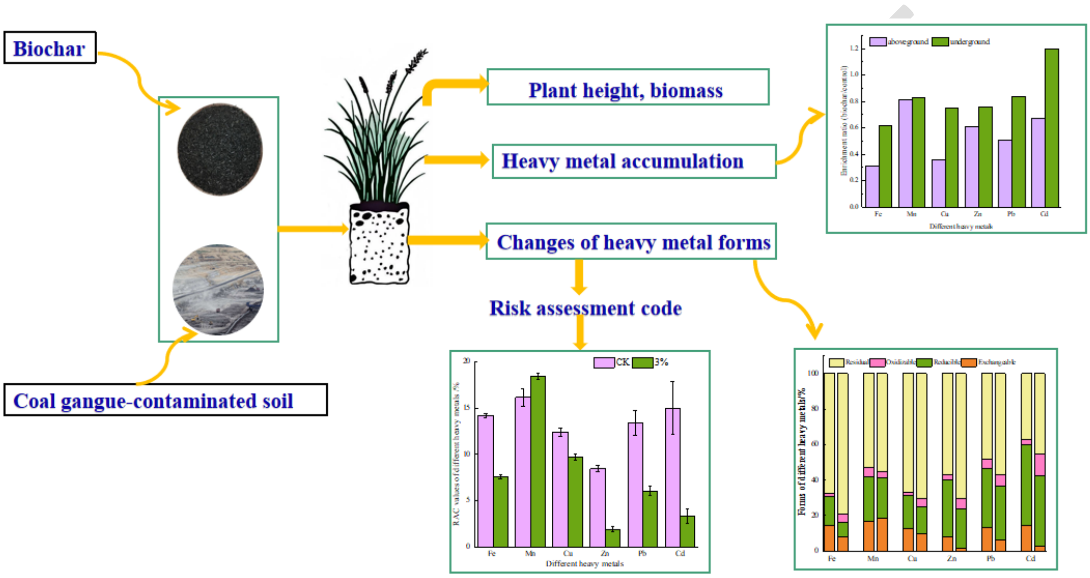
Biochar remediation of heavy metal-contaminated soils in a coal gangue-affected area

Graphical Abstract



Biochar remediation of heavy metal-contaminated soils in a coal gangue-affected area

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Abstract: Ryegrass was used as a test material to investigate biochar remediation of heavy metal-contaminated soils in a coal gangue-affected area. Five biochar additions were set: 0% (CK), 1% (B1), 2% (B2), 3% (B3), and 5% (B4). The effects of biochar on soil physicochemical properties, heavy metal forms, plant biomass, and heavy metal accumulation were analyzed. Results showed that soil pH, organic carbon content, and plant biomass increased significantly (P<0.05) with increasing biochar addition. The low supplemental level (1%) promoted iron (Fe), manganese (Mn), zinc (Zn), and cadmium (Cd) enrichment in ryegrass roots, while higher supplemental levels (>2%) significantly (P<0.05) inhibited heavy metal migration to plants. The exchangeable Fe, lead (Pb), and Cd concentrations in coal gangue-contaminated soil decreased significantly (P<0.05) with increasing biochar addition, while the reducible Mn concentration decreased. The risk assessment revealed that the potential ecological risks of Fe, Zn, Pb, and Cd decreased from moderate to mild when the biochar addition exceeded 2%. Under the experimental conditions, biochar additions exceeding 2% effectively reduced heavy metal bioavailability in coal gangue-contaminated soil and significantly inhibited the enrichment and transport of heavy metals in ryegrass through enhanced immobilization mechanisms. Additions of 2−3% biochar should be applied in actual remediation projects.

Keywords: straw biochar; coal gangue; heavy metals; bioavailability; ryegrass

1. Introduction

Coal is a primary energy source driving social development. In 2023, China's national raw coal production reached 4.71 billion tons. As a byproduct of coal mining and washing, coal gangue accounts for 15−20% of total coal production. In 2023, the total amount of coal gangue in China exceeded 7 billion tons (Jia et al. 2024). The main uses of coal gangue include the recovery of heat for power generation, construction materials, and as a filling raw material for subsidence mines (Wang et al. 2022). However, these applications utilize less than 30% of the annual stockpile. Furthermore, the utilization of coal gangue faces several challenges. These include serious environmental concerns, low utilization rates of valuable elements, and high costs due to large capital investments and insufficient consumption capacity. These issues collectively limit its rapid development (Zheng et al. 2024). The stockpiling of coal gangue poses significant environmental challenges, including the occupation of land resources and the release of heavy metals such as Fe, Mn, Cu, and Zn through leaching and erosion processes induced by rainwater (Tian et al. 2020; Wang et al. 2019). Consequently, these pollutants are transported in water runoff to surrounding areas, resulting in serious soil pollution around the mining area. Ren et al. (2016) investigated the concentrations of Pb, Zn, chromium (Cr), and Cu in soils surrounding a coal gangue stockpile in Huozhou, Shanxi Province. Their findings revealed that, compared to the background values of Shanxi Province, all four heavy metals exhibited varying degrees of enrichment, with levels exceeding established soil quality standards. Heavy metals contamination causes serious deterioration of the physical and chemical properties of soil, which not only affects the absorption of nutrients by crops but also leads to declining crop quality. In some parts of China, Cu, Cd, arsenic (As) and Pb concentrations in soil exceed the relevant quality standards, resulting in low levels of agricultural production and even crop failure (Zou *et al.* 2021). Therefore, ecological remediation of coal gangue-contaminated soils in mining areas is critically important to mitigate heavy metal toxicity and safeguard agricultural systems.

Currently, remediation of soils contaminated by heavy metals include physical, chemical, and biological ways (Azhar et al. 2022). Physical remediation has high efficiency but cannot remove all pollutants. It is also too expensive for large-scale use, so it is only suitable for small areas; Chemical remediation can effectively immobilize heavy metals in contaminated soils through the application of stabilizing agents such as iron sulfate, ferrous sulfate, lime, and cement. However, this method has significant drawbacks, including serious soil disturbance and potential toxicity to the soil (Li et al. 2015). Bioremediation includes phytoremediation, animal remediation, and microbial remediation, which have the advantages of low costs and low risk of secondary pollution in situ remediation(Cui et al. 2021). Phytoremediation is also highly valued by scholars due to its low cost, easy operation, and ability to beautify the environment. Xing et al. (2014) proved that phytoremediation can stabilize or remove pollutants through plant extraction, fixation, volatilization, absorption, and degradation, reducing the harm of pollutants to the environment. Phytoremediation is considered to be an economical and effective method for soil heavy metal removal due to its safety, environmental protection and large-scale in-situ remediation (Li et al. 2023). Coal gangue contains various elements, including Zn, Fe, and Cu, which are essential nutrients for plant growth. Therefore, it presents an excellent method for enhancing its properties and utilizing it in plant cultivation (Li et al. 2021).

Biochar is a carbon-rich solid product produced by the pyrolysis of biomass in an oxygen limited or oxygen free environment (≤700°C). Due to the abundance of raw materials for production, simple production process, and low cost, biochar has great potential for improving soil quality and promoting plant growth (Huang et al. 2024; Wu et al. 2015). Furthermore, biochar can significantly influence the chemical form, enrichment, and migration of heavy metals in soil. Studies have demonstrated that biochar amendment effectively reduces the mobility and bioavailability of Cu and Pb in contaminated soils (Peng et al. 2024; Puga et al. 2016). Cheng et al. (2023) added rice straw biochar to the surface soil of Pb and Zn tailings in a simulation experiment, and found that the Pb and Cd concentrations in the surface soil were significantly reduced. Furthermore, compared with a 1% addition amount, a 5% biochar addition ratio can significantly reduce the bioavailability of Cu and Pb (Zhao et al. 2016). Previous studies of biochar in the field of heavy metal-contaminated soil remediation have primarily focused on single metal pollution systems indoor simulations. However, the passivation effect of biochar and the migration of heavy metals have not been systematically studied, particularly in coal gangue dumps with their complex mixtures of heavy metals. This study focused on coal gangue-contaminated soil in a typical coal mine area. Through a pot experiment, the study investigated the effect of biochar addition on the availability of heavy metals in coal gangue-contaminated soil, as well as its influence on their bioaccumulation and translocation in the soil-plant system. The findings have important theoretical and practical significance for promoting soil ecological security and sustainable management in mining areas.

2 Materials and methods

2.1 Test materials

The coal gangue-contaminated soil was collected from an abandoned coal mine in Qingzhen City, Guizhou Province, China. After sampling, the soil was transported to the laboratory where it was air-dried. Sand, gravel, and large particles were removed, and it was then passed through a 2 mm mesh. The physical and chemical properties of the coal gangue-contaminated soil were as follows: pH = 5.46, EC = 1.427 dS/m, organic carbon = 9.7 g/kg, Fe = 32168 mg/kg, Mn = 62.11 mg/kg, Cu = 57.40 mg/kg, Zn = 107.30 mg/kg, Pb = 55.60 mg/kg and Cd = 0.39 mg/kg. The test biochar was corn straw charcoal (purchased from Shenyang Longtai Biotechnology Engineering Company, China), and its basic physicochemical properties were pH 8.77, total carbon 546.38 g/kg, total nitrogen 8.66 g/kg, total phosphorus 8.03 g/kg, and total potassium 27.28 g/kg.

2.2 Experimental design

Two kilograms of coal gangue-contaminated soil was placed into each of 15 plastic plant pots. Four different biochar treatments were established by adding 1%, 2%, 3%, and 5% to the soils, while soil without biochar was used as a control (CK). There were a total of five treatments, with three replicates per treatment (Table 1). Ryegrass seeds were sterilized by soaking in 75% alcohol for 30 s and rinsed with deionized water. Ryegrass seeds with full grains and consistent maturity were selected to be sown in pots, with 180 seeds per pot. The pot experiment was carried out under natural conditions, and the seedlings were thinned after 15 d. During the whole experiment, the positions of the pots were randomly changed and watered regularly. The plants were harvested 90 days after planting.

Table 1. Addition ratios of different biochar

Numbers	Different treatments	Proportion of biochar (%)
1	CK	0
2	B1	1%
3	B2	2%
4	B3	3%
5	B4	5%

2.3 Sample collection and analysis

Following 15 days of growth, seedling emergence rates were recorded for each pot. After 90 days of cultivation, plant height measurements were taken across all treatment groups. Subsequently, ryegrass were carefully harvested using stainless steel scissors, separating above-ground and underground biomass. All plant materials were thoroughly rinsed with deionized water, and then weighed to determine fresh biomass for both components. After weighing, the underground and above-ground parts of the plants were placed in the oven respectively. The plants were deoxidized at 105℃ for 30 min, dried at 75℃ to constant weight, and crushed through a 100-mesh sieve, and stored in a ziplock bag for later use. The rhizosphere soil samples were naturally air-dried and screened 100 mesh for use.

Soil pH and EC values were mixed in a ratio of 1:2.5, soil to liquid (deionized water), and measured using a pH meter (SH2601) and conductivity meter (DDS11A) after full oscillation. Soil organic carbon was determined using the K_2CrO_7 volumetric method. Soil was sieved through a 100-mesh sieve and then digested with nitric acid and hydrofluoric acid (with a volume ratio of 3:1), and various chemical forms of heavy metals were sequentially extracted using the improved European Community Bureau of Reference (BCR) method (Zhang et al., 2012). The extraction sequence was as follows: exchangeable, reducible, oxidizable, and residual states. The specific extraction steps are shown in Table 2. The residual state of heavy metals was determined after digestion with nitric acid, hydrofluoric acid, and perchloric acid. The heavy metals Mn, Cu, Zn, Pb, and Cd were determined using an inductively coupled plasma mass spectrometer (ICP-MS) (iCAP RQ, Thermo Fisher Scientific, Waltham, USA) with a detection limit of 0.01 μg/L, while Fe was quantified using an atomic absorption spectrophotometer (WFX-110, Ruisi, Beijing, China).

Table 2. Improved BCR sequential extraction method

Procedure	Chemical Form	Method
1	Exchangeable state	Add 40 mL 0.11 mol/L acetic acid to 1 g of soil sample, shake at room temperature for 16 h, 4000 r/min, centrifuge for 20 min.
2	Reducible state	Add 40 mL 0.5mol/L hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), shake at room temperature for 16 h, 4000 r/min, centrifuge for 20 min.
3	Oxidizable state	Add 10 mL 8.8 mol /L H_2O_2, leave at room temperature for 1 h, and dissolve in a water bath for 1 h. Add another 10 mL 8.8mol /L H_2O_2 and dissolve in a water bath to about 1 Mr. Add 40 mL 1 mol/L ammonium acetate (NH_4Ac), shake at room temperature for 16 h, 4000 r/min, centrifuge for 20 min.
4	Residual state	Nitrate-hydrofluoric acid-perchloric acid digestion

During the experiment, quality control was carried out using reagent blanks, parallel samples, and national standard soil samples (ESS-4). During the analysis process, a reagent blank sample, a standard substance sample, and a parallel sample were randomly inserted into every 10 samples. The experimental water was all ultrapure water, and the reagents used were all of analytical purity. The experimental vessels were soaked in 10% nitric acid or sulfuric acid solution for more than 24 h, then washed with ultrapure water and dried for subsequent use.

The germination and passivation rates were calculated as follows:

$$\text{Germination rate} = (\text{total number of germinations} / \text{total number of seeds}) \times 100\% \quad (1)$$

$$\text{Bioconcentration factor (BCF)} = \text{characteristic metal content of plant underground parts} / \text{characteristic metal content of soil} \quad (2)$$

$$\text{Transformation factor(TF)} = \text{characteristic metal content of plant aerial parts} / \text{heavy metal content of plant roots} \quad (3)$$

2.4 Potential ecological risk assessment of heavy metals

The risk assessment code (RAC), developed through environmental morphological studies (Duan et al., 2021; Liu et al., 2011), is an ecological risk assessment methodology that evaluates heavy metal bioavailability based on their labile fractions in environmental matrices. This approach specifically analyzes the geochemically active forms of heavy metals that directly influence ecological risk potential. The environmental risk posed by heavy metals increases significantly when their bioavailable fractions constitute a high proportion of the total metal content. The calculation formula is as follows:

$$RAC = C_{exchangeable} / C_{total} \times 100\% \quad (4)$$

In the formula: RAC represents the risk assessment code value; $C_{exchangeable}$ is the exchangeable form content of heavy metals extracted by BCR sequential extraction method, mg/kg; C_{total} is the total amount of heavy metals, mg/kg.

The relationship between the proportion of active forms of heavy metals and the degree of pollution is shown in Table 3.

Table 3 Relationship between the degree of pollution and the proportion (%) of the active form of heavy metals

%	<1	1−10	10−30	30−50	≥50
Degree of pollution	None	Mild	Moderate	Severe	Extremely serious

2.5 Data processing and analysis

For data statistics and analysis, IBM SPSS statistics 25 was employed, whereas Origin 2023 was utilized for mapping purposes. The bioaccumulation capacity and transformation efficiency of ryegrass were systematically analyzed and comprehensively evaluated by BCF and TF.

3 Results and Analysis

3.1 Changes in the plant biomass in the different treatment groups

After 90 days of planting, the changes of plant emergence rate, plant height and biomass in each treatment group were shown in Figure 1. The ryegrass emergence rates for all groups were significantly different ($P<0.05$). As shown in Figure 1-a, the ryegrass emergence rate was 36.66% for the CK group and 74.62% for B4. The plant emergence rate increased significantly with the increase in straw biochar addition. As shown in Figure 1-b, the average plant height of ryegrass in the CK group was 31.10 cm, and the plant heights in each of B1, B2, and B3 were significantly higher than in the CK group. At the 5% straw biochar addition rate, the height of ryegrass was significantly reduced. Compared with the CK group, the biomass increases in B1, B2, B3, and B4 were 142.30%, 106.01%, 169.78%, and 132.45%, respectively (Figure 1-c), and the ryegrass biomass in B3 was slightly higher than in the other treatment groups.

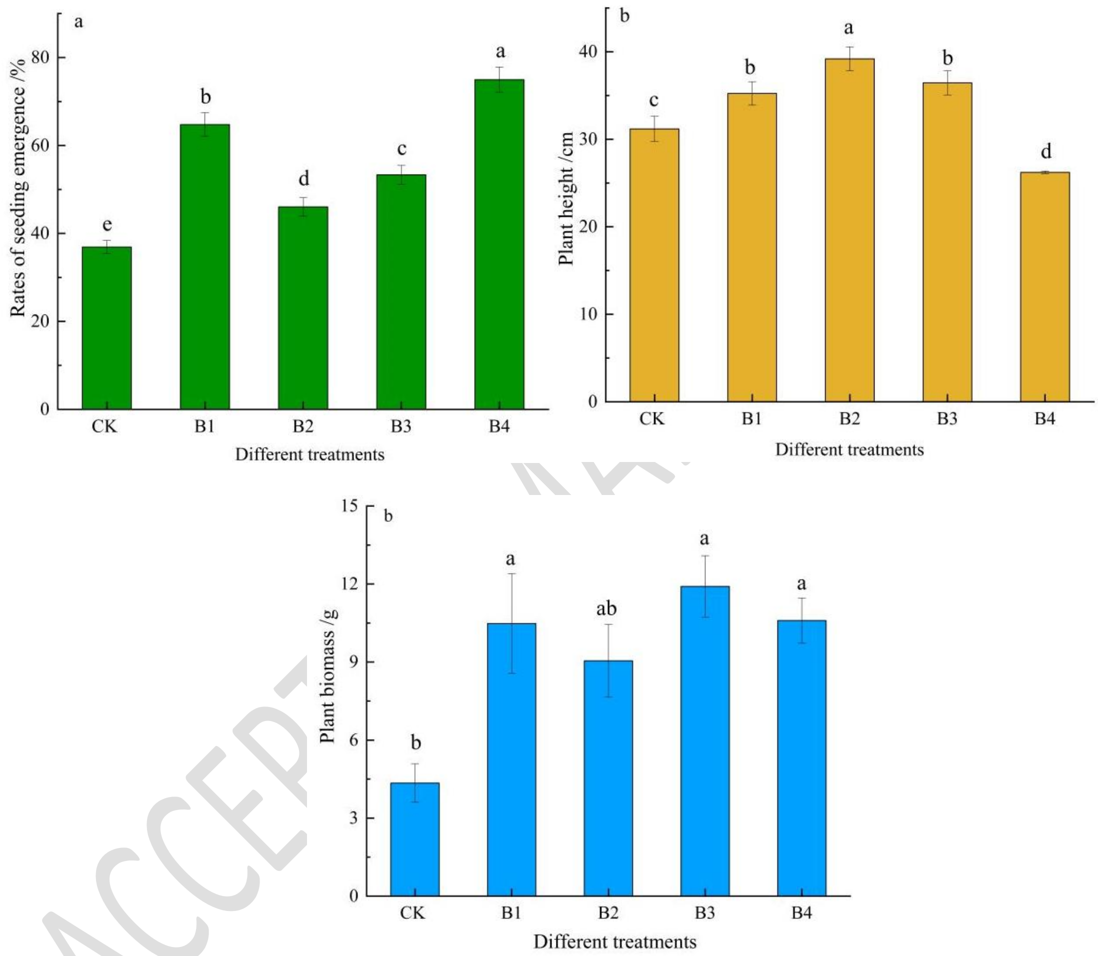
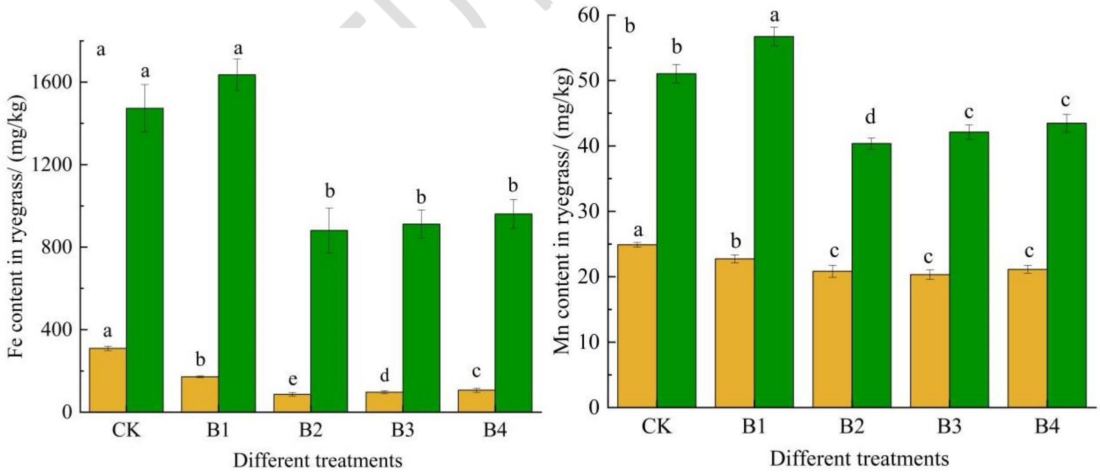


Figure 1: Effects of straw biochar additions on the germination rate, plant height, and ryegrass biomass

Note: The data are averages, different lowercase letters in the same column of the table indicate significant differences among treatments (P<0.05).

2.2 Accumulation and migration characteristics of heavy metals in ryegrass under different treatments

The ability of plants to accumulate heavy metals provides an important index for evaluating the ecological remediation of heavy metal-contaminated soil. The ability of plants to accumulate heavy metals is related to the physical and chemical characteristics of the rhizosphere soil (Adamczyk et al. 2015), plant species (Thatoi et al. 1995), and heavy metal concentration in the rhizosphere soil (Xu et al. 2014). The heavy metal concentrations in ryegrass grown on coal gangue-contaminated soil in each treatment group are shown in Figure 2. Compared with the CK group, in B1, the Fe concentration was increased in the underground parts of plants, while the Fe concentration in the aboveground and underground parts of ryegrass in B2, B3, and B4 significantly decreased (P<0.05). In B4, the Fe concentration in the aboveground and underground parts of plants decreased by 65.55% and 34.74%, respectively. A low biochar addition rate promoted an increase in the Fe concentration in plants, while a high biochar addition rate inhibited the absorption and enrichment of Fe by plants. The effects of straw biochar addition on the Mn concentration in ryegrass are shown in Figure 2-b. When the biochar addition rate was 1%, the Mn concentration in the underground part of plants was significantly higher than in the CK group. When the biochar addition rate was >2%, the Mn concentration in the underground and aboveground parts of ryegrass in B2, B3, and B4 was significantly reduced (P<0.05). The aboveground Cu concentration in ryegrass in all treatment groups was significantly lower than in the CK group (P<0.05), and the aboveground Cu concentration in ryegrass in B4 was reduced by 61.23% (Figure 2-c). The Cd concentration in the underground part of ryegrass increased with the addition of straw biochar. The most significant increase (71.38%) was observed in B4, although there was no change observed in the Cd concentration in the aboveground part of ryegrass. The results showed that the addition of straw biochar influenced the enrichment of heavy metals by ryegrass in polluted soil, with varying effects depending on the type of heavy metal and the amount of biochar added. When the addition rate of straw biochar was 1%, the Mn and Zn concentrations in the underground part of ryegrass were significantly higher than in the CK group. And when the addition rate of straw biochar was ≥2%, the content of heavy metals in ryegrass decreased significantly, indicating that the addition of high proportion of biochar inhibited the absorption and enrichment of heavy metals by plants.



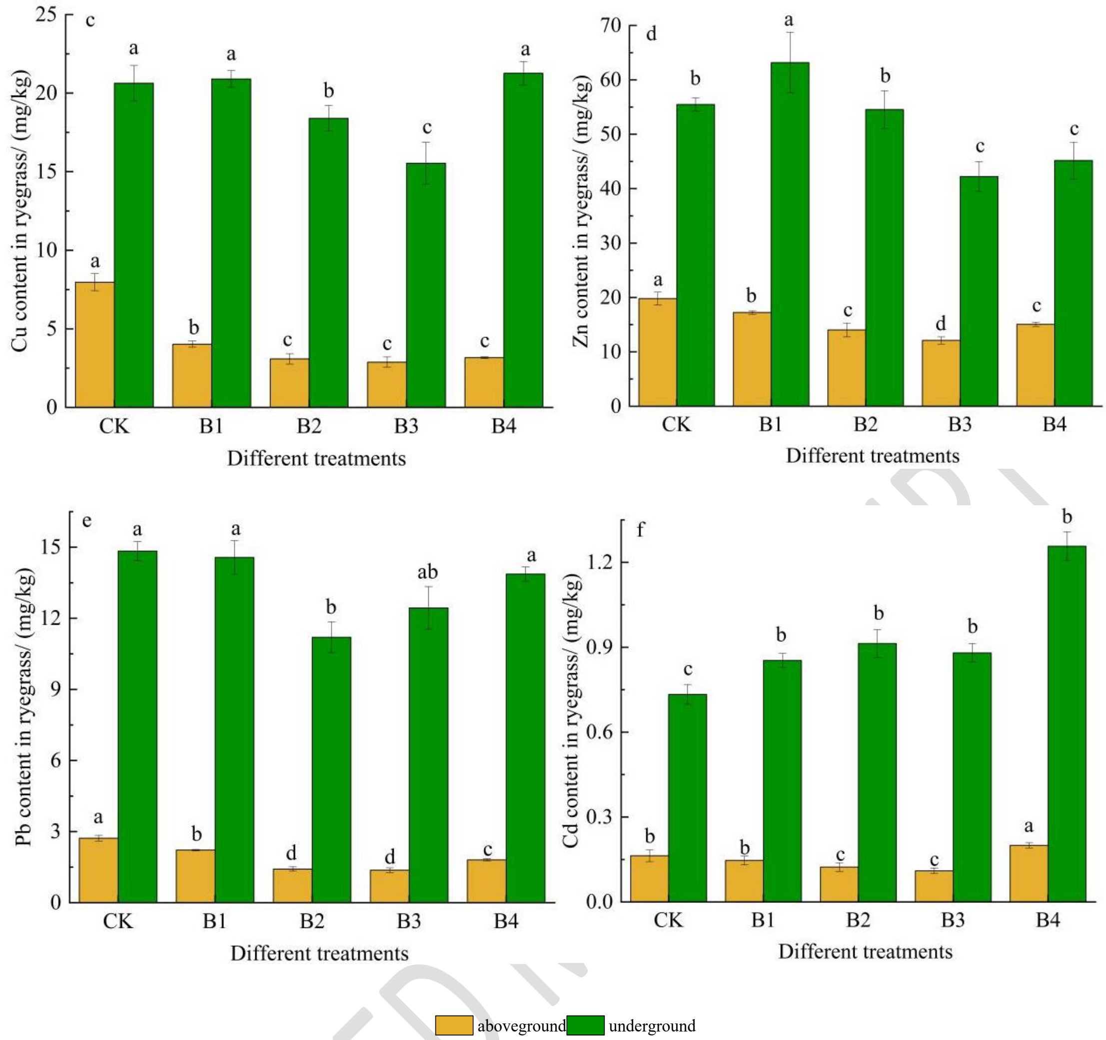


Figure 2. Effect of straw biochar addition on heavy metal accumulation in ryegrass

Note: The data are averages, different lowercase letters in the same column of the table indicate significant differences among treatments (P<0.05).

The BCF of plants for heavy metals is used to evaluate the propensity for heavy metals to migrate from soil to plant tissues. And the TF is the ratio of the concentration of a heavy metal in the stems and leaves of plants to the concentration in the roots, indicating the difference in the heavy metal uptake capacity between the shoots and roots of plants. The heavy metal concentrations in ryegrass and polluted soil in the different treatment groups were calculated using formulas (2) and (3). Additionally, the BCF of heavy metals in plant roots and the TF of the underground to aboveground parts of plants in the different treatment groups were also obtained. All results are shown in Table 4. The addition of straw biochar had a specific effect on the BCF of heavy metals in ryegrass. The BCFs for the six heavy metals in polluted soil in the different treatment groups were significantly different. The enrichment coefficients of five heavy metals (Fe, Mn, Cu, Zn, and Cd) in ryegrass roots in B1 were higher than in the CK group. The results indicated that the addition of 1% biochar promoted the enrichment and absorption of five characteristic metals in the underground part of ryegrass. However, with increasing biochar addition (≥2%), the enrichment coefficients of Fe, Mn, Cu and Zn in ryegrass roots were lower than those in the CK group, indicating that biochar inhibited the enrichment and absorption of these four characteristic metals in ryegrass, but promoted the enrichment of Cd in ryegrass. In conclusion, the addition of straw biochar has a certain effect on the transport of characteristic metals in ryegrass. When the addition ratio of biochar exceeded 2%, the addition of biochar inhibits the transfer of characteristic metals from coal gangue polluted soil to ryegrass, and the inhibition effect is more obvious with the increase of the addition amount.

Table 4 The effect of straw biochar addition on enrichment and transport coefficients in ryegrass

Elements	Indicator	Different treatments				
		CK	B1	B2	B3	B4
Fe	BCF	0.046	0.051	0.027	0.028	0.030
	TF	0.21	0.10	0.10	0.11	0.11
Mn	BCF	0.822	0.914	0.650	0.678	0.700
	TF	0.49	0.40	0.52	0.49	0.49

Cu	BCF	0.360	0.364	0.321	0.270	0.371
	TF	0.39	0.19	0.17	0.19	0.15
Zn	BCF	0.517	0.589	0.508	0.394	0.421
	TF	0.36	0.27	0.26	0.29	0.33
Pb	BCF	0.267	0.262	0.201	0.224	0.249
	TF	0.18	0.15	0.13	0.11	0.13
Cd	BCF	1.880	2.188	2.342	2.250	3.222
	TF	0.22	0.17	0.14	0.13	0.16

2.3 Effect of biochar addition on the physicochemical properties of coal gangue-contaminated soil

Soil pH value is an important parameter affecting the activity of heavy metals in soil. The effect of biochar addition on the pH of coal gangue-contaminated soil in this study is shown in Figure 3-a. The pH values of B2, B3, and B4 were significantly higher than in the CK group and B1, and the higher the proportion of biochar addition, the more obvious the increase in pH. When the biochar addition rate was > 2%, the soil EC value was significantly lower than in the CK group, and the EC value in B4 decreased by 29.78% compared with the CK group. The higher the proportion of biochar added, the more pronounced the increase in the organic carbon content in soil polluted by coal gangue. When the amount of biochar added reached 5%, the organic carbon content in the soil increased to 16.27 g/kg, which was 1.53 times that of the CK treatment group.

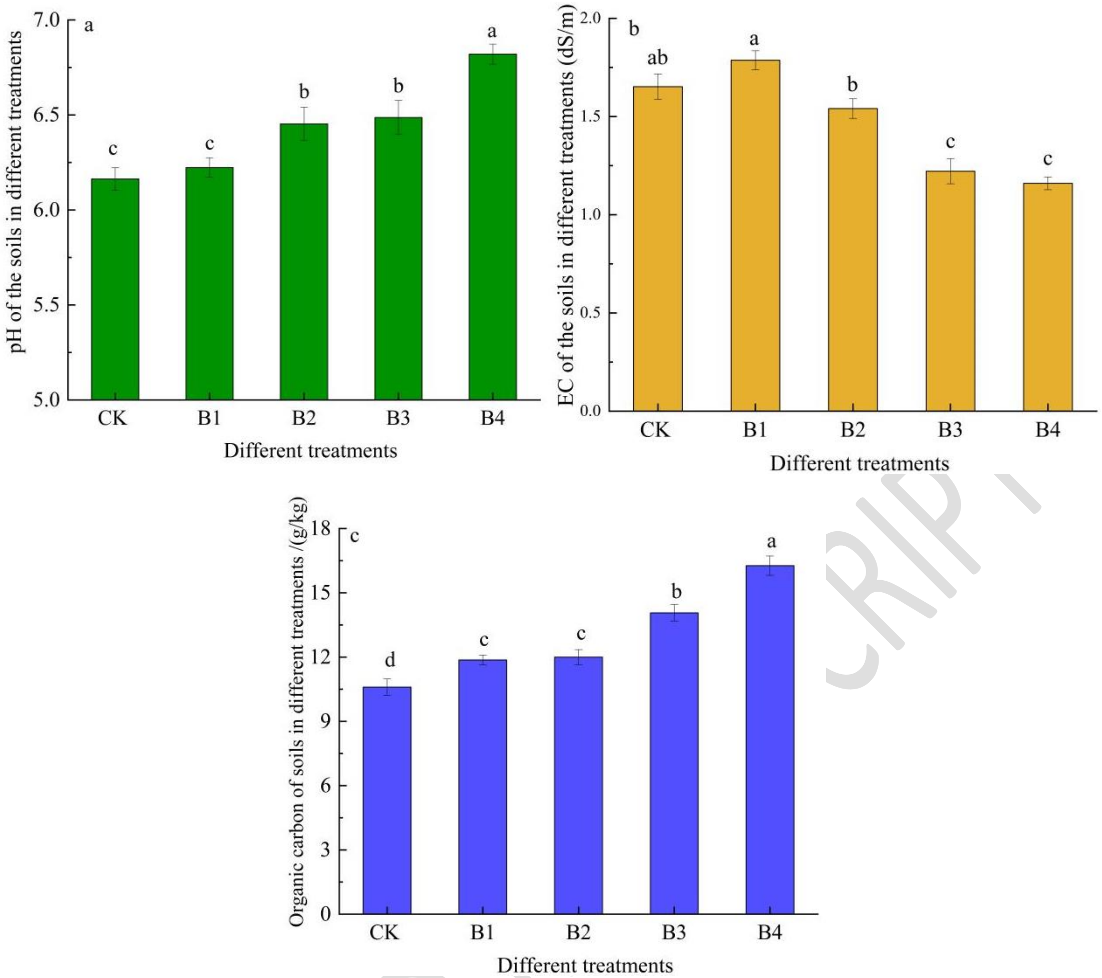


Figure 3. Effect of biochar on the pH, EC and organic carbon of coal gangue-contaminated soil.

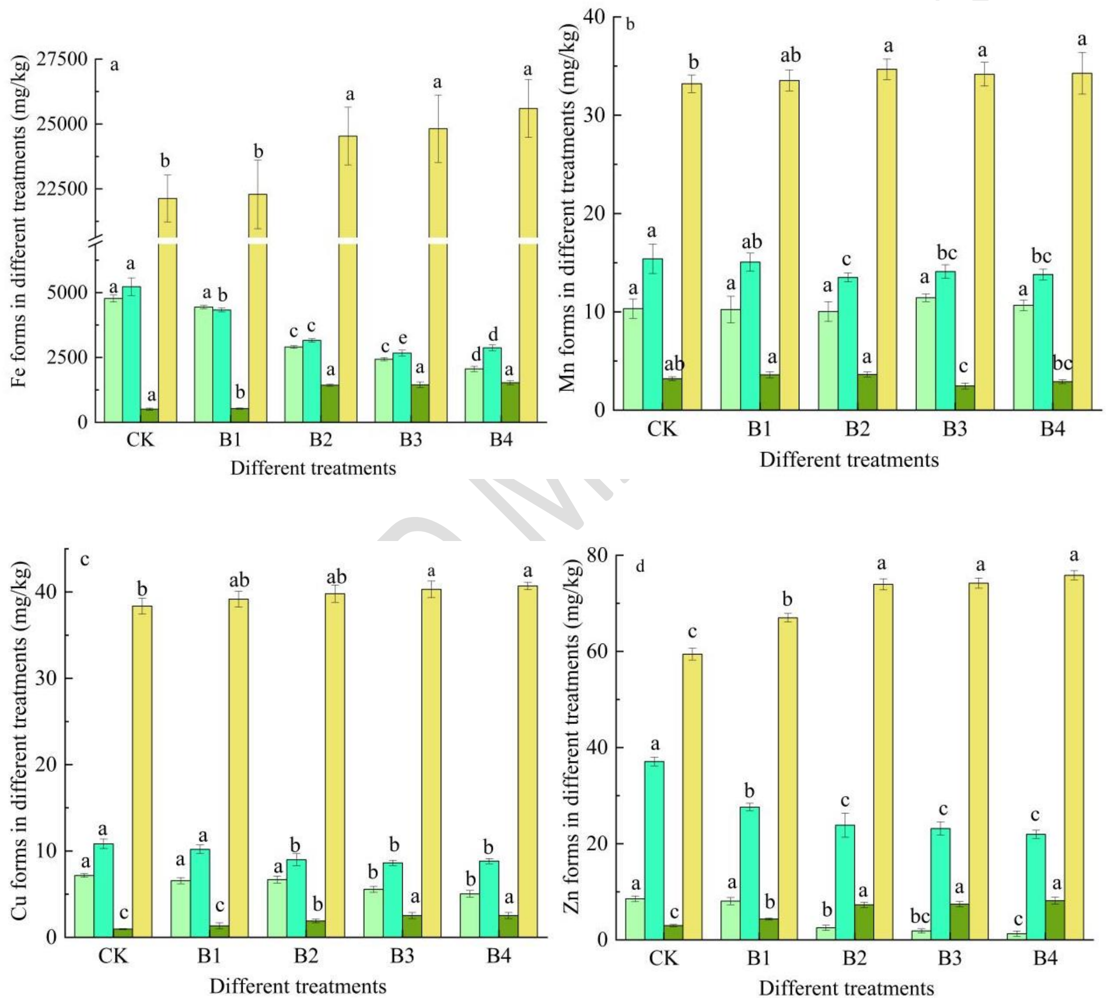
Note: The data are averages, different lowercase letters in the same column of the table indicate significant differences among treatments (P<0.05).

2.4 Effect of biochar on heavy metals in coal gangue-contaminated soil

2.4.1 Effect of biochar on the speciation of heavy metals in coal gangue-contaminated soil

The BCR extraction results showed that the heavy metals in the coal gangue-contaminated soil were transformed to a more stable form by the addition of biochar (Figure 4). The changes of Fe morphology in coal gangue-contaminated soil were shown in Figure 4-a. Compared with the CK group, the residual Fe concentration was significantly increased when the biochar addition rate was >2%

(P<0.05). The residual Fe concentrations in B2, B3, and B4 were 11.61%, 12.9%, and 16.43% higher than in the CK group, respectively. The exchangeable Fe concentration in coal gangue-contaminated soil decreased significantly, and the oxidizable Fe concentration gradually increased with increasing biochar addition. Compared with the CK group, the oxidizable Fe concentration in B4 increased by 208.10%. As shown in Figure 4-b, the addition of biochar had little effect on the exchangeable Mn concentration in soil. However, with the increasing addition of biochar, the reducible Mn concentration in the coal gangue-contaminated soil gradually decreased, while the residual Mn concentration slightly increased. Compared with the CK group, the exchangeable and reducible Cu concentrations in coal gangue-contaminated soil were significantly decreased (P<0.05), while the oxidizable and residual Cu concentrations were significantly increased (P<0.05) when the biochar addition level was >3% (Figure 4-c). The exchangeable and reducible Cu concentrations in B3 decreased by 22.32% and 20.39%, respectively, while the oxidized Cu concentration increased from 0.97 to 1.90 mg/kg, an increase of 95.88%. The addition of biochar further stabilized the Zn concentration in the coal gangue-contaminated soil (Figure 4-d). The Zn in all treatment groups changed from highly active and commutative states to the more stable oxidizable and residual states. The residual Zn concentration in the coal gangue-contaminated soil gradually increased from 59.43 mg/kg in the CK group to 75.83 mg/kg in B4. The more biochar that was added, the more apparent the morphological changes were. When the amount of biochar added was >2%, the exchangeable Pb concentration in soil decreased to varying degrees, with a more pronounced decline observed as the biochar addition increased (Figure 4-e). Compared with the CK group, the exchangeable Pb concentration in B4 decreased by 61.96%, while the oxidizable and residual Pb concentrations increased to varying degrees. Biochar addition reduced the exchangeable Cd concentration in coal gangue-contaminated soil by different magnitudes, with the exchangeable Cd concentrations in B2, B3, and B4 being significantly lower than in the CK group ($P<0.05$). The exchangeable Cd concentrations in these three treatments decreased by 40.00%, 61.82%, and 74.55%, respectively. The oxidizable and residual Cd concentrations increased by different magnitudes in each treatment group.



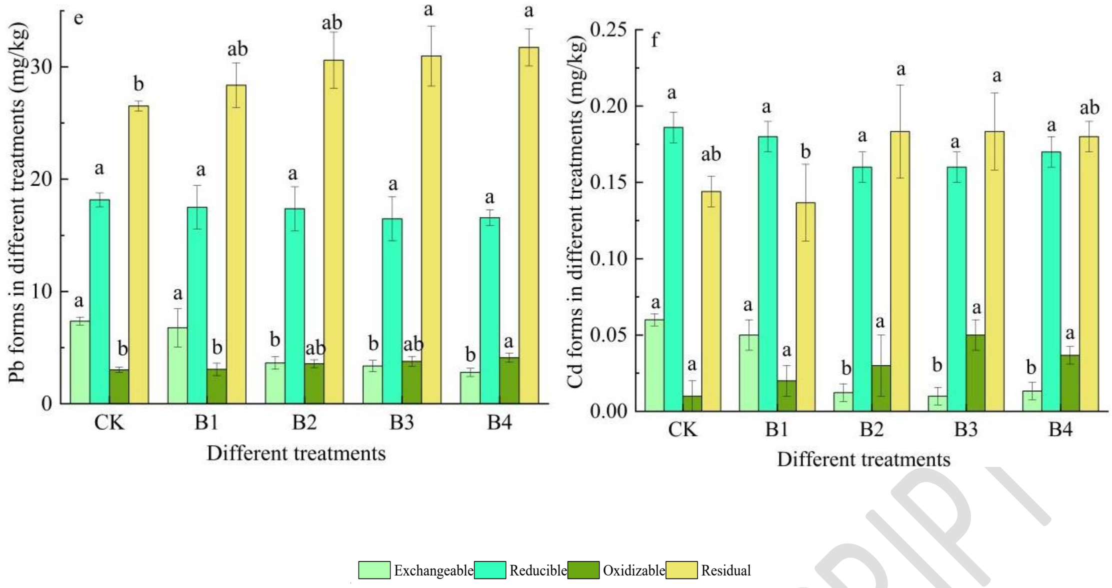
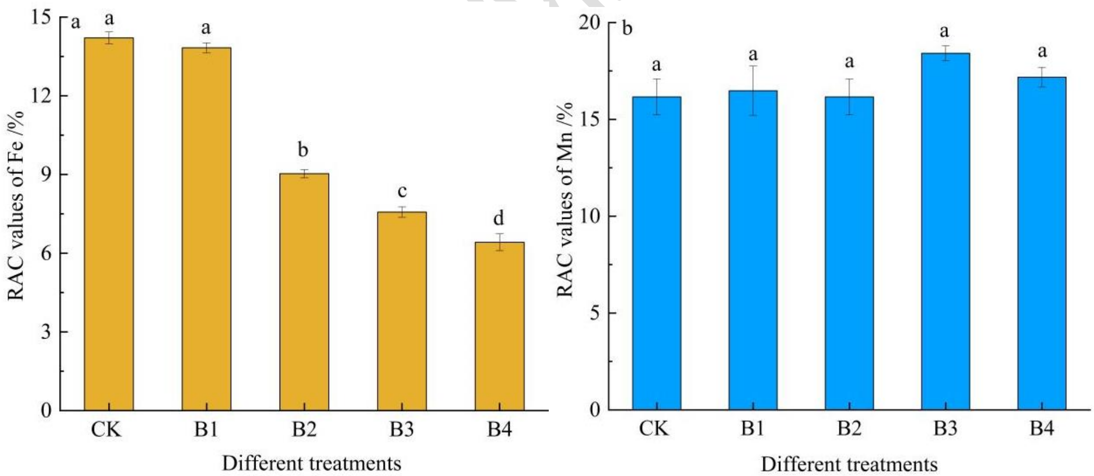


Figure 4. The influence of biochar addition on the morphological changes of heavy metals in coal gangue-contaminated soil.

Note: The data are averages, different lowercase letters in the same column of the table indicate significant differences among treatments (P<0.05).

2.4.2 Ecological assessment of heavy metals after the addition of biochar to coal gangue-contaminated soil

The environmental impact of heavy metals depends not only on their total concentration, but also on their chemical speciation, which determines their mobility and toxicity. The RAC is an evaluation method that was developed based on morphological studies. The greater the proportion of active forms of heavy metals, the stronger their migration ability and the higher the potential risk to the ecological environment. The proportion of active forms of heavy metals in coal gangue at the end of the experiment is shown in Figure 5. The proportion of active forms of the heavy metals followed the order of Mn > Zn > Cu > Fe > Cd > Pb. The ecological risk of Fe in the treatment groups with a biochar content >2% decreased significantly compared to the treatments with lower biochar contents (P<0.05), and the RAC value was <10%, indicating that the potential ecological risk of Fe in coal gangue changed from moderate to light (Figure 5-a). Biochar addition had little effect on the Mn concentration in coal gangue, and the RAC value of Mn in all treatment groups was >10%, which represented a moderate risk. The ecological risk of Cu decreased from moderate to mild when the biochar addition rate was >3%. And when the biochar addition rate was >2%, the ecological activities of Zn, Pb, and Cd in all treatment groups decreased significantly from moderate to mild. Therefore, when the biochar addition rate exceeded 2%, the ecological activities of Fe, Zn, Pb, and Cd in coal gangue-contaminated soil were significantly inhibited.



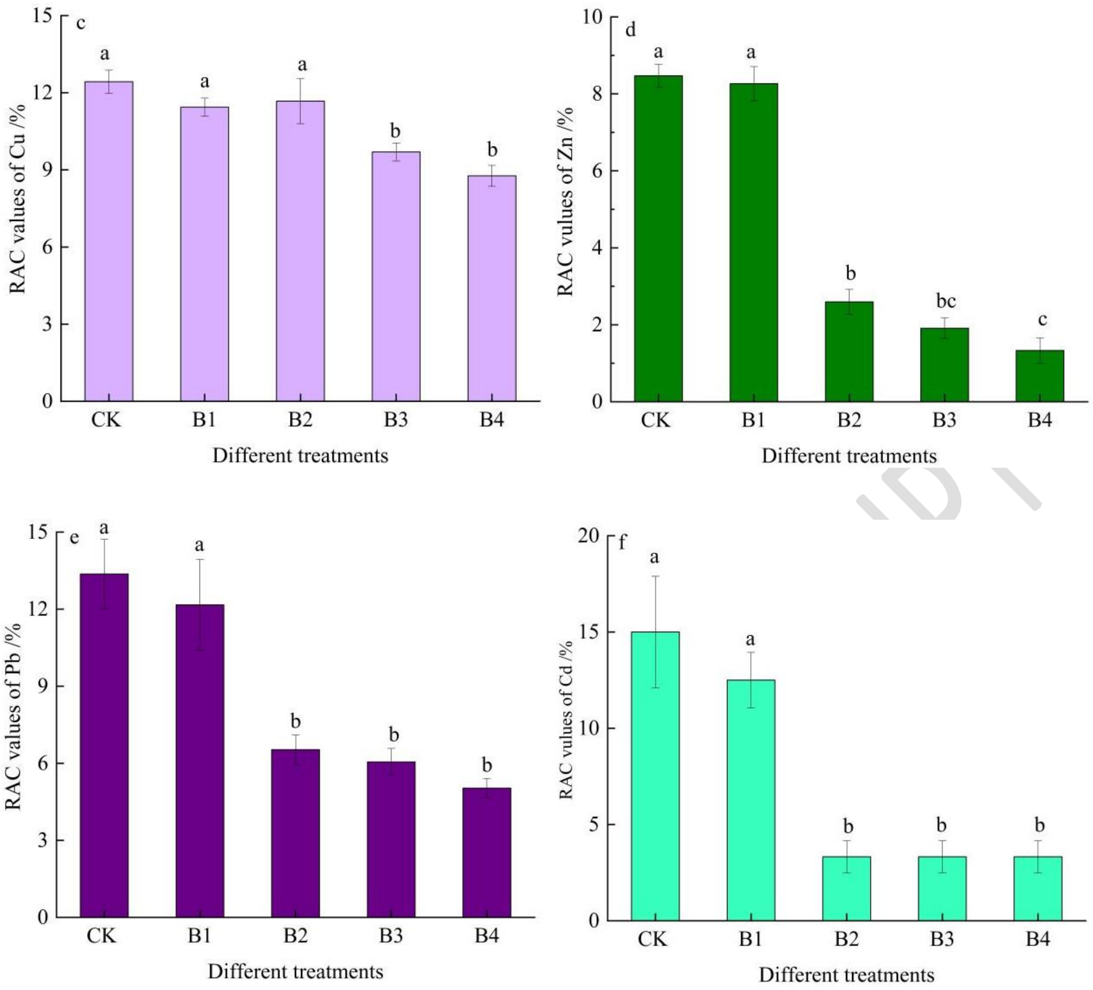


Figure 5. RAC values of heavy metals in different treatments

4. Discussion

After planting ryegrass in the coal gangue-contaminated soil with the addition of biochar, the germination rate and biomass of ryegrass increased significantly with the increase of the biological addition amount. Some studies have shown that biochar can improve the soil environment due to its unique adsorption properties (Zhang et al. 2009). Biochar can enhance the retention capacity of soil moisture and provide essential mineral elements (such as K, Ca, and Mg) that are necessary for crop growth (Wu et al. 2022). Biochar exhibits significant adsorption capacity for nutrients, including ammonium (Lehmann, 2022), nitrate (Mizuta et al., 2004), and phosphorus (Wei et al., 2023). This property enhances soil fertility by improving fertilizer retention and reducing nutrient leaching. Additionally, it can adsorb pesticides and heavy metals (Mohan et al. 2007), reducing soil and environmental pollution and mitigating the toxic effects on ryegrass.

When the biochar addition rate was 1%, the Fe, Mn, Zn, and Cd concentrations in ryegrass roots increased. Li et al.(2022) showed that nickel (Ni), Pb, Cd, and Cr in coal gangue mainly exist in stable states, characterized by bioavailability and limited concentrations. Because the utilization of soil nutrients is largely catalyzed by enzymes, soil enzyme activity serves as an important indicator of soil quality changes (Samuel et al. 2008). Feng et al. (2021) reported that soil enzyme activity increased with biochar addition and the increase in soil enzyme activity promoted the absorption of heavy metals by ryegrass roots. Biochar provides habitats for microorganisms while releasing substantial amounts of free-state metals available for plant uptake (Liu et al. 2014). Therefore, the Fe, Mn, Zn, and Cd concentrations in ryegrass roots tended to increase when the biochar addition rate was 1%. When the biochar addition rate was >2%, the migration of Fe, Mn, Cu, Zn, and Pb from the soil to the roots and aboveground parts of ryegrass was inhibited. This may be attributed to the competitive binding of free metal elements by the increasing amount of biochar. Notably, Cd is resistant to metal inhibition in ryegrass and can inhibit the enrichment of Fe, Mn, Cu, Zn, and Pb by competing for transport sites and disrupting the root iron plaque (Zhang et al. 2021). As a result, the Cd concentration in ryegrass continued to increase while the Fe, Mn, Cu, Zn, and Pb concentrations continuously decreased.

Biochar effectively reduces the bioavailability of Fe, Cu, Zn, Pb, Cd by promoting the transformation of heavy metals into stable forms. When the biochar addition rate was ≥2%, the residual Fe concentration increased significantly, the exchangeable and reducible Fe concentrations continued to decrease. This was mainly because the biochar content increased with the increase in the organic matter content in the soil. As a result, the oxidizable Fe concentration in soil increased, which was also reported in previous studies (Chatzistathis et al. 2017; Zhu et al. 2020). Additionally, there were significant differences in the responses of the different metals to biochar. The morphological transformation of Mn was relatively limited, and its exchangeable state did not change significantly, which may be related to the high migration rate of Mn and the activity of Mn-oxidizing bacteria in soil. Cd is highly toxic and bioavailable (Jia et al. 2019). When the biochar addition rate was 3%, the exchangeable Cd concentration in the soil decreased by 74.55%, primarily because the addition of biochar increased the soil pH (Figure 3), enhancing the stability of soil Cd (Rizwan et al. 2016). Furthermore, biochar increases the soil pH value, resulting in Cd being present in the form of hydroxide or carbonate precipitation, while Pb can complex with the surface functional groups of biochar, further reducing its activity (Xu et al. 2020). It has also been shown that increases in soil pH and organic carbon content are the main factors influencing Zn fixation (Wu et al. 2017).

This study showed that biochar addition has a significant remediation effect on heavy metals in coal gangue-contaminated soil. By promoting the transformation of heavy metals into stable forms, biochar effectively reduced the bioavailability of heavy metal. Additionally, the addition of biochar also had a positive effect on the physical and chemical properties of soil and growth of ryegrass. Therefore, biochar has broad application prospects in the remediation of coal gangue-contaminated soil.

5. Conclusion

(1) Straw biochar additions to coal gangue-contaminated soil significantly increased seedling emergence of ryegrass and also contributed to an increase in ryegrass biomass.

(2) When the biochar addition rate was 1%, biochar promoted the uptake of iron and manganese by ryegrass roots. However, when the biochar addition rate was >2%, biochar inhibited the enrichment of iron, manganese, copper, zinc, and lead in both the roots and aboveground parts of plants.

(3) Based on the risk assessment, the addition of biochar at rates exceeding 2% reduced the potential ecological risk of iron, zinc, lead, and cadmium from a moderate to a mild level. Under experimental conditions, such amendment rates effectively decreased heavy metal bioavailability in the coal gangue-contaminated soil and significantly suppressed the enrichment and translocation of heavy metals in ryegrass.

Therefore, this study recommends using 2-3% straw biochar as the addition ratio for remediating coal gangue contaminated-soil. This ratio can not only effectively stabilize various heavy metals and reduce their bioavailability, but also significantly promote the growth of ryegrass, which has important practical significance for promoting the green and sustainable management of contaminated soil in mining areas. However, we also recognize that the current research does not fully explain the microscopic mechanism by which biochar affects the migration and transformation of heavy metals. Therefore, in the future, it is planned to further explore its microscopic mechanism of action and systematically evaluate the restoration potential of different combinations of biochar and plants, with the aim of providing more comprehensive and reliable scientific basis for practical site applications.

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