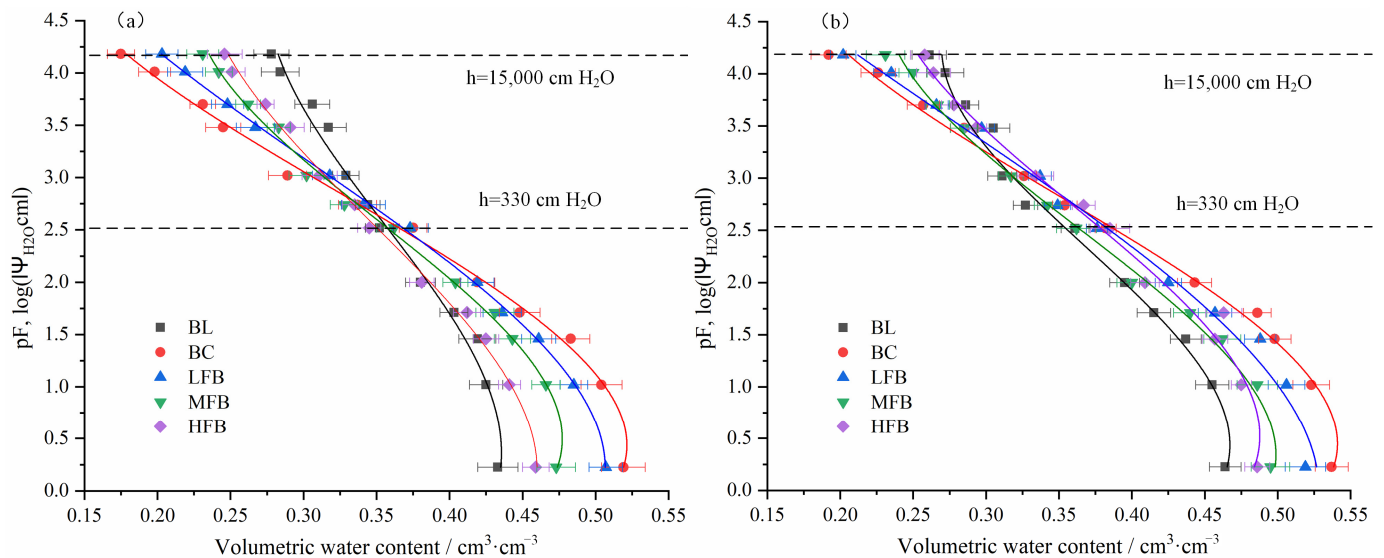


Figure 5. Soil water characteristic curves. (a) Soil water retention characteristics at the seedling stage and (b) soil water retention characteristics at maturity.

The fitting results of soil water characteristic parameters showed that the θ_s value of soil increased by 18.25%, 13.24%, 7.75%, and 5.99% in the BC, LFB, MFB, and HFB treatments, respectively, compared with the BL group, while the θ_r value of soil showed an opposite trend. As mentioned above, biochar improves soil water retention owing to an increase in total soil porosity and a change in the distribution of aggregates, thus increasing the water storage capacity of soil pores [37,55]. In addition, by comparing the difference in soil water storage in the high suction and low suction stages under different treatment conditions, we also found that the soil water storage capacity in different suction stages under the BC treatment was the largest, which further confirmed that the biochar–soil system affected particle accumulation and changed the mesoporous volume of soil. It also increased the availability of soil water [56,57]. Zhang et al. [58] found that the carbon-based materials improved soil water retention to varying degrees, and the effect was significant with an increase in biochar content.

Table 3. Soil moisture characteristic parameters.

Treatment	Seedling Stage				Maturity Stage			
	$\theta_s/\text{cm}^3 \cdot \text{cm}^{-3}$	$\theta_r/\text{cm}^3 \cdot \text{cm}^{-3}$	α/cm^{-1}	n	$\theta_s/\text{cm}^3 \cdot \text{cm}^{-3}$	$\theta_r/\text{cm}^3 \cdot \text{cm}^{-3}$	α/cm^{-1}	n
BL	44.26	14.59	0.0682	1.459	43.12	13.86	0.595	1.412
BC	52.34	8.64	0.0812	1.315	50.15	7.68	0.798	1.287
LFB	50.12	10.15	0.0768	1.368	48.92	9.57	0.659	1.336
MFB	47.69	11.59	0.0742	1.395	45.32	10.39	0.721	1.375
HFB	46.91	13.48	0.0616	1.425	44.37	12.11	0.863	1.356

4.2. Soil Cation Exchange Capacity

The CEC values of the soil samples under different treatment conditions are shown in Figure 6. First, under BL treatment, the CEC value of 0–10-cm soil at the seedling stage was $14.72 \text{ cmol} \cdot \text{kg}^{-1}$ while under BC treatment, the value significantly increased to $25.69 \text{ cmol} \cdot \text{kg}^{-1}$. Biochar application promoted the formation of soil aggregates and provided more ion adsorption sites, enhancing soil cation exchange capacity [59]. Under ferric chloride modification, the soil cation exchange capacity decreased to a certain extent. Compared with the BC treatment, soil cation exchange capacity under the LFB, MFB, and HFB treatments decreased by 13.74%, 27.01%, and 32.15%, respectively, but the values were still higher than that of the control group. This may be because the coupling between ferric chloride and biochar occupies some of the adsorption sites of biochar, hindering the exchange and adsorption between metal cations and soil particles [60,61]. Compared with previous studies, the improvement of soil cation exchange capacity by rice husk biochar is 8–10% [62], while the improvement effect of ferric chloride-modified biochar is significantly enhanced.

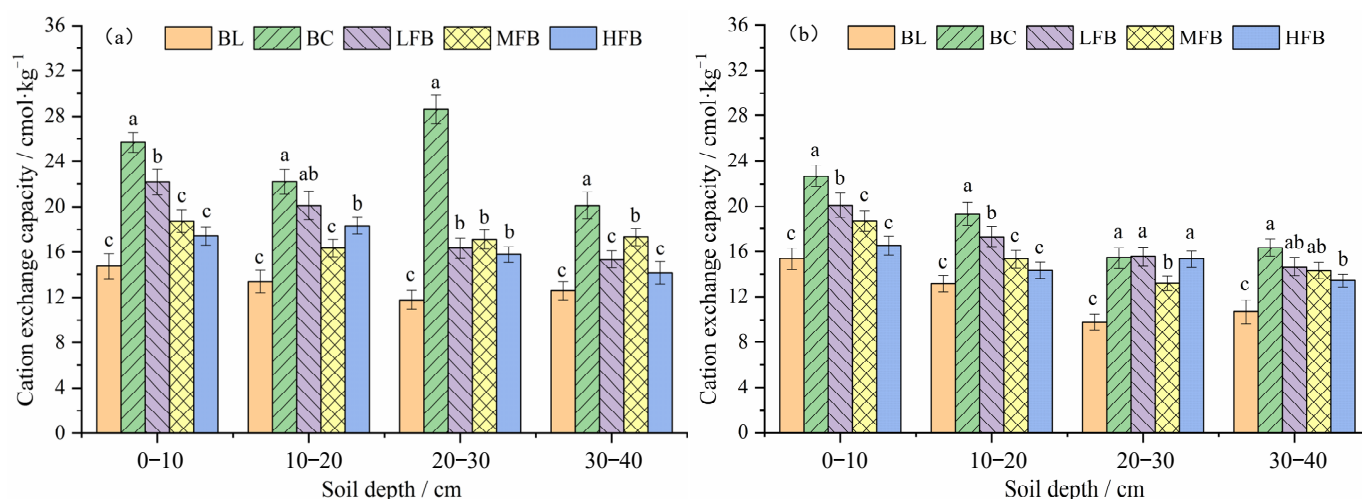


Figure 6. Soil cation exchange capacity. (a) Soil cation exchange capacity at the seedling stage and (b) soil cation exchange capacity at maturity. In addition, a, b, ab and c indicate that the parameters are significantly different under the same treatment ($p < 0.05$). BL, BC, LFB, MFB and HFB represent the treatments set up in the research.

4.3. Adsorption/Desorption Process of Modified Biochar

The adsorption isotherms of Cd and As at different concentrations of biochar and modified biochar are shown in Figure 7. The adsorption capacities for Cd and As increased with increasing mass concentrations of the equilibrium solution. When the equilibrium liquid concentration is low, the adsorption capacity increases rapidly with increasing mass concentration; when the equilibrium liquid mass concentration reaches a certain threshold value, the adsorption capacity increases slowly and finally reaches equilibrium [63]. This is because, under certain conditions, the soil adsorption sites for Cd and As are fixed. With an increase in metal concentration, the adsorption capacity also increases while the number of adsorption sites gradually decreases, and the adsorption capacity of the soil for metals decreases [64,65]. For Cd, the adsorption capacity of the original biochar was higher than that of the modified biochars (LFB, MFB, and HFB), whereas the adsorption capacity of the modified biochar was better than that of the original biochar.

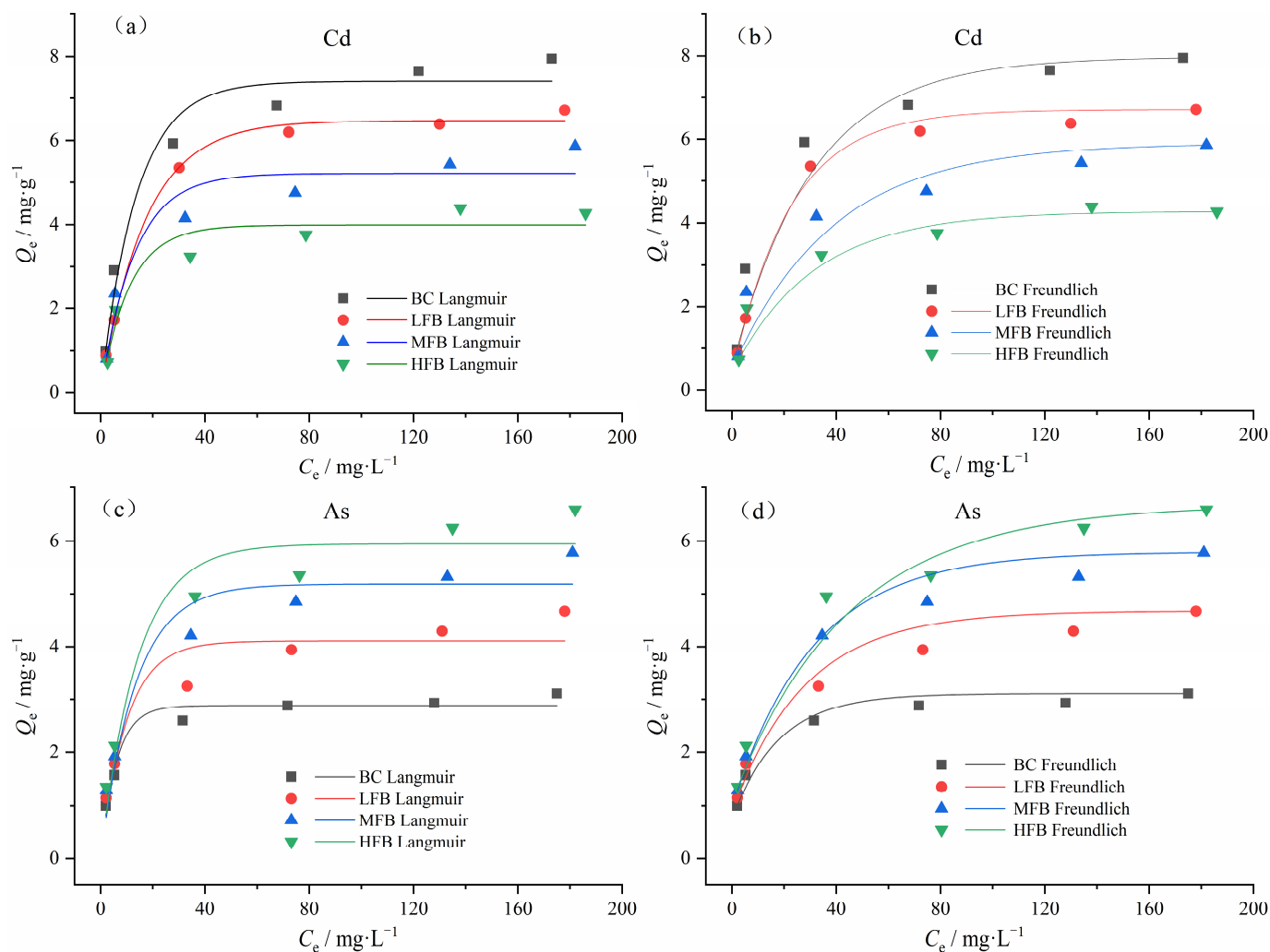


Figure 7. Isothermal adsorption model of Cd and As on carbon-based materials. (a) Langmuir isothermal adsorption curve of Cd, (b) Freundlich isothermal adsorption curve of Cd, (c) Langmuir isothermal adsorption curve of As, and (d) Freundlich isothermal adsorption curve of As.

The Langmuir and Freundlich equations were used to fit the adsorption isotherms, and the differences in the adsorption of Cd and As after biochar modification were compared. The fitting parameters are listed in Table 4. As shown in the table, the two isothermal adsorption equations have an extremely significant correlation with the degrees of fit for Cd and As in the four materials. Compared with the saturated adsorption capacity Q_m of Cd in the Langmuir equation, the Q_m of the BC material is increased by 13.10%, 20.91%, and 23.34% compared to those of LFB, MFB, and HFB, respectively. In addition, the adsorption capacity (K_f) of the BC material increased by 30.42~71.15% compared with the modified biochar material, indicating that the adsorption capacity of the original biochar for heavy metal Cd is better than that of the modified biochar. This is in line with the findings of Park et al. [66], who concluded that alkaline minerals in biochar carry negative charges on the surface and enhance the immobilization of Cd through precipitation or electrostatic action, thereby enhancing the ability of the material to retain Cd. In contrast, the saturated adsorption capacity of BC for As decreased by 7.89%, 30.12%, and 45.74% compared to those of LFB, MFB, and HFB, respectively. Meanwhile, the adsorption capacities (K_f) of various carbon-based materials for As were in the order of HFB > MFB > LFB > BC, from largest to smallest. This also confirms the previous inference that ferrous and manganese ions have nonlinear specific adsorption and adsorption effects on arsenic [67]. Most importantly, the organic combination of biochar and ferric chloride effectively solves the synergistic

immobilization relationship between arsenic and cadmium, and the effect is significantly better than that of using a single material alone. Moreover, soils with a high specific gravity content of biochar are unfavorable for the adsorption of As [68].

Table 4. Fitting parameters of the isothermal adsorption equation for Cd and As adsorbed by carbon-based materials.

Treatment	Heavy Metal Cd						Heavy Metal As					
	Langmuir Model			Freundlich Model			Langmuir Model			Freundlich Model		
	Q_m	K_l	R^2	K_f	n	R^2	Q_m	K_l	R^2	K_f	n	R^2
BC	0.613	0.472	0.905 *	1.792	3.257	0.927 *	0.478	0.357	0.923 *	1.104	4.784	0.931 *
LFB	0.542	0.533	0.949 *	1.374	3.096	0.952 **	0.519	0.281	0.956 **	1.133	3.598	0.981 **
MFB	0.507	0.395	0.973 **	1.244	2.890	0.937 **	0.684	0.412	0.971 **	1.292	3.389	0.967 **
HFB	0.497	0.372	0.968 **	1.047	3.521	0.935 *	0.881	0.339	0.965 **	1.407	3.279	0.952 *

Note: Asterisks denote a significant difference between different treatments: * $p < 0.05$, ** $p < 0.01$.

Overall, it can be concluded that ferric chloride-modified biochar can effectively enhance the water holding capacity of the soil root zone, suppress the synergistic effect of soil and water loss, and reduce the accumulation of heavy metals in plant fruits by simultaneously immobilizing As and Cd. This study is of great significance for improving the soil root zone microenvironment and ensuring the healthy and sustainable development of agricultural ecosystems [69,70].

5. Conclusions

The results showed that both the original and modified biochar could better hold soil water, reduce the free diffusion capacity of soil inorganic nitrogen and available phosphorus, and effectively inhibit the loss of soil water and fertilizer by 26.34~48.29% and 18.91~38.14%, respectively, during the crop growth period. Biochar enhanced soil water-holding performance and increased the available nitrogen and phosphorus contents through adsorption and ion exchange. The soil water and fertilizer retention effects from high to low were as follows: BC > HFB > MFB > LFB. Biochar is rich mainly in hydroxyl, carboxyl, and carbonyl functional groups. Cd is directly immobilized through surface complexation and immobilization to inhibit the enrichment of metals in plant organs, whereas some Fe^{3+} ions react directly with As to produce insoluble iron–arsenic compounds. In addition, the REDOX effect of Fe^{3+} promotes the conversion of As(III) into As(V). The As activity in the soil decreased; therefore, ferric chloride-modified biochar can significantly reduce the bioavailability of As. Based on the above factors, modified biochar can effectively reduce the concentrations of available As and Cd by 64.58~72.92% and 55.54~68.18%, respectively. What is more, it can be seen that LFB and MFB treatments can take into account the maintenance of soil water and fertilizer and the stabilization effect of the heavy metals Cd and As and are expected to become a long-term control technology model for farmland health caused by combined Cd and As pollution.

Author Contributions: Conceptualization, W.H., Y.J. and C.N.; data curation, Y.W. and C.F.; formal analysis, H.Z.; investigation, H.Z.; methodology, W.H.; resources, Y.J. and C.N.; software, C.F.; validation, C.N.; visualization, W.H. and Y.W.; writing—original draft, W.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (51779272), the Independent Research Project of State Key Laboratory of Simulations and Regulation of Water Cycle in River Basin (SKL2020ZY04), the Special Support Funds for National High-level Talents 60 (WR0166A012019), the Major Science and Technology Project of the Ministry of Water Resources (SKS-2022056), and the Water Conservancy Science and Technology Project of Guizhou Province (KT202314, KT202316 and KT202203).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data will be made available on request.

Acknowledgments: We would like to express our gratitude to the State Key Laboratory of Simulation and Regulation of Water Cycle in River Basin, China Institute of Water Resources and Hydropower Research, and the Guizhou Institute of Water Conservancy Science for their assistance in providing the experimental facilities and equipment for this study. We also thank the editor, associate editor, and reviewers for helpful comments.

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

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