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# Arsenic Immobilization for Paddy Field and Improvement of Rice (*Oryza sativa* L.) Growth through Cerium–Manganese Modified Wheat Straw Biochar Application

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**Abstract:** Arsenic (As) frequently emerges in paddy soils, necessitating measures to combat soil pollution and protect rice crops from As contamination. In this study, a novel functional biochar (MBC) by loading cerium manganese oxide was prepared, and its effects on soil As immobilization and As uptake by rice in two different As-contaminated paddy soils of 68.99 and 158.52 mgAs·kg$^{-1}$ (marked as soil-L and soil-H, respectively) were detected. The pot experiment manifested that MBC performed better in stabilizing soil As than original biochar. The incorporation of MBC facilitated the conversion of soil active As to the stable state, promoted the growth of rice plants, and reduced As uptake by rice. Specifically, the total plant biomasses for MBC treatment were increased by 16.13–70.07% and 12.36–92.58% in soil-L and soil-H compared with CK (without material input), respectively. MBC treatments resulted in a reduction of As contents by 34.67–60.13% in roots, 43.68–66.90% in stems, and 54.72–64.65% in leaves for soil-L. Furthermore, in soil-H, the As content in rice roots, stems, and leaves showed a decrease by 49.26–79.03%, 87.10–94.63%, and 75.79–85.71% respectively. This study provides important insights for the remediation of As-contaminated paddy soil using MBC.

**Keywords:** modified biochar; arsenic; immobilization; rice



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## 1. Introduction

Arsenic (As) pollution has emerged as a global environmental issue, and a large number of countries and regions are facing serious consequences [1,2]. China is one of the countries seriously affected by As pollution [3]. In addition to natural geochemical processes, emissions of As resulting from human activities, including industrial operations, mining waste, and intensified agricultural production, have become a significant concern [4,5]. According to the National Soil Contamination Bulletin (2014) conducted by the Ministry of Environmental Protection and the Ministry of Land and Resources of China, arsenic (As) is identified as one of the most hazardous heavy metal pollutants. It poses a significant threat to agricultural soils and human health due to its ability to accumulate in the food chain. Hunan province is known as a non-ferrous metal mine and a major rice (*Oryza sativa* L.) producing region in China, and some of its farmland soils have been polluted by As as a result of previous mining and metal processing activities, farmers are still growing crops in many regions with high As risk [6]. In previous reports, As concentration in paddy soils reached 34–2268 mg·kg$^{-1}$, significantly exceeding the standards of agricultural soil in China (30 mg·kg$^{-1}$) [7]. Due to its higher efficiency in absorbing and transporting As compared to other crops, rice is particularly susceptible to As contamination [8], and rice is one of the main ways humans consume arsenic through the food chain.

The safety of rice production in China has been seriously threatened. It has raised great concerns for the remediation of As polluted farmland and the reduction of As uptake by crops for food safety. From multiple perspectives, it is imperative to develop effective and environmentally friendly approaches for the remediation of As-contaminated soil.

Chemical immobilization presents a more viable technique for mitigating heavy metal-contaminated soil compared to bioremediation and phytoremediation, and the research and development of more efficient passivation materials is becoming the top priority [9–12]. In recent years, biochar has proven to be a successful tool for immobilizing heavy metals in soils. Biochar is a carbon-rich product derived from the pyrolysis of organic materials, such as crop straw and wood, under anoxic or anaerobic conditions [13–16]. Owing to its high porosity, extensive specific surface area, robust adsorption capacity, anti-oxidation, and resistance to biological decomposition, biochar is widely used in soil fertility improvement, carbon sequestration, emissions reduction, and remediation of heavy metal-contaminated soil [17–20]. Researchers found that in the As-contaminated soil, the application of biochar significantly decreased the arsenic (As) content in tomatoes ($p < 0.05$), and the biological toxicity and transfer risks were significantly reduced [21]. It is worth noting that biochar has great advantages with low cost and high adsorption capacity, but the immobilization performance of As is scant due to the limitations in surface chemical structure, pore structure, and functional groups [22], and remediation of As-contaminated soils with biochar remains a challenge [23]. Therefore, using certain methods to modify and design biochar to overcome its limitations and enhance its ability to fix As has become very important and crucial [24,25]. In recent years, numerous studies have focused on modifying biochar to enhance its adsorption capacity [25–27]. These modifications have resulted in biochar with increased surface area and improved functionality, thereby enhancing its effectiveness in remediating heavy metal-contaminated soil [28–30]. For instance, goethite-modified biochar has good adsorption performance for As in water, and the available As content in contaminated soil declined by 58.7% after goethite-modified biochar treatment [31]. Meanwhile, other research manifested that modified biochar not only significantly restricted the migration of As in the soil, reducing its accumulation in brown rice by 30% to 52%, but also increased the rice yield [32]. Overall, modified biochar has shown great advantages and good application potential for the remediation of As-contaminated soil.

Both manganese oxides and cerium oxides are promising materials that can be utilized for the remediation of As pollution in water bodies and soils [28,29]. Biochar modification of their single metal element and its use for arsenic pollution remediation have been reported in the past, and the remediation effect is excellent [27]. Therefore, in order to explore more effective technology for remediating As contaminated paddy soil, a novel composite material named cerium–manganese modified biochar (MBC) was manufactured by combining metal and rare earth oxides based on wheat straws. Although our previous research proved that MBC had much higher As(V) adsorption compacity than other materials [33], the impact of MBC on the mobility and transfer of arsenic (As) in the soil-rice system has not been fully understood. This study aims to investigate the effects of MBC application on the transformation of As species in soils and the uptake of As by rice plants through a pot experiment. The main objectives were to (1) clarify the effects of MBC on rice growth and nutrient accumulation; (2) explore the impacts of MBC on physiochemical properties of paddy soil; and (3) reveal the effect of MBC on As immobilization in soil and As uptake by rice plants. The results of this study will provide a scientific approach for the remediation of paddy soil contaminated with As.

## 2. Materials and Methods

### 2.1. Sample Preparation

The paddy soil used in this study was collected from a paddy field located near the realgar mine in Shimen County, Hunan Province, China. The soil samples were air-dried, sieved through a 2 mm mesh, and subsequently stored at room temperature. The process of preparing BC and MBC is described in a previous study [33]. The physicochemical properties of soil and biochar were shown in Table 1.

**Table 1.** Physicochemical properties of soil and biochar in the experiment.

| Properties | Soil-L | Soil-H | BC | MBC |
|---|---|---|---|---|
| pH | 6.59 | 6.42 | 9.26 | 6.06 |
| TN (Nitrogen) ($g \cdot kg^{-1}$) | 0.53 | 0.54 | 7.41 | 3.96 |
| TP (Phosphorus) ($g \cdot kg^{-1}$) | 0.51 | 0.60 | 2.64 | 1.00 |
| TK (Potassium) ($g \cdot kg^{-1}$) | 3.02 | 2.92 | 19.34 | 22.02 |
| TN (Soil organic matter) ($g \cdot kg^{-1}$) | 4.65 | 4.38 | 358 | 233 |
| As ($mg \cdot kg^{-1}$) | 68.99 | 158.52 | 0.11 | 0.10 |
| $S_{BET}$ ($m^2 \cdot g^{-1}$) | / | / | 5.53 | 6.88 |

Notes: $S_{BET}$, the specific surface area.

### 2.2. Experimental Design

Seeds of rice (*Oryza sativa* L. Zhuoliangyou 336) were sterilized in $H_2O_2$ for 30 min and then washed thoroughly with de-ionized water. Subsequently, seeds were placed in a petri dish that was then placed in an incubator at 30 °C until the dew white was transferred to the seedling tray to prepare rice nursery. After two weeks, the uniform-sized rice seedlings were selected to move to the plastic pots of 19–23 cm, which were filled with As-contaminated soil.

Fourteen treatments were prepared in triplicate within the pot trials, with different dosages of the biochar in soil and different As levels: control (CK); BC was added at a rate of 0.125% (0.125% BC), 0.25% (0.25% BC), 0.5% (0.5% BC) (*w*/*w*), different dosages of MBC were treated as above. Each treatment was replicated three times. Soil with low and high As concentrations were marked as soil-L and soil-H, respectively. Each treatment contained 3.00 kg of soil and varying amounts of BC or MBC. And the fertilizer was added to all the treatments with 0.2 $g \cdot kg^{-1}$ N ($CH_4N_2O$), 0.1 $g \cdot kg^{-1}$ $P_2O_5$ ($KH_2PO_4$), and 0.2 $g \cdot kg^{-1}$ $K_2O$ (KCl), respectively. The experiment was performed in the greenhouse of the Institute of Environment and Sustainable Development in Agriculture, CAAS Beijing. Fertilizer and biochar (BC and MBC) were thoroughly mixed with the soil and then deionized water was added to keep the soil in the flooded state. Throughout the entire growth period of rice, the paddy fields were flooded on a daily basis, maintaining a water layer of 3–5 cm during rice growth.

### 2.3. Chemical Analysis

#### 2.3.1. Analysis of Basic Physical and Chemical Properties

Soil physicochemical properties were analyzed following the procedures outlined in the study [34]. pH measurements were conducted using a pH meter. Water-soluble arsenic (Ws-As) was extracted from the soil samples using deionized water at a ratio of 1:10 (*w*/*v*). SOC was determined by the $K_2Cr_2O_7$ external heating method, the Kjeldahl method for TN, the molybdenum antimony anti-colorimetric method for TP, and flame atomic absorption for TK. In addition, soil-dissolved organic carbon (DOC) was quantified using an automatic analyzer specifically designed for liquid samples (Multi N/C3100 TOC-V CSN Analyzer, Analytik Jena, Jena, Germany). The soil samples were treated with the $HNO_3$-HCl digestion method (EPA 3010a), and total As was determined using a hydride generator-atomic fluorescence instrument HG-AFS (9120) (Beijing Jitian Instruments, Beijing, China) with a detection limit of 0.02 $\mu g \cdot L^{-1}$ and the standard curve correlation coefficient of 0.9998. And one standard reference soil, GBW07391(GSS-35) (National Research Center for Standards in China), was used for analytical quality control; the recoveries of the method ranged from 95.60% to 100.80%, which met the quality control requirements. Soil As forms were determined using the HPLC-HG-AFS (High-Performance Liquid Chromatography-Hydride Generation Coupled with Atomic Fluorescence Spectrometry) technique. Scanning electron microscopy (SEM) was used to observe the structural morphology of BC and MBC

(ZEISS Gemini 300, Jena, Germany) in Shiyanjia Lab (www.shiyanjia.com, accessed on 24 December 2022). The specific surface area ($S_{BET}$) was tested via a surface area analyzer (Quantachrome, Boynton Beach, FL, USA).

2.3.2. Plant Sampling and Analysis

After a two-month growth period, plant samples were collected and divided into roots, stems, and leaves. They were then rinsed with deionized water to remove impurities. Subsequently, the plant samples were dried in an oven at 105 °C for 30 min and further baked at 75 °C until a constant weight was achieved. For the analysis of arsenic (As) concentrations, the plant samples were digested using a mixture of $HNO_3$-HCl (EPA 3010a) and measured using atomic fluorescence spectroscopy. Nitrogen (N), phosphorus (P), and potassium (K) concentrations were determined by digesting the samples with $H_2SO_4$-$H_2O_2$ and analyzed using a flow analyzer for N and P and a flame photometer for K.

2.3.3. As Fraction

As fractions were analyzed in accordance with the sequential extraction procedure described by the previous study [35]. The As fractions were extracted through the following five steps: (F1: non-specifically adsorbed) Soil sample (1 g) and $(NH_4)_2SO_4$ (0.05 M) were added to a 50-mL centrifuge tube and shaken at 25 °C for 4 h, then centrifuged to obtain the extract and solid residue was further shaken with ultra-pure water and centrifuged. (F2: specifically adsorbed) Solid residue from Step 1 and $NH_4H_2PO_4$ (0.05 M) solution were mixed and shaken at 25 °C for 16 h. The extract and solid residue were obtained as described in Step 1. (F3: amorphous and poorly crystalline hydrous oxides of Fe and Al) $NH_4^+$-oxalate buffer solution (0.2 M) was added to solid residue from Step 2 and shaken for 4 h. (F4: well-crystallized hydrous oxides of Fe and Al) Solid residue from Step 3 and ascorbic acid (0.1 M) + $NH_4^+$-oxalate buffer solution (0.2 M) were mixed and incubated at 96 °C for 0.5 h. (F5: residual As) Solid residue from Step 4 was digested in an acid mixture ($HNO_3$-HCl) in a digestion system to obtain the extract.

*2.4. Data Analysis*

Statistical analysis was conducted using SPSS 22.0 software. One-way analysis of variance (ANOVA) was employed, and Duncan's multiple comparisons were performed ($p \leq 0.05$). Plotting was carried out by using Origin (ver. 9.5).

The immobilization efficiency ($\eta$) of soil available As by biochar material was calculated as (1):

$$\eta(\%) = \frac{C_0 - C_e}{C_o} \times 100\% \quad (1)$$

where $C_0$ and $C_e$ are the available As content (mg·kg$^{-1}$) of the control soil and the soil sample with charcoal material, respectively.

Bioconcentration factors (*BCF*) were utilized to assess the capacity of rice plants to uptake and accumulate arsenic (As) from the soil. The *BCF* was calculated using the following Formula (2):

$$BCF = \frac{C_{root/stem/leaf}}{C_{soil}} \quad (2)$$

where $C_{root/stem/leaf}$ and $C_{soil}$ are the total As content in the root, stem, or leaf of the rice (mg·kg$^{-1}$) and the total As content in the soil (mg·kg$^{-1}$), respectively.

Translocation factors (*TF*) of As from root to shoot were calculated by the Formulas (3) and (4):

$$TF_{root-stem} = \frac{C_{stem}}{C_{root}} \quad (3)$$

$$TF_{root-leaf} = \frac{C_{leaf}}{C_{root}} \quad (4)$$

where $C_{root}$, $C_{stem}$, and $C_{leaf}$ represent the total As content in the different tissues of the rice ($mg \cdot kg^{-1}$), respectively.

The mobility factor $M$ indicates the transport properties of exchangeable As in soil [36]; the $M$ value was calculated using the following Equation (5):

$$M = \frac{F1 + F2}{F1 + F2 + F3 + F4 + F5}\% \quad (5)$$

$F1$–$F5$ ($mg \cdot kg^{-1}$) were the As contents of five fractions.

## 3. Results

### 3.1. Soil Physiochemical Properties

As shown in Table 2, almost all the soil quality parameters like SOC, TN, available phosphorus (AP), and available potassium (AK) increased after being treated with either MBC or BC. For soil pH under these two different soil types, the application of MBC led to a decrease but enhancement for BC treatment. Meanwhile, DOC all obviously declined. At the dosage of 0.5% in soil-L, the soil SOC, TN, and AK were greatly improved by 26.71%, 12.30%, and 50.86%, respectively, compared with CK when MBC applied into soils. In soil-H, 0.5% MBC enhanced the soil SOC, TN, AK, and AP by 33.76%, 23.73%, 119.51%, and 54.50%, respectively. The soil pH and DOC concentrations were decreased by 4.20% and 37.56% in soil-L ($p < 0.05$), while 0.5%BC treatment increased DOC by 15.23% and 30.24% in soil-L and soil-H. To improve soil quality by improving nutrient supply, the function of MBC is similar to BC, though they exhibited opposite patterns in soil pH and DOC.

**Table 2.** Effects of different treatments on soil physic-chemical properties.

| Treatments | | SOC $g\ kg^{-1}$ | TN $g\ kg^{-1}$ | AP $mg\ kg^{-1}$ | AK $mg\ kg^{-1}$ | DOC $mg\ kg^{-1}$ | pH / |
|---|---|---|---|---|---|---|---|
| L | CK | 4.77 ± 0.09 d | 0.83 ± 0.02 bc | 7.37 ± 0.52 abc | 154.67 ± 2.40 e | 37.81 ± 1.10 e | 6.75 ± 0.04 b |
| | 0.125%BC | 5.00 ± 0.03 cd | 0.83 ± 0.03 c | 6.53 ± 0.15 c | 156.00 ± 3.51 e | 36.86 ± 1.31 b | 6.93 ± 0.09 a |
| | 0.25%BC | 5.44 ± 0.13 c | 0.85 ± 0.02 abc | 7.67 ± 0.58 ab | 154.67 ± 2.40 e | 38.08 ± 0.61 b | 6.94 ± 0.05 a |
| | 0.5%BC | 6.67 ± 0.06 a | 0.92 ± 0.01 ab | 8.30 ± 0.32 a | 168.00 ± 1.00 d | 43.56 ± 3.31 a | 6.97 ± 0.03 a |
| | 0.125%MBC | 4.59 ± 0.14 d | 0.85 ± 0.00 abc | 7.73 ± 0.23 ab | 178.33 ± 0.33 c | 36.90 ± 0.99 b | 6.72 ± 0.01 bc |
| | 0.25%MBC | 5.05 ± 0.25 cd | 0.92 ± 0.01 a | 6.90 ± 0.10 bc | 191.67 ± 3.53 b | 34.66 ± 1.41 b | 6.61 ± 0.03 c |
| | 0.5%MBC | 6.05 ± 0.30 b | 0.93 ± 0.06 a | 7.80 ± 0.21 ab | 233.33 ± 5.36 a | 23.61 ± 0.82 c | 6.47 ± 0.01 d |
| H | CK | 4.66 ± 0.25 c | 0.71 ± 0.00 c | 7.40 ± 0.15 c | 95.67 ± 4.98 d | 42.07 ± 1.64 bc | 6.82 ± 0.06 a |
| | 0.125%BC | 4.76 ± 0.13 c | 0.77 ± 0.02 c | 14.47 ± 1.97 a | 174.00 ± 14.64 b | 41.51 ± 1.02 bc | 6.84 ± 0.03 a |
| | 0.25%BC | 6.23 ± 0.06 b | 0.73 ± 0.03 c | 7.90 ± 0.76 c | 93.33 ± 1.45 d | 46.39 ± 2.24 b | 6.87 ± 0.02 a |
| | 0.5%BC | 7.10 ± 0.21 a | 0.95 ± 0.03 a | 10.17 ± 2.47 bc | 168.00 ± 2.65 b | 54.79 ± 2.18 b | 6.90 ± 0.04 a |
| | 0.125%MBC | 5.10 ± 0.16 c | 0.77 ± 0.00 c | 12.33 ± 0.38 ab | 172.33 ± 0.67 b | 40.29 ± 1.30 cd | 6.76 ± 0.03 a |
| | 0.25%MBC | 5.11 ± 0.27 c | 0.74 ± 0.03 c | 9.20 ± 1.47 bc | 135.00 ± 6.11 c | 38.23 ± 1.80 cd | 6.65 ± 0.22 a |
| | 0.5%MBC | 6.24 ± 0.09 b | 0.88 ± 0.02 b | 11.43 ± 0.93 abc | 210.00 ± 5.57 a | 36.19 ± 1.40 d | 6.62 ± 0.01 a |

Note: The error indicates the standard deviation. The same letter represents non-significant differences, whereas different letters represent significant differences (LSD Test; $p < 0.05$).

### 3.2. Ws-As in Soils

Ws-As is one of the main available forms of As and is readily absorbed by plants [36]. As shown in Figure 1, it was obvious that different doses of MBC had various effects on the Ws-As content in the soil. From Figure 1, it can be seen that Ws-As concentrations decreased with applied MBC improved. For soil-L treated with MBC of 0.125% to 0.5%, the As immobilization efficiency ranged from 11.36% to 35.10%, and for soil-H, the As immobilization efficiency reached 11.07–27.12%. Corresponding to the above pattern, the As species with water extraction like As(III) and As(V) in soils amended with MBC at the rate of 0.125–0.5% decreased by 63.01–75.09% and 15.18–34.81%, respectively ($p < 0.05$) (Figure S1). On the contrary, the application of original BC had caused Ws-As content to increase to some extent, unlike MBC, causing great reduction.

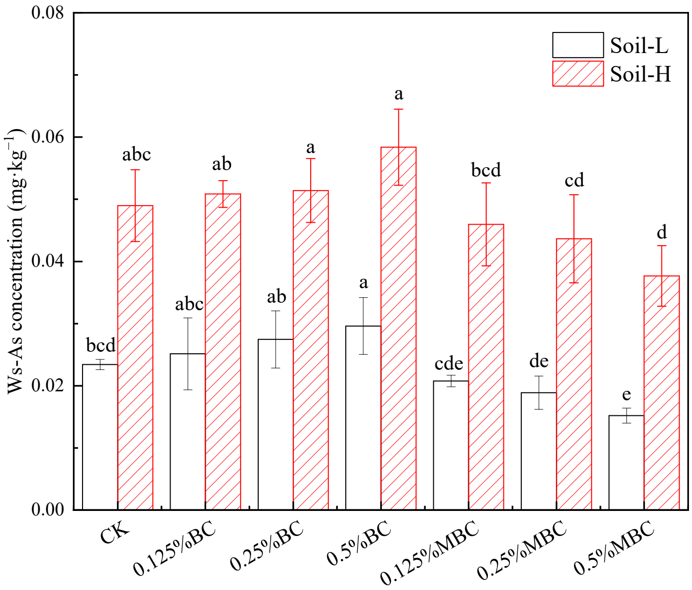


**Figure 1.** Effects of materials under different amendments at seeding stage on Ws-As concentration in soil. Note: The error indicates the standard deviation. The same letter represents non-significant differences, whereas different letters represent significant differences (LSD Test; $p < 0.05$).

### *3.3. As Fractions*

As shown in Figure 2, As forms in soil are mainly presented in F3 and F5. Compared with CK, the application of MBC caused a sharp decrease in the As concentration in F1 and F2 forms in the soil. MBC resulted in a significant decrease of 67.60% and 28.47% in F1 and F2 and an increase of 39.31% and 14.36% in F4 and F5 at 0.5% addition for soil-L ($p < 0.05$). Although 0.5%BC reduced the F1 in soil-L by 46.42%, after being treated with 0.125–0.5%MBC, the F1 in soil-H decreased by up to 61.20%, and 0.5%MBC treatment increased F5 by 24.43%, respectively. Correspondingly, the mobility factor (M value) of As also decreased, indicating that MBC caused an obvious passivation of As and a decrease in the mobility of As in the soil ($p < 0.05$) (Table 3). 0.5% MBC treatment reduced the *M* values from 21.80% (CK) to 15.14% in soil-L and from 24.61% (CK) to 20.75% in soil-H, respectively. In comparison with BC, the newly manufactured MBC promoted the more active As to a stable forms in soil, thus reducing the bioavailability of soil As. Though the application of BC can stabilize arsenic to some extent, MBC showed more excellent immobilization ability by converting much more active As into more stable As forms in paddy soils with less M values.

**Table 3.** Effects of amendments on mobility factor M.

| Soil | CK | 0.125%BC | 0.25%BC | 0.5%BC | 0.125%MBC | 0.25%MBC | 0.5%MBC |
|---|---|---|---|---|---|---|---|
| Soil-L | 21.80% | 17.63% | 18.67% | 18.12% | 18.21% | 17.20% | 15.14% |
| Soil-H | 24.61% | 23.13% | 20.11% | 19.51% | 25.05% | 21.92% | 20.75% |

### *3.4. Rice Biomass and Nutrient Accumulation*

The addition of MBC and BC both significantly raised the biomass of total rice plant and root ($p < 0.05$) (Table 4). For soil-L, compared to CK, MBC treatment increased the total plant by 16.13–70.07% and improved the root biomass by 19.13–50.23%. In soil-H, MBC treatments also improved rice biomass, especially for 0.5% dosage; the total rice plant and root increased by 187.17% and 50.34%, respectively. The results were similar for the BC treatment, the increased percentage of biomass ranged from 27.81% to 64.88% for the total plant, and the root biomass was enhanced from 17.49% to 39.20% in comparison with CK. Thus, it can be concluded that the addition of MBC effectively enhanced the biomass of rice at the seeding stage and facilitated the growth of the crop.

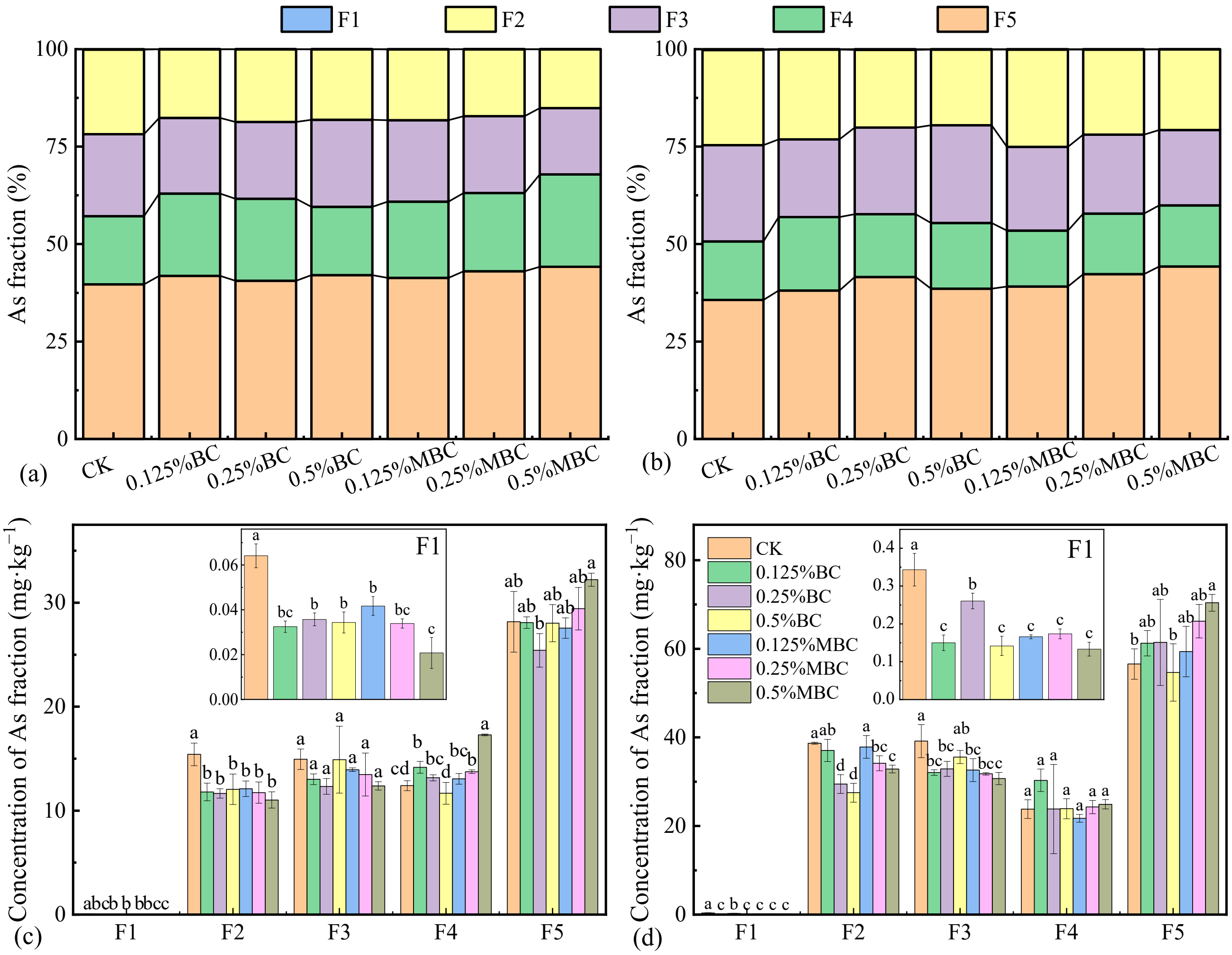


**Figure 2.** Effects of amendments on the proportion and concentrations of As fractions in soil. (**a**,**c**) represent low levels of As-contaminated soil, and (**b**,**d**) represent high levels, respectively. Note: The error indicates the standard deviation. The same letter represents non-significant differences, whereas different letters represent significant differences (LSD Test; $p < 0.05$).

**Table 4.** Effects of amendments on rice biomass.

| Treatments | Total Plant (g) | | Root (g) | |
|---|---|---|---|---|
| | Soil-L | Soil-H | Soil-L | Soil-H |
| CK | 7.39 ± 0.74 c | 6.47 ± 0.87 d | 1.42 ± 0.24 c | 1.47 ± 0.18 b |
| 0.125%BC | 9.45 ± 0.35 b | 7.27 ± 0.89 d | 1.67 ± 0.04 bc | 1.62 ± 0.06 b |
| 0.25%BC | 11.32 ± 0.61 a | 11.65 ± 0.61 b | 1.74 ± 0.19 bc | 1.72 ± 0.25 ab |
| 0.5%BC | 12.18 ± 0.54 a | 12.46 ± 1.08 b | 1.98 ± 0.21 ab | 1.96 ± 0.15 ab |
| 0.125%MBC | 8.58 ± 0.98 bc | 10.21 ± 0.79 c | 1.69 ± 0.21 bc | 1.63 ± 0.19 b |
| 0.25%MBC | 11.37 ± 0.96 a | 12.40 ± 0.38 b | 1.89 ± 0.18 ab | 1.76 ± 0.28 ab |
| 0.5%MBC | 12.57 ± 0.62 a | 18.58 ± 0.54 a | 2.13 ± 0.19 a | 2.21 ± 0.53 a |

Note: The error indicates the standard deviation. The same letter represents non-significant differences, whereas different letters represent significant differences (LSD Test; $p < 0.05$).

For the nutrient accumulation in different parts of rice, the addition of MBC significantly raised the accumulation of total N, P, and K in rice roots, stems, and leaves, as well as BC. The accumulation content was significantly enhanced with the dosage of biochar or MBC increased ($p < 0.05$) (Figure 3). Compared to the control treatment CK for soil-H, application dosage of 0.125% to 0.5% MBC caused the N, P, and K accumulation of rice roots were increased by 6.47–44.72%, 12.58–74.23%, and 31.27–116.80%. In contrast, BC application also caused enhancement of the N, P, and K in rice roots with percentages of 3.67–18.94%, 5.17–33.87%, and 5.79–58.97%, respectively. In total, MBC exhibited the highest nutrient accumulation, indicating that the incorporation of MBC can promote the uptake and utilization of N, P, and K by rice to a certain extent, which is beneficial to the growth of rice.

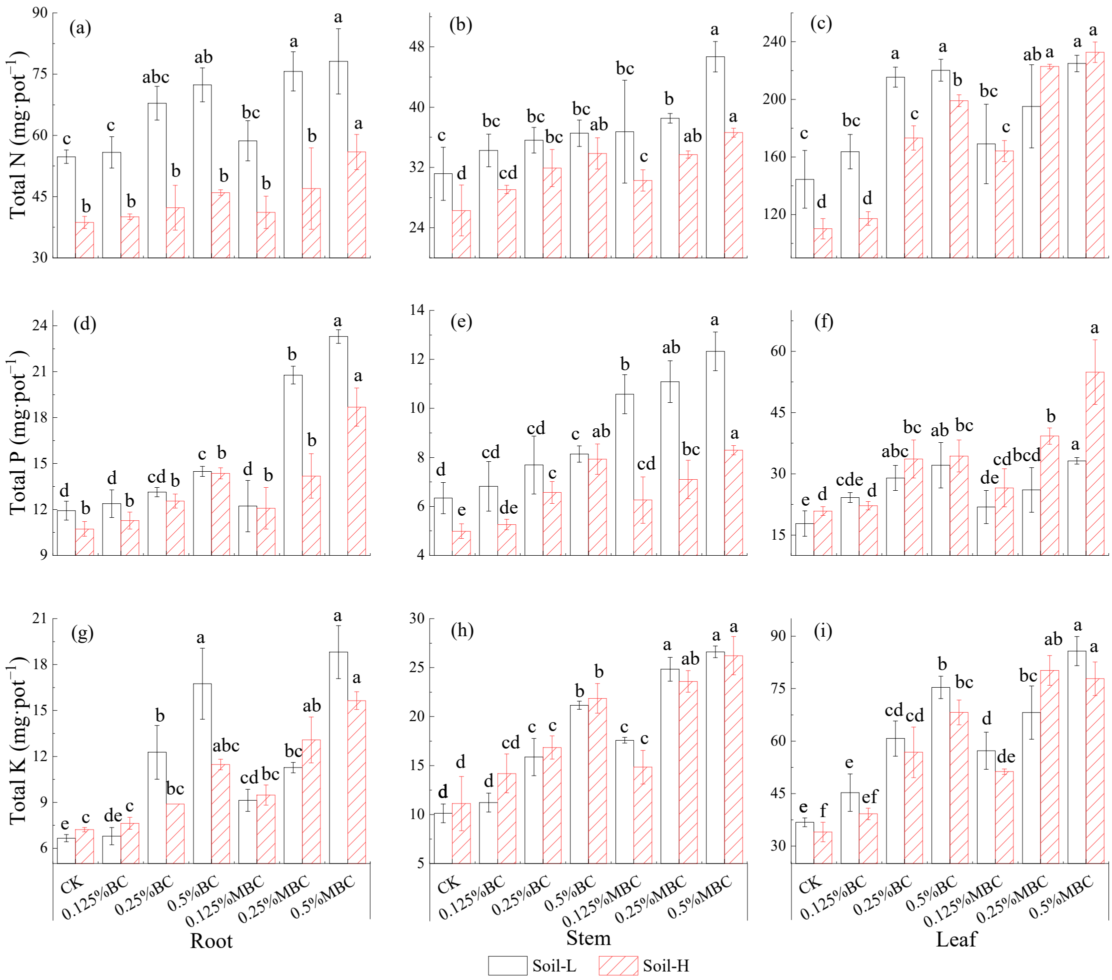


**Figure 3.** Effect of different amendments on nutrient accumulation in different tissues of rice. (**a**–**c**) were total N in root, stem, and leaf, respectively. (**d**–**f**) were total P in root, stem, and leaf, respectively. (**g**–**i**) were total K in root, stem, and leaf, respectively. Note: The error indicates the standard deviation. The same letter represents non-significant differences, whereas different letters represent significant differences (LSD Test; $p < 0.05$).

### *3.5. As Uptake, Enrichment, and Transfer Coefficients in Rice Plants*

Under various treatments with MBC and BC, shown in Figure 4, there are significant differences in the effects on arsenic absorption by rice. For two different levels of As-contaminated soils, MBC treatments declined the As content in rice parts. As uptake amount in different parts of rice ranked as follows: root > stem > leaf (Figure 4). With the addition of MBC increased, As uptake by rice plants decreased significantly ($p < 0.05$). When the soil-L was amended with 0.5% MBC, As content in root, stem, and leaf was significantly decreased by 60.13%, 66.99%, and 64.71%, separately, and0.5%MBC in soil-H also reduced the As concentrations in the rice root, stem, and leaf by 79.03%, 94.63%, and 85.68%, respectively, compared with CK ($p < 0.05$). For BC treatment under 0.5% dosage, the As content for different parts of rice was also reduced to a certain degree, while MBC is more effective in fixing arsenic and inhibiting As adsorption of root and rice seedlings.

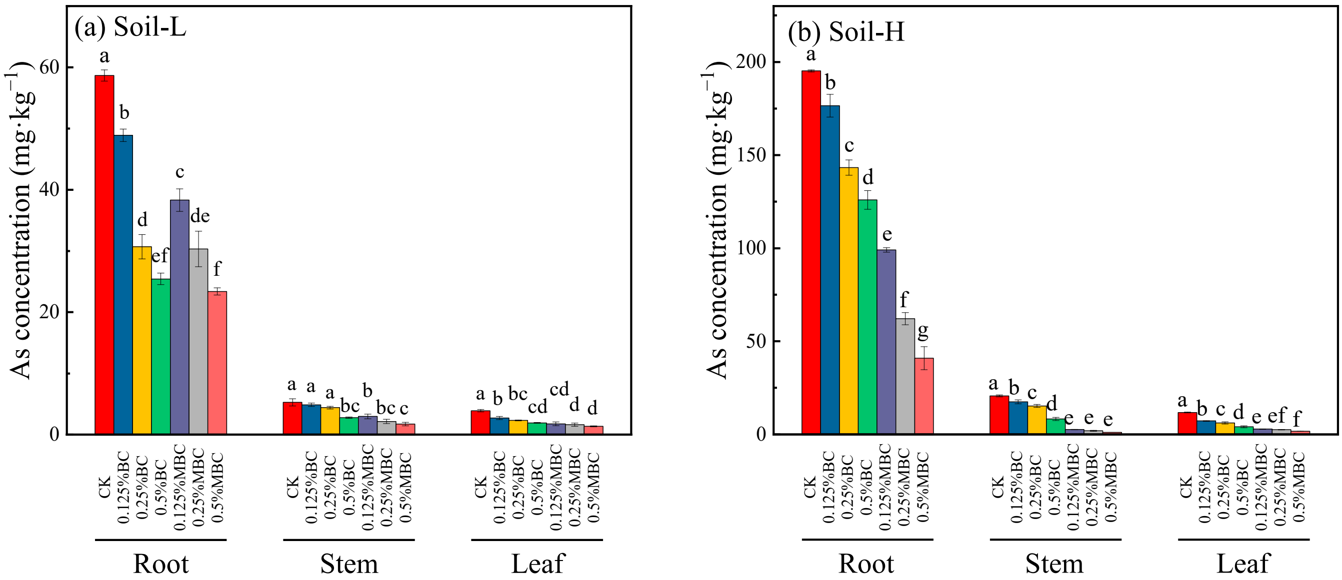


**Figure 4.** As concentrations in rice in different tissues. (**a**): soil-L, (**b**): soil-H. Note: The error indicates the standard deviation. The same letter represents non-significant differences, whereas different letters represent significant differences (LSD Test; $p < 0.05$).

Besides, MBC and BC application also had a great influence on the enrichment coefficients of soil-root, soil-stem, and soil-leaf for grown rice (*Oryza sativa* L.). For example, 0.5%MBC in soil-L reduced the enrichment coefficients of soil-root, soil-stem, and soil-leaf by 60.39%%, 65.21%, and 62.50%, respectively, compared with CK (Table 5). Under the 0.125–0.5% BC treatment in soil-L, the enrichment coefficients for root, stem, and leaf were reduced by 16.47–56.86%, 8.70–47.83%, and 331.24–43.75%, respectively compared with CK. In addition, under the treatment of MBC treatment in soil-H, the enrichment coefficients of soil-root, soil-stem, and soil-leaf decreased by 48.78–78.86%, 84.62–92.31%, and 71.43–85.71%, respectively ($p < 0.05$). In comparison with blank, the transfer coefficients of root-stem and root-leaf with 0.5%MBC treatment were decreased by 72.73% and 33.33%, respectively ($p < 0.05$). Comparatively speaking, the *BCF* and *TF* were lower in MBC treatments than that observed in BC treatment. Therefore, MBC was more beneficial for the safe production of rice in As-contaminated soil.

**Table 5.** Effects of treatments on As bioconcentration factors and translocation factors.

| Type | Treatments | $BCF_{soil\text{-}root}$ | $BCF_{soil\text{-}stem}$ | $BCF_{soil\text{-}leaf}$ | $TF_{root\text{-}stem}$ | $TF_{root\text{-}leaf}$ |
|---|---|---|---|---|---|---|
| Soil-L | CK | 0.85 ± 0.012 a | 0.08 ± 0.009 a | 0.05 ± 0.003 a | 0.09 ± 0.010 bcd | 0.07 ± 0.007 ab |
| | 0.125%BC | 0.71 ± 0.015 b | 0.07 ± 0.006 a | 0.04 ± 0.003 b | 0.1 ± 0.006 bc | 0.06 ± 0.009 ab |
| | 0.25%BC | 0.44 ± 0.027 d | 0.07 ± 0.003 a | 0.03 ± 0.003 bc | 0.14 ± 0.007 a | 0.07 ± 0.003 a |
| | 0.5%BC | 0.37 ± 0.015 e | 0.04 ± 0.000 b | 0.03 ± 0.000 bc | 0.11 ± 0.000 b | 0.08 ± 0.003 a |
| | 0.125%MBC | 0.56 ± 0.027 c | 0.04 ± 0.006 b | 0.03 ± 0.003 cd | 0.08 ± 0.010 cd | 0.06 ± 0.009 b |
| | 0.25%MBC | 0.44 ± 0.042 d | 0.03 ± 0.006 b | 0.03 ± 0.003 cd | 0.07 ± 0.010 d | 0.06 ± 0.012 ab |
| | 0.5%MBC | 0.34 ± 0.009 e | 0.03 ± 0.003 b | 0.02 ± 0.000 d | 0.07 ± 0.009 d | 0.06 ± 0.006 ab |
| Soil-H | CK | 1.23 ± 0.006 a | 0.13 ± 0.003 a | 0.07 ± 0.003 a | 0.11 ± 0.003 a | 0.06 ± 0.000 a |
| | 0.125%BC | 1.11 ± 0.039 b | 0.11 ± 0.006 b | 0.05 ± 0.003 b | 0.10 ± 0.009 a | 0.04 ± 0.000 bc |
| | 0.25%BC | 0.90 ± 0.024 c | 0.10 ± 0.003 c | 0.04 ± 0.006 b | 0.11 ± 0.009 a | 0.04 ± 0.003 b |
| | 0.5%BC | 0.79 ± 0.032 d | 0.05 ± 0.006 d | 0.02 ± 0.003 c | 0.07 ± 0.012 b | 0.03 ± 0.003 bc |
| | 0.125%MBC | 0.63 ± 0.007 e | 0.02 ± 0.000 e | 0.02 ± 0.000 cd | 0.03 ± 0.000 c | 0.03 ± 0.000 c |
| | 0.25%MBC | 0.39 ± 0.022 f | 0.01 ± 0.003 e | 0.02 ± 0.003 cd | 0.03 ± 0.003 c | 0.04 ± 0.003 b |
| | 0.5%MBC | 0.26 ± 0.038 g | 0.01 ± 0.000 e | 0.01 ± 0.000 d | 0.03 ± 0.006 c | 0.04 ± 0.008 b |

Note: The error indicates the standard deviation. The same letter represents non-significant differences, whereas different letters represent significant differences (LSD Test; $p < 0.05$).

### *3.6. Relationships between Soil Physicochemical Properties and As Bioavailability*

The correlation graph clearly showed a strong negative relationship between pH and Ws-As. Among various fractions of As, F1-As, and F2-As were highly positively related to root As, stem As, and leaf As in soil-L. Also, AK was negatively associated with F1-As and remarkably negatively correlated with rice plant As ($p < 0.01$) (Figure 5). Moreover, soil nutrients were positively correlated with rice nutrient accumulation in soil-L and soil-H (Figure S2). Soil nutrients positively affected the biomass of different parts of the rice plant. In Figure S3a–d, the positive correlation between pH and Ws-As was verified using linear correlation analysis (soil-L: $r^2 = 0.9416$, $p < 0.001$; soil-H: $r^2 = 0.8532$, $p < 0.01$), and DOC was extremely negatively correlated with Ws-As (soil-L: $r^2 = 0.7402$, $p < 0.01$; soil-H: $r^2 = 0.8377$, $p < 0.01$).

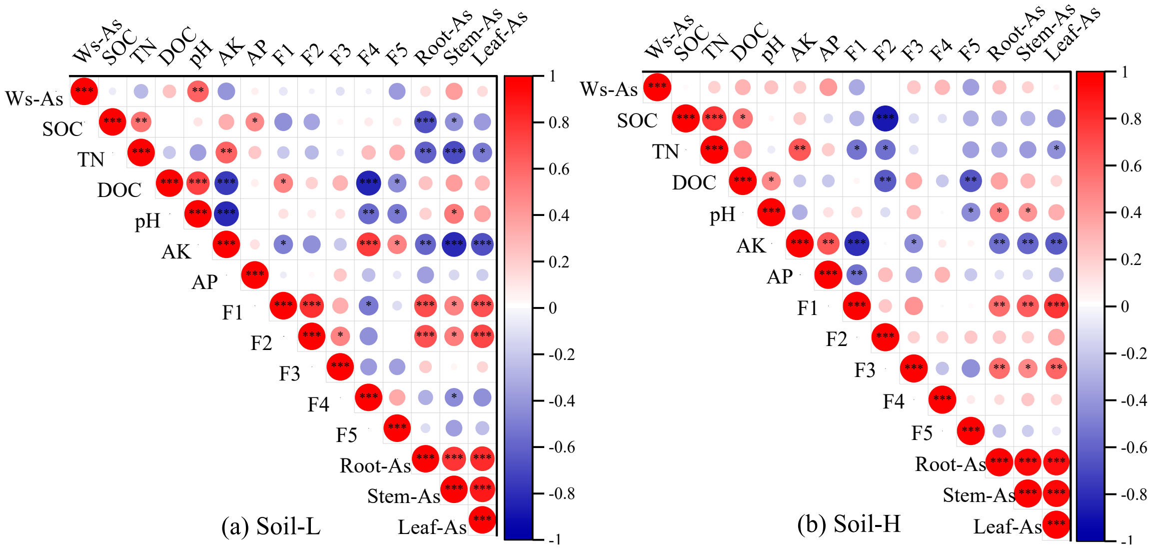


**Figure 5.** Correlation heat map of As bioavailability and soil properties. (**a**): soil-L, (**b**): soil-H. Blue and red represent negative and positive correlations, respectively. Darker shades indicate stronger correlations. *, $p < 0.05$, **, $p < 0.01$, ***, $p < 0.001$.

The correlation graph was conducted to clarify the correlation among multiple indexes (Figure 5), and the graph illustrated that F1 was extremely positively correlated with rice As (Root-As, Stem-As, and Leaf-As). Furthermore, TN and AK were significantly negative with rice As in soil-L, and a similar trend for AK appeared in soil-H. The Redundancy analysis (RDA) was utilized to identify potential environmental factors influencing the uptake of arsenic (As) in different tissues of rice (Figure 6). For soil-L, RDA1 and RDA2 explained 86.18% and 0.45% of the total variations in soil properties, respectively. In terms of soil-H, the first and second axes accounted for 80.76% and 0.12%, respectively. Furthermore, rice As was significantly influenced by F1 and TN for soil-L (F1: 48.1%, F = 17.6, $p = 0.002$; TN: 23.5%, F = 14.9, $p = 0.002$), for soil-H, F1 and Ws-As were significantly affected to rice As (F1: 33.7%, F = 9.7, $p = 0.006$; Ws-As: 23.5%, F = 9.9, $p = 0.004$). Consequently, among all the soil properties, F1 played a crucial role in regulating the uptake of As by rice plants.

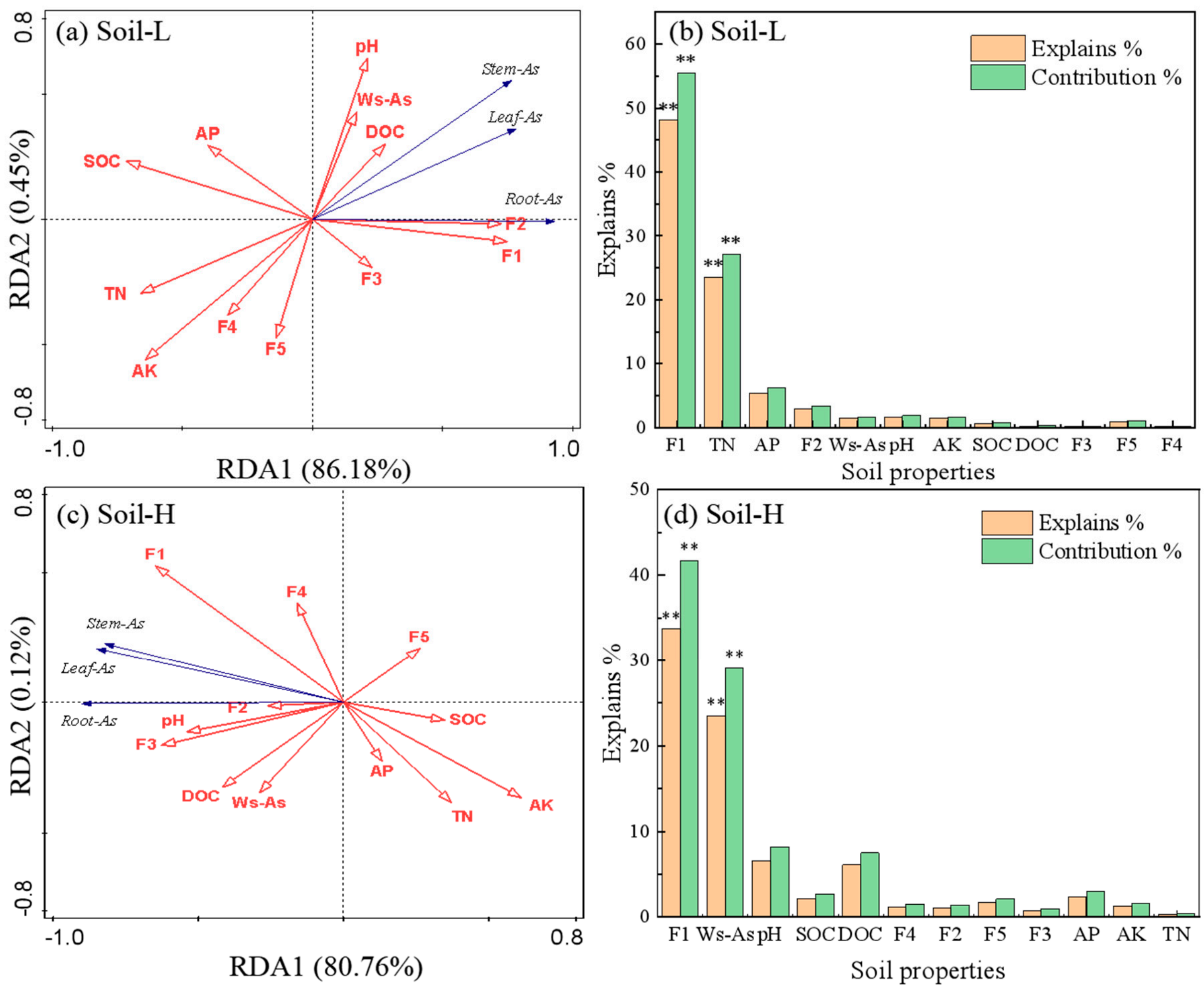


**Figure 6.** RDA of the correlations between soil properties and rice As ((**a**,**b**): soil-L; (**c**,**d**): soil-H). **, $p < 0.01$.

## 4. Discussion

### *4.1. MBC-Mediated Effects on Rice Growth and Nutrient Uptake*

The above results suggested that the addition of MBC at low application rates could achieve significant positive effects on the rice biomass and nutrient accumulation. The reasons were various. Arsenic stress led to a significant reduction in the uptake of nitrogen and potassium in rice, which in turn affected rice growth, whereas this negative effect was greatly reduced by MBC. Biochar, a multifunctional material, can influence nutrients in the soil by various means. For example, as a nutrient source, biochar can supply the macro-nutrients, secondary nutrients, and micronutrients for soil microorganisms and crops [37,38]. Also, biochar can alter the soil properties and improve the soil's capacity to retain nutrients through its unique physico-chemical properties, thus releasing nutrients slowly and influencing element availability for plants [18,39].

Biochar has been widely used in agricultural soils to improve the bioavailability of nitrogen and promote crop growth in recent years [38]. Previous studies have demonstrated that the addition of biochar and its composites to heavy metal-contaminated soils can effectively supply nutrients to crops, improve soil physical and chemical properties, and enhance crop growth concurrently [39,40]. In the present study, the increase in biomass can be attributed to the enhanced soil fertility resulting from the application of MBC, consistent with the findings that biochar-based compound fertilizer could improve soil fertility and maize growth [41]. We speculated that the application of MBC enriched the functional microorganisms related to nutrient transformation, thus increasing nutrient bioavailability and improving plant growth. In addition, As stress affected crop nutrient uptake, but modified biochar enhanced nutrient uptake while mitigating As stress, thus being more favorable to crop growth [42]. MBC also provides plants with a certain amount of manganese, which promotes plant growth [43]. In conclusion, MBC could be used as a functional material to increase rice biomass and nutrient accumulation in two arsenic-contaminated soils.

### *4.2. As Immobilization Effect by MBC Application*

Biochar has been extensively researched as a soil amendment to mitigate the bioavailability of As due to its large surface area, high sorption capacity, and strong cation exchange capacity [44]. For example, iron-modified magnetic biochar has been reported to significantly reduce multiple heavy metal concentrations (As, Cd, and Pb) compared to untreated soil [27]. Meanwhile, metal oxides such as iron and cerium have shown excellent potential for As passivation function [45,46], e.g., copper oxide and alumina composite adsorbents showed high removal of both As(III) and As(V) [47]. Our research combined metal oxides with biochar to take advantage of their respective strengths and enhance the As passivation performance. Ws-As played a crucial role in controlling the uptake of As by rice plants. In this study, MBC significantly decreased the Ws-As concentration, but BC treatment did not exhibit the advantage of reducing Ws-As. However, interestingly, both BC and MBC significantly reduced the rice As, so Ws-As was not the only factor affecting the As uptake by rice plants.

As fractions serve as indicators of the mobility and availability of arsenic (As) in the environment in which non-specifically adsorbed specie-As and specifically adsorbed specie-As are considered to be the most phytoavailable As [25]. A previous study found that the addition of biochar could cause a redistribution of As between the different fractions [48]. Our results reflected that BC and MBC treatment obviously changed the As fraction. In the present study, the *M* value decreased from an averaged 21.80% in the control test to an averaged 15.14% with MBC amendment in soil-L, and a similar decrease in *M* value was observed in soil-H, and this facilitated the decrease in As uptake by rice plants. Although both MBC and BC treatments have effectively reduced the levels of arsenic (As) in rice, the MBC treatment was found to be more effective. This result is consistent with findings from previous studies [36]. Zhang et al. [48] also reported that Fe-Mn-Ce modified biochar composite enhanced residual As concentration and outperformed pristine biochar, which is similar to that of this research. In the present study, F4 and F5 in soil treated with biochar were greatly increased compared with CK, particularly for MBC. Therefore, our results reflected that MBC could promote the conversation of As forms from an active As to a stable form and then led to a decline in As mobility, thus reducing the bioavailability and safety risks of soil As.

### *4.3. The Possible Mechanism of As Passivation by MBC Application*

The input of biochar could change the soil's physicochemical properties, and the changes might affect the bioavailability and phytotoxicity of As [49]. As reported, the application of biochar had an impact on the soil pH value, which showed a significant and positive correlation with the concentration of exchangeable As [50]. The higher pH was more favorable for the release of As, which led to the increase of available As concentration in soil [51,52], this phenomenon is also confirmed in this study. Our results showed that BC elevated the soil Ws-As with the increasing pH, and MBC was the opposite. Moreover, the addition of biochar resulted in an increase in pH, which was more obvious in soil-L and the amount of MBC was inversely related to pH (Table 2). Previous studies have reported that the application of original biochar might stimulate the As availability in soils [40], and the reasons could be summarized in multiple aspects; for example, soil pH is one of the key factors affecting As mobility, and change in pH can affect As sorption by the soil, and the high soil pH created by biochar could increase the negative charge on the surface of soil matrixes, resulting in reducing the adsorption of As on soil solid.

In addition, DOC is one of the important factors in controlling the availability of As, which can reduce As adsorption on the surface of a solid phase (minerals, biochar, etc.) through competitive adsorption, thus increasing dissolved As concentration [36]. Moreover, soil As is prone to complexation and precipitation with DOM, which changes its redox state and affects morphology and bioavailability [53]. The present findings are consistent with previous reports that DOC was significantly increased with the addition of BC and led to the dissolution of As ($p < 0.05$), while the incorporation of MBC reduced the DOC and immobilized more As, thus reducing its bioavailability [54]. The reason for declining DOC created by MBC might be related to the decomposition and loss of organic matter during the pre-preparation-process of MBC, such as soaking in acid and washing.

Multiple studies have demonstrated that biochar has the potential to immobilize heavy metals in soils through various mechanisms, including electrostatic attraction, ion exchange, complexation, and precipitation [55,56]. And modified biochar tended to exert better As fixation ability attributed to the modification [57]. For example, manganese oxide-modified biochar exhibited higher As(V) sorption capacity compared with the original biochar [58]. Furthermore, the application of Fe-Mn-Ce oxide–modified biochar significantly decreased the As fluidity in As-contaminated soils compared with CK [59], which was in excellent agreement with the present result. Previous studies elaborated on the adsorption process of MBC, in which chemical adsorption played a vital role, and the efficient adsorption capacity was found to be closely associated with the loading of cerium and manganese oxide [33]. On the one hand, the modification process resulted in an increase in the specific surface area, providing a greater number of adsorption sites. MBC has a higher specific surface area than BC, 24.4% higher than BC, thus contributing to the As adsorption. On the other hand, As ions would precipitate or co-precipitate with cerium–manganese oxides to form stable complexes [46]. Moreover, researchers have reported that impregnating biochar with metal oxides improves surface morphology, modifies functional groups, and alters elemental composition [60]. This can effectively reduce the mobility and bioavailability of As [61]. Consistent with previous findings, the rich functional groups (e.g., hydroxyl groups) of MBC also played a crucial role in this process [33]. The SEM result also showed that compared with the original biochar, MBC had a layer of particles, i.e., cerium–manganese oxide (Figure S4).

As is widely recognized, the risk of heavy metal pollution is not solely dependent on the total amount of heavy metals present but is also closely correlated with their chemical forms [41]. The researchers focused on the fact that the toxicity of trivalent As ranks first among the four forms of As; previous studies have found that manganese oxides have a strong oxidation capacity for As and can oxidize As(III) to As(V) [62]. Our study also reflected this point. In the current study, As was mainly present in the form of As(III) in the control soil. It should be emphasized that the soil treated with MBC not only greatly reduced the total As concentration, but more gratifyingly, the main form of As in the soil was As(V) (Figure S1). Hence, the application of MBC has led to the immobilization of As in paddy soils and the transformation of As from As(III) to As(V) in soil, resulting in the detoxification of As in soil on one hand and less mobility from soil to plant by reducing health risk from food chain on the other hand.

Additionally, the original biochar increased the available As. But the As concentration in rice decreased significantly; it can be speculated that the iron plaque of the rice root system may play the role of a barrier. It is also consistent with previous literature that although the As concentration in soil pore water was greatly increased, the uptake of As by plants was significantly decreased [21]. However, the reduction of As uptake by rice plants under MBC application is due to the dual actions of As fixation and the barrier effect of iron plaque [63,64]. In our study, the application of BC and MBC enhanced the growth of rice, especially at the seeding stage; we speculated that high oxygen secretion from the rich root system enhanced the formation of iron plaque on the rice root surface, which further limited the migration of As and reduced its concentration in rice tissues [32]. Meanwhile, MBC application reduced As uptake by the rice crop and reduced the translocation of

As from roots to other tissues (Table 5), possibly owing to the regulatory influence of biochar on the expression of transporters involved in As uptake and translocation, thereby inhibiting As translocation from root to aboveground [40,65]. The findings of reducing As transport coefficient and As concentrations in various tissues of rice through the application of modified biochar were also reflected in other studies [66]. Meanwhile, previous literature reported that biochar application could enhance the biomass yield of rice plants, achieving a dilution effect on the As accumulation in rice tissues [67]. The current results showed that the addition of MBC at low dosage could achieve significant positive effects on the rice biomass and nutrient accumulation (Figure S2). From the correlation heat map of rice biomass, nutrients, and As (Figure S3), the rice As concentrations were significantly negatively correlated with rice biomass and nutrients. And the increasing soil nutrients might promote the growth of soil microorganisms associated with As immobilization [68]. In our study, for two different levels of As-contaminated soils, both BC and MBC were able to increase the biomass and nutrient accumulation of rice similarly, which was in excellent agreement with the other study [69]. It is worth mentioning that BC caused less As uptake of rice, which may be related to this dilution effect due to rice biomass enhancement, though the soluble As in soils was increased to some degree. This phenomenon is similar to another research [36]. In comparison with BC, the newly manufactured material MBC has more advantages for the immobilization of As. According to our previous research, the aging process of Ce–Mn-modified biochar increased As(V) adsorption and immobilization, which offered evidence for its better recyclability, long-lasting, and preferable adsorption selectivity [70]. In arsenic contamination remediation of agricultural land, the cost of MBC is acceptable. Meanwhile, in the remediation of arsenic contamination in mining areas, this cost is relatively low. Thus, MBC might be an excellent long-term environmental functional material to remediate the As-contamination soil and improve crop growth.

## 5. Conclusions

This study assessed the effect of MBC on the As uptake by rice plants with three application dosages in two As-polluted soils. The experiment unequivocally demonstrated that applying low doses of MBC resulted in a significant enhancement in rice nutrient accumulation and growth. Meanwhile, MBC immobilized As in soil and promoted the transformation of active As to a more stable form, which reduced the mobility of As in soil, thereby reducing the As uptake by rice different tissues and safety risks. Overall, the findings suggested that MBC prepared based on agricultural waste can be used as a green, efficient, sustainable, and promising passivating agent for promoting the growth of rice and alleviating the As bioavailability in contaminated soil. Furthermore, this finding is in line with the principles of circular development, waste treatment, and ecological agriculture, making it highly promising for the actual remediation of As-contaminated soil. It holds immense practical and scientific significance in addressing the issue of As contamination in farmland.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/su152316161/s1, Figure S1. Effects of amendments at the tillering stage on different As contents. (a) and (b) are BC and MBC treatments to low-concentration As contaminated soil, respectively, (c) and (d) are BC and MBC treatments to high-concentration As contaminated soil, respectively. Figure S2. Correlation heat map of rice biomass, soil nutrients, and nutrient accumulation in rice. Blue and red represent negative and positive correlations, respectively. Darker colors represent higher correlations. *, $p < 0.05$, **, $p < 0.01$, ***, $p < 0.001$. Figure S3. Soil pH and DOC and their relationships with Ws-As concentrations. Figure S4. SEM images of BC (a) and MBC (b). Note: Red arrows point out some of the particles. The magnification is 2000 times.

**Author Contributions:** Methodology, L.L.; Validation, T.L. and L.L.; Formal analysis, T.L.; Resources, L.L.; Data curation, T.L.; Writing—original draft, T.L.; Writing—review & editing, T.L. and L.L.; Project administration, L.L.; Funding acquisition, L.L. All authors have read and agreed to the published version of the manuscript.

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