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The Effects of the Combined Application of Biochar and Phosphogypsum on the Physicochemical Properties of Cd-Contaminated Soil and the Yield Quality of Chinese Cabbage

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Abstract: Chinese cabbage (*Brassica pekinensis* (Lour.) Rupr.) is rich in many vitamins and many minerals and is an important green vegetable in people's daily diet. Soil heavy metal Cd content exceeding safe values has a toxic effect on the growth of vegetables, which seriously affects human health. Biochar can effectively stabilize heavy metals in polluted soil, and phosphogypsum can improve the physical and chemical properties of soil and promote the growth of crops. To explore the remediation effect of biochar combined with different amounts of phosphogypsum on Cd-contaminated soil and the safe production of agricultural products, a pot experiment was conducted with corn straw biochar and harmless phosphogypsum as the test materials, and Chinese cabbage as the test plant. The soil pH; the alkali-hydrolyzed nitrogen content; the available phosphorus, potassium, and Cd content in the soil; the fresh weight of the Chinese cabbage; the Cd content in the edible part of the Chinese cabbage; and the vitamin C, chlorophyll, and soluble sugar contents in the leaves were measured and analyzed. The results showed that among all the treatments, the T3 and T4 treatments were the most effective in enhancing the soil pH and soil available nutrient content. Compared with CK, the T3 and T4 treatments significantly enhanced the soil pH by 0.27 and 0.29 units, respectively, and significantly increased alkali-hydrolyzed nitrogen content by 16.25% and 14.04%, available phosphorus content by 22.98% and 22.87%; and available potassium content by 8.50% and 10.13%. In addition, among all the treatments, the T3 treatment had the best effect on reducing the soil available Cd content and the Cd content in the edible part of the Chinese cabbage, which were significantly reduced by 17.05% and 49.35%, respectively, compared with CK, and the T3 treatment had the best effect on improving the yield and quality of the Chinese cabbage, significantly increasing the fresh weight of the Chinese cabbage by 31.86%, the soluble sugar level by 9.54%, the vitamin C level by 15.38%, and the chlorophyll level by 13.28%, compared with CK. In summary, 3000 kg/hm^2 of biochar combined with 3000 kg/hm^2 of phosphogypsum can significantly reduce the effectiveness of soil Cd, prevent the transfer of Cd to Chinese cabbage, reduce the ecological risk of Cd, and improve the yield and quality of Chinese cabbage. The results provide a theoretical basis for the safe production of agricultural products in Cd-contaminated soil and promote the recycling of resources for the benefit of the environment.

Keywords: biochar; phosphogypsum; Chinese cabbage; Cd

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1. Introduction

With rapid industrialization and large-scale agricultural intensification, human activities, such as mining and the extensive use of chemical fertilizers and pesticides, have caused serious pollution to soil [1]. Among the types of pollution, heavy metal pollution in soil is particularly prominent and has already posed a serious challenge to food production and food security [2,3]. Heavy metal pollution in soil has evolved into an environmental problem that poses a major threat to the future sustainable development of agriculture and human health due to its multiple characteristics such as invisibility, persistence, irreversibility, and enrichment [4]. In recent years, the remediation of heavy metal-contaminated soil and the restoration of its original function have become the focus of research at home and abroad [5]. Currently, various remediation methods are available for heavy metal-contaminated soils, including soil replacement, water washing, passivation, electrokinetic remediation, bioremediation, microbial remediation, synthesis, etc. [6–9]. However, these methods usually require the use of costly chemical agents and are accompanied by the need for a large amount of energy and capital investment [10,11]. Therefore, finding a remediation technology that not only effectively reduces the bioeffectiveness of heavy metals but also improves soil fertility has great theoretical significance and practical value [12].

As a major leafy vegetable in China, Chinese cabbage has been widely cultivated and consumed due to its short growth cycle, low cost, and rich nutritional value [13]. However, Chinese cabbage growing on Cd-contaminated land shows extremely high Cd accumulation potential in its edible parts [14]. Therefore, finding a management strategy to reduce the absorption of Cd in the edible parts of Chinese cabbage is necessary.

Biochar is a carbon-rich solid substance that is generated through the thermal cracking of biomass in an oxygen-deficient environment and is mainly composed of carbon molecules [15]. Its surface is rich in hydroxyl groups, olefins, organic oxygen functional groups, and pore structures, and these properties help biochar stabilize heavy metals in contaminated soil, improve the physicochemical properties of soil and soil fertility, and promote the growth and development of plants; hence, biochar has a wide range of applications in the remediation of heavy metal-contaminated soil [16,17]. Phosphogypsum is a by-product of phosphorus compound fertilizers and the phosphorus chemical industry, and 4.5–5.0 t of phosphogypsum is by-produced for every 1 t of phosphoric acid produced [18]. China is not only the world's largest producer of phosphate fertilizers, but also the world's largest by-producer of phosphogypsum, especially in Yunnan, Sichuan, Hubei, and Guizhou, with a combined output of up to 78 million t of phosphogypsum in 2018, an unutilized rate of more than 80%, and a cumulative stockpile of more than 830 million t [19]. Currently, phosphogypsum is used as a soil amendment in most parts of the world, and phosphogypsum application can improve certain soil properties and increase crop yields [20]. Numerous studies have been conducted to show that biochar and phosphogypsum provide a better way to use resources in agriculture. For example, Awad et al. [21] found that biochar pyrolyzed at 400 °C reduced the hazard of heavy metals in contaminated soils. Chaudhary et al. [22] found that biochar from different biowaste materials adsorbed heavy metal ions mainly through surface complexation and precipitation processes, which resulted in reductions in heavy metal content. Michalovicz et al. [23] showed that phosphogypsum can be used as a soil conditioner or slow-release fertilizer in agriculture, which improves soil fertility by providing basic cations and reducing Al^{3+} effectiveness.

However, while many studies have reported the effects of biochar or phosphogypsum alone on crop yield, quality, and soil nutrients [24,25], few studies have reported the effects of biochar combined with phosphogypsum on heavy metal-contaminated soil, and crop growth and development. Here, through a pot experiment based on previous research on the field remediation and improvement effects of corn straw biochar as a passivator on vegetables polluted by heavy metals for many years, the most suitable amount of biochar was selected and different amounts of phosphogypsum were applied to explore the remediation and improvement effects of biochar combined with different amounts of phosphogypsum on Cd-contaminated soil and the effect on the yield and quality of Chinese cabbage. The aim of this study was to provide a theoretical basis and a technical reference for promoting the safe production of agricultural products and for using solid waste resources in Cd-contaminated farmland.

2. Materials and Methods

2.1. Preparation of Biochar

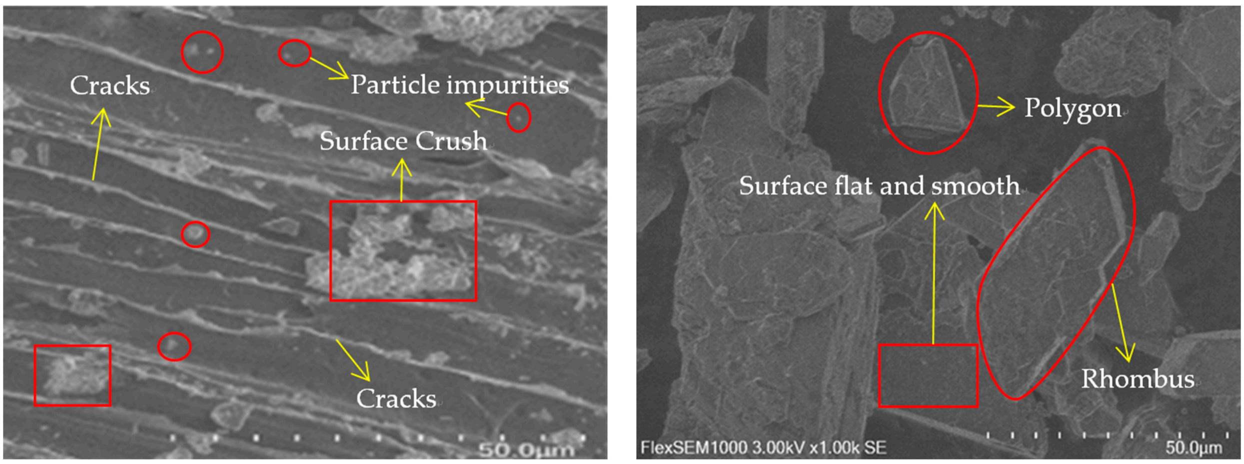
Corn straw was selected as the biochar material and prepared at the Soil Fertilization and Pollution Remediation Engineering Research Center of Yunnan Province. The corn straw was ground through a 100-mesh sieve, and then the powdered corn straw was placed in a tube furnace and heated to 500 °C for 2 h. During the preparation process, N_2 was introduced to ensure that the whole pyrolysis process was carried out under anaerobic conditions [26]. The prepared corn straw biochar was sealed and dried in a wide-necked bottle for use.

2.2. Harmless Disposal of Phosphogypsum

The phosphogypsum was reduced in acidity and water-soluble phosphorus, fluorine, and other impurities by washing and flotation; then high-temperature roasting was used to remove volatile components from the phosphogypsum, decompose organic matter, and convert some of the phosphorus, fluorine, and other impurities into insoluble or insoluble substances [18]. The harmless treatment of phosphogypsum was carried out by Yuntianhua Co., Kunming, China. (The company used a complete process that can effectively reduce more than 99% of water-soluble phosphorus and more than 90% of fluoride content in phosphogypsum and, at the same time, recover 0.3% of water-soluble phosphorus so that the pH value of phosphorus-containing wastewater reaches a neutral level close to 7. Not only can harmful substances be safely stockpiled but also harmless phosphogypsum can be obtained through alkaline curing. The phosphogypsum used in this test is harmless treated phosphogypsum).

2.3. Scanning Electron Microscopy of Biochar and Phosphogypsum

The principle of scanning electron microscopy for biochar and phosphogypsum was to scan the samples with a slender electron beam. The specific operation was to place the corn stover biochar and phosphogypsum materials on the carrier stage, first sprayed with gold, and then after drying, they were placed under the scanning electron microscope to observe the surface morphology and structural characteristics of the biochar under microscopic conditions [27]. The surface morphology analysis of the biochar and phosphogypsum is shown in Figure 1.



(**a**) (**b**)

Figure 1. Scanning electron micrographs of biochar and phosphogypsum. (**a**) Scanning electron micrograph of biochar; (**b**) scanning electron micrograph of phosphogypsum.

2.4. Test Material

A potting test was carried out in the greenhouse at the back of Yunnan Agricultural University, and the soil for testing was taken from Datun Town, Honghe Hani, and Yi Autonomous Prefecture, Yunnan Province, where the soil was acidic red soil and, due to mining carried out around the area in the early years, had more serious Cd contamination. The soil was taken from 0 to 20 cm of the top soil of the farmland in the area, and the soil samples were dried naturally to remove any debris, mixed uniformly, passed through a 2 mm sieve, and used for the potting tests. The physicochemical properties of the soil are shown in Table 1.

Table 1. The nature of the materials to be tested.

	pH	OM (g/kg)	AN (mg/kg)	AP (mg/kg)	AK (mg/kg)	Total Cd (mg/kg)
Soil	6.34	21.6	68.87	25.4	233.67	2.32
Phosphogypsum	7.53	211.5	24.26	84.41	67.12	0.11
Biochar	8.56	617.3	73.62	36.81	51.74	0.09

Vegetables: The vegetables used for testing were Chinese cabbage of the "Beijing Research Fast Vegetable No. 6 F1" variety, and the Chinese cabbage seeds were purchased from the Beijing Research Yinong (Beijing) Seed Industry Science and Technology Co., Beijing, China.

Biochar and phosphogypsum for testing: The corn stover biochar prepared by the Yunnan Soil Fertilization and Pollution Remediation Engineering Research Center and the phosphogypsum harmlessly treated by Yuntianhua Co., Kunming, China, were selected as the objects of this study, the basic properties of which are shown in Table 1.

2.5. Experimental Design

The pot experiment was conducted in July–September 2023 in a sunny greenhouse (the temperature in the greenhouse was (25 ± 3) °C and (20 ± 2) °C during the day and at night, respectively; the light cycle was 13 h) at the back of Yunnan Agricultural University, where biochar and phosphogypsum were mixed and applied in combination with basal fertilizer (a 15-15-15 chemical fertilizer was used as the basal fertilizer), and the experiment was set up with five treatments: no application of phosphogypsum or biochar (CK), no phosphogypsum + application of 3000 kg/hm^2 of biochar (T1), application of 1500 kg/hm^2 of phosphogypsum + 3000 kg/hm^2 of biochar (T2), application of 3000 kg/hm^2 of phosphogypsum + 3000 kg/hm^2 of biochar (T3), and application of 4500 kg/hm^2 of phosphogypsum + 3000 kg/hm^2 of biochar (T4). Three replications were carried out for each treatment, totaling 15 pots. The pots were filled with 5 kg of soil. Biochar, phosphogypsum, and sieved soil were added to plastic pots (20 cm in diameter and 20 cm in height), mixed evenly, and irrigated with deionized water. The pot water was adjusted to 65% of the field's water-holding capacity. After 2 weeks of balancing the soil properties, 30 Chinese cabbages were sown in each pot, and the seedlings were removed after 7 days of emergence to keep the number of seedlings in each pot at 3. During the growth period, the plants were regularly watered, and the Chinese cabbage plant samples were harvested after 30 days.

2.6. Sample Collection and Analysis

Plant and soil sample collection: When harvesting the Chinese cabbage, the two most representative Chinese cabbages were selected from each pot, and the Chinese cabbages were divided into two parts: their roots and their edible parts. The roots and edible parts were washed with tap water first and then washed with deionized water three times, and finally, the water on the surface of the plant was dried with dust-free paper. One of the cabbages was weighed, and then the fresh edible part was immediately stored in a refrigerator at 4 °C for quality determination. The other one, together with its roots, was treated in an oven at 105 °C for 30 min and then dried at 70 °C to a constant weight. After crushing, it was used for the determination of heavy metal content. The soil around the rhizosphere of the Chinese cabbage was collected from each pot. After being taken back, it was ground via natural ventilation, dried, sieved using 2 mm and 0.149 mm sieves, and sub-packed in a disposable plastic bag for testing [28].

Determination and analysis: The soil physical and chemical properties, vitamin C content, and soluble sugar content of the Chinese cabbages were determined according to "soil agrochemical analysis" [29]. The chlorophyll content of the Chinese cabbages was determined using a portable chlorophyll meter. The total amount of soil Cd referenced the standard "soil quality determination of lead and Cd graphite furnace atomic absorption spectrophotometry" (GB/T 17141-1997) [30]. The determination of available Cd content in the soil referred to the standard "Determination of available lead and Cd in soil by atomic absorption spectrometry" (GB/T 3739-2009) [31]. The determination of the Cd content in the Chinese cabbage was based on the national food safety standard "Determination of Cd in food" (GB 5009.15-2014) [32,33].

2.7. Data Analysis

The experimental data were analyzed using Excel 2016 for data statistics; SPSS Statistics 26 was used to determine the mean and standard deviation and used for significance analysis of the data; and Duncan's multiple comparisons were used to analyze the differences between the treatments, with the level of significance difference being $p < 0.05$. Origin 2021 was used to draw graphs.

3. Analysis of Results

3.1. Effect of Biochar with Phosphogypsum Application on pH of Cd-Contaminated Soil

The different treatments had different effects on the pH of the Cd-contaminated soil, as shown in Figure 2. Both the application of only biochar and the application of biochar with phosphogypsum significantly increased the pH of the Cd-contaminated soil. Among all the treatments, compared with the CK treatment, the T3 and T4 treatments had the best effect on increasing the pH of the Cd-contaminated soil, which was significantly increased by 0.27 and 0.29 units compared with the CK treatment, respectively, indicating that the application of 3000 kg/hm^2 and 4500 kg/hm^2 of phosphogypsum with biochar had the best effect on increasing the pH of the Cd-contaminated soil.

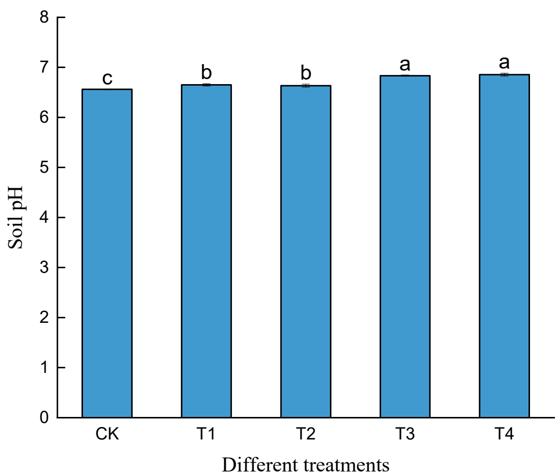
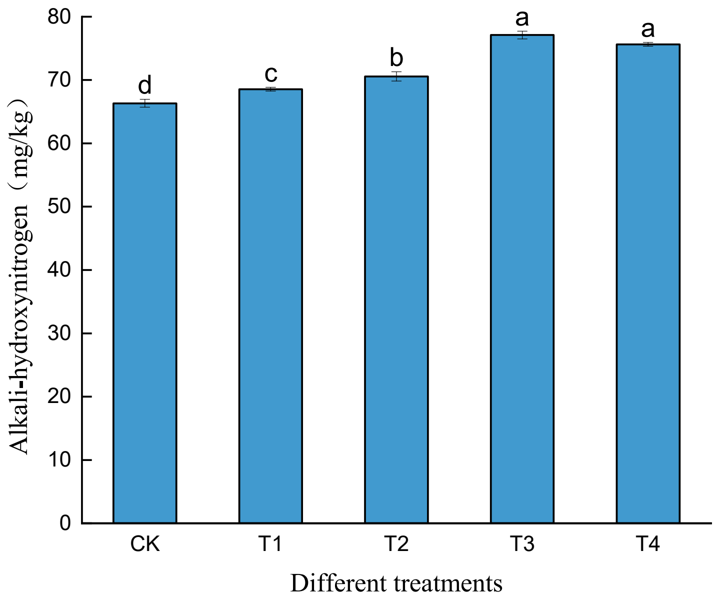


Figure 2. Effect of different treatments on pH of Cd-contaminated soil. No phosphogypsum and biochar (CK), no phosphogypsum + biochar application amount of 3000 kg/hm^2 (T1), phosphogypsum application amount of 1500 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T2), phosphogypsum application amount of 3000 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T3), and phosphogypsum application amount of 4500 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T4). The values are the means ± standard deviations (n = 3). Different small letters indicate significant differences at the level of $p < 0.05$.

3.2. The Effects of Biochar Combined with Phosphogypsum on the Contents of Alkali-Hydrolyzable Nitrogen, Available Phosphorus, and Available Potassium in Cd-Contaminated Soil

The effects of different treatments on the contents of alkali-hydrolyzable nitrogen, available phosphorus, and available potassium in the Cd-contaminated soil were different, as shown in Figure 3. The application of only biochar and the application of biochar with phosphogypsum increased the content of available phosphorus and available potassium in the Cd-contaminated soil and significantly increased the content of alkali-hydrolyzable nitrogen in the Cd-contaminated soil. Among all the treatments, compared with the CK treatment, the T3 and T4 treatments had the best effect on increasing the contents of alkali-hydrolyzable nitrogen, available phosphorus, and available potassium in the Cd-contaminated soil, which were significantly increased by 16.25%, 22.98%, and 8.50% and by 14.04%, 22.87%, and 10.13%, respectively, compared with the CK treatment. This shows that the application of 3000 kg/hm^2 and 4500 kg/hm^2 of phosphogypsum with biochar has the best effect on increasing the content of alkali-hydrolyzable nitrogen, available phosphorus, and available potassium in Cd-contaminated soil.



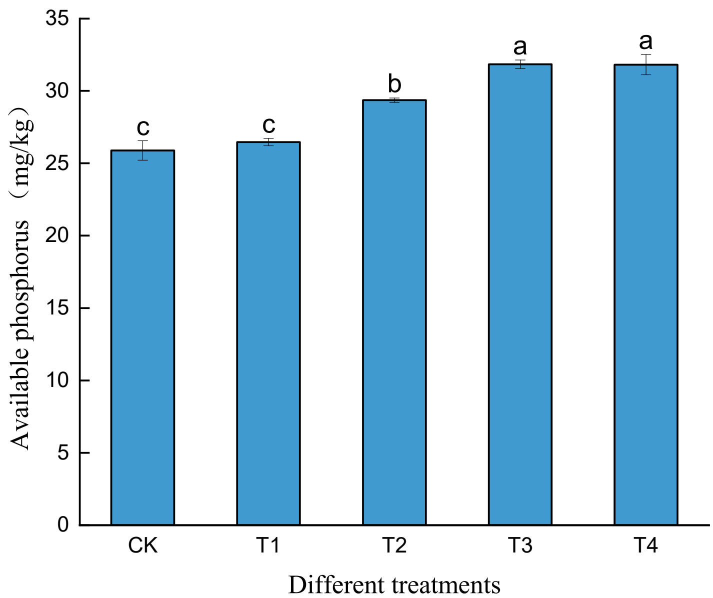


Figure 3. *Cont.*

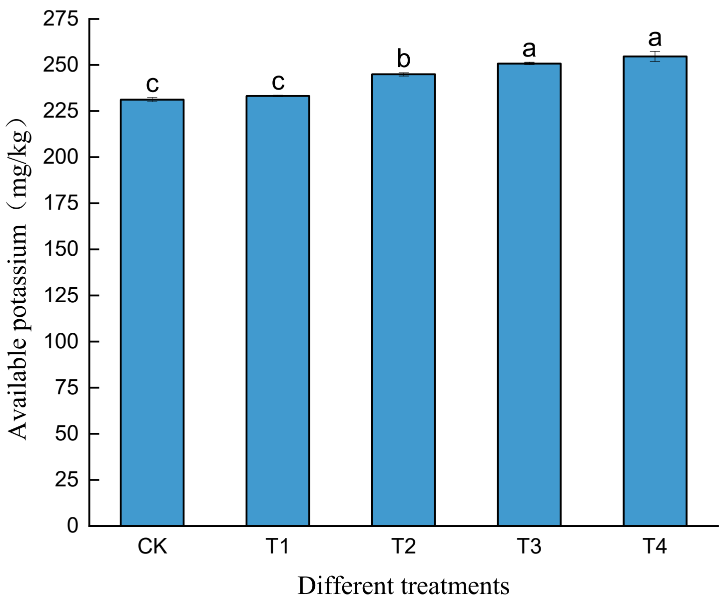


Figure 3. The effects of different treatments on the contents of alkali-hydrolyzable nitrogen, available phosphorus, and available potassium in Cd-contaminated soil. No phosphogypsum and biochar (CK), no phosphogypsum + biochar application amount of 3000 kg/hm^2 (T1), phosphogypsum application amount of 1500 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T2), phosphogypsum application amount of 3000 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T3), and phosphogypsum application amount of 4500 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T4). The values are the means ± standard deviations (n = 3). Different small letters indicate significant differences at the level of $p < 0.05$.

3.3. Effect of Biochar Combined with Phosphogypsum on Available Cd Content in Cd-Contaminated Soil

Different treatments had different degrees of effects on the Cd content in the available Cd-contaminated soil, as shown in Figure 4. Both the application of only biochar and the application of biochar with phosphogypsum significantly reduced the Cd content of Cd-contaminated soil in the available state. Among all the treatments, compared with the CK treatment, the T1, T2, and T3 treatments had the best effect on reducing the available Cd content in the Cd-contaminated soil, which was significantly lower than that of the CK treatment by 13.41%, 14.77, and 17.05%, respectively. This indicates that the application of only biochar and the application of 1500 kg/hm^2 and 3000 kg/hm^2 of phosphogypsum with biochar had the best effects on reducing the available Cd content in Cd-contaminated soil.

3.4. The Effect of the Application of Biochar with Phosphogypsum on the Cd Content in the Edible Part of Chinese Cabbage

Different treatments had different effects on the Cd content in the edible part of the Chinese cabbages, as shown in Figure 5. Both the application of only biochar and the application of biochar with phosphogypsum significantly reduced the Cd content in the edible part of the Chinese cabbages. Among all the treatments, the T3 treatment significantly reduced the Cd content in the edible part of the Chinese cabbages by 49.35% compared with the CK treatment. This indicates that the application of 3000 kg/hm^2 of phosphogypsum on top of biochar has the best effect on reducing the Cd content in the edible part of Chinese cabbage.

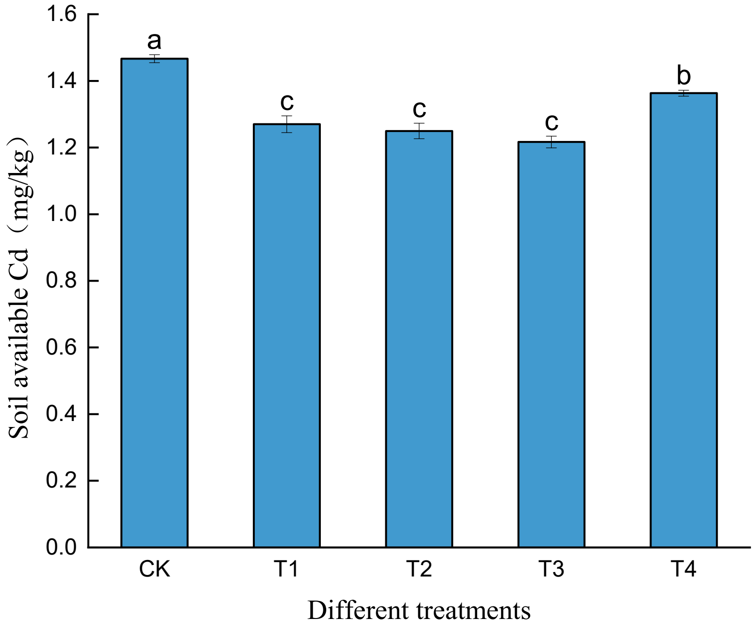


Figure 4. The effects of different treatments on the content of available Cd in Cd-contaminated soil. No phosphogypsum and biochar (CK), no phosphogypsum + biochar application amount of 3000 kg/hm^2 (T1), phosphogypsum application amount of 1500 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T2), phosphogypsum application amount of 3000 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T3), and phosphogypsum application amount of 4500 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T4). The values are the means ± standard deviations (n = 3). Different small letters indicate significant differences at the level of $p < 0.05$.

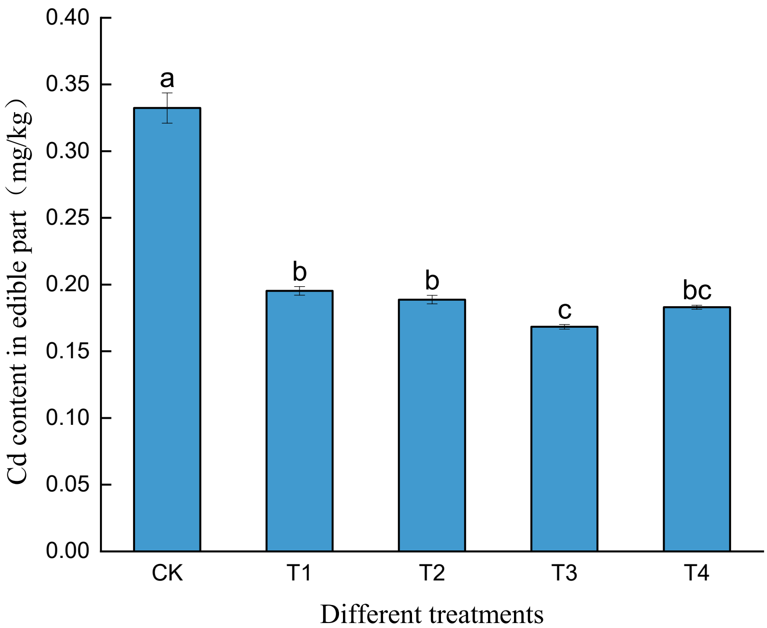


Figure 5. The effects of different treatments on Cd content in the edible part of Chinese cabbage. No phosphogypsum and biochar (CK), no phosphogypsum + biochar application amount of 3000 kg/hm^2 (T1), phosphogypsum application amount of 1500 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T2), phosphogypsum application amount of 3000 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T3), and phosphogypsum application amount of 4500 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T4). The values are the means ± standard deviations (n = 3). Different small letters indicate significant differences at the level of $p < 0.05$.

3.5. The Effect of the Application of Biochar with Phosphogypsum on the Yield and Quality of Chinese Cabbage

The effects of different treatments on the yield and quality of Chinese cabbage were different (Table 2). The application of only biochar and the application of biochar with phosphogypsum significantly increased the yield of Chinese cabbage. Among all the treatments, the T3 treatment had the most significant effect on the yield of Chinese cabbage, which was significantly higher than those of the CK, T1, T2, and T4 treatments by 31.86%, 20.89%, 29.32%, and 11.85%, respectively. The effect of biochar combined with phosphogypsum on the yield of Chinese cabbage was as follows: T3 > T1 > T2. The effect of biochar combined with phosphogypsum on the yield of Chinese cabbage increased first and then decreased with the increase in the rate of phosphogypsum application, indicating that an appropriate amount of phosphogypsum can significantly increase the yield of Chinese cabbage. However, a greater amount of phosphogypsum reduced the yield of Chinese cabbage.

Table 2. The effects of different treatments on the yield and quality of Chinese cabbage.

	Yield (g)	Soluble Sugar (%)	Vitamin C (mg/100 g)	Chlorophyll (mg/100 g)
CK	18.83 ± 0.24 d	2.83 ± 0.04 c	2.60 ± 0.04 c	2.86 ± 0.01 c
T1	20.54 ± 0.27 c	2.90 ± 0.06 bc	2.83 ± 0.02 b	3.09 ± 0.01 b
T2	19.20 ± 0.17 d	2.95 ± 0.06 abc	2.76 ± 0.03 b	3.07 ± 0.02 b
T3	24.83 ± 0.68 a	3.10 ± 0.02 a	3.00 ± 0.02 a	3.24 ± 0.02 a
T4	22.20 ± 0.34 b	3.07 ± 0.06 ab	3.03 ± 0.05 a	3.12 ± 0.01 b

Note: No phosphogypsum and biochar (CK), no phosphogypsum + biochar application amount of 3000 kg/hm^2 (T1), phosphogypsum application amount of 1500 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T2), phosphogypsum application amount of 3000 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T3), and phosphogypsum application amount of 4500 kg/hm^2 + biochar application amount of 3000 kg/hm^2 (T4). The values are the means ± standard deviations (n = 3). Different small letters indicate significant differences at the level of $p < 0.05$.

In addition, the application of only biochar and the application of biochar with phosphogypsum significantly increased the content of vitamin C, chlorophyll, and soluble sugar in Chinese cabbage. Among all the treatments, the T3 treatment had the best effect on improving the soluble sugar, vitamin C, and chlorophyll contents of Chinese cabbage, which was significantly higher than those in the CK treatment by 9.54%, 15.38%, and 13.28%, respectively. We can also see from Table 2 that among all the treatments, the T3 treatment increased the soluble sugar and chlorophyll content of the Chinese cabbages compared with the T1, T2, and T4 treatments, showing a trend of increasing first and then decreasing. The content of vitamin C showed an increasing trend with the increase in phosphogypsum application.

In conclusion, the best effect on improving the yield and quality of Chinese cabbage was achieved by applying 3000 kg/hm^2 of phosphogypsum on top of biochar.

4. Discussion

In this study, treatments with biochar and phosphogypsum significantly increased the pH of Cd-contaminated soil (Figure 2), which may be due to the large amount of soluble alkaline ions contained in the biochar. The soil used in this experiment was red soil. When biochar and phosphogypsum were mixed and added to the soil, the alkaline ions in the biochar were released in the form of carbonates and oxides. The cation was exchanged with the acidic ions in the soil, which effectively neutralized the acidity of the soil and increased the pH of the soil [34]. Another reason for this increase in pH may be because the pH of phosphogypsum was maintained between 7 and 8 during its treatment to become harmless and the pH of the biochar was greater than 8, so the pH of the Cd-contaminated soil increased significantly with the increase in phosphogypsum application. Guo et al. [35] showed that the application of biochar could significantly change the basic physical and chemical properties of the soil (pH, EC, and organic matter content), and the change range was more obvious with the increase in biochar application, results that were similar to the results of this study. The application of biochar combined with phosphogypsum significantly increased the pH of the Cd-contaminated soil.

Soil pH and organic matter content are key factors affecting plants' capacity to absorb heavy metals and their available states [36]. This study showed that the application of 3000 kg/hm^2 of phosphogypsum with biochar had the best effect on reducing the available Cd content in soil and the Cd content in the edible part of Chinese cabbage (Figures 4 and 5). This is because the functional groups, such as -OH and -COOH, contained in biochar not only contribute to the transformation of Cd in the soil to more stable hydroxides and carbonates but also form complexes with Cd^{2+}, thereby reducing the content of available Cd in the soil [37]. This result is the same as that found in the research by Jiao et al. [38]. They found that the application of biochar can reduce the content of available Cd in the soil. Biochar can effectively change the form of heavy metals in the soil and reduce its bioavailability due to its large porosity, specific surface area, and abundant surface functional groups. At the same time, the removal of heavy metal ions by phosphogypsum is mainly achieved through adsorption, precipitation, and ion exchange. For example, sulfate ions and other anions in phosphogypsum can react with heavy metal ions to precipitate on the surface of phosphogypsum in the form of hydroxyl complexes, further reducing the bioavailability of heavy metals [39].

In addition, biochar combined with phosphogypsum can significantly increase the content of available nutrients in Cd-contaminated soil (Figure 3), which may be due to the porous structure of biochar, which can adsorb many minerals in the soil, such as nitrogen, phosphorus, potassium, etc., thereby enhancing its nutrient fixation capacity [40]; the oxygen-containing functional groups (such as -COOH, -COH, and -OH) on the surface of biochar can combine with iron, aluminum, and other elements in the soil to promote the release of nutrients, such as the release of iron–aluminum-bound phosphorus; and increase the content of available phosphorus in the soil [41]. Biochar indirectly promotes plant growth by improving soil fertility and its physical structure [42,43]. Another reason may be because phosphogypsum contains many Ca and S elements, which are important nutrient elements for plant growth. Ca is an important component of the plant cell wall and plays an important role in maintaining the stability and integrity of the cell structure. S is necessary for plants to synthesize biologically active substances such as proteins, vitamins, and enzymes. The addition of phosphogypsum can release these nutrients for plant absorption and utilization, thus improving the growth performance of plants [44]. Luo et al. [45] showed that the cultivation of Sudan grass on an electrolytic manganese slag, phosphogypsum, and pepper straw biochar matrix significantly increased the fresh weight of Sudan grass. The nutritional components of the electrolytic manganese slag itself were incomplete (such as low available phosphorus content), and the content of heavy metals such as Mn was still high, which showed limited support for plant growth. Promoting plant growth depends on the roles of biochar and phosphogypsum. Wang et al. [46] found that the combination of desulfurization gypsum and biochar significantly improved the soil physical and chemical properties; significantly increased the soil water-soluble K^+, water holding capacity, available phosphorus, available potassium, and organic matter content; and promoted peanut growth. The fresh weight, dry weight, plant height, and leaf area of the peanut plant were higher than those of the control treatment. The combination of desulfurization gypsum and biochar can increase the availability and content of nitrogen, phosphorus, and potassium, thereby promoting crop growth. Their research results are consistent with those of this experiment. In addition, studies have shown that when the amount of biochar added is 2.5%, the soluble sugar content of Chinese cabbage is the highest and, when the amount of biochar added is 5%, the vitamin C content of Chinese cabbage is the highest [47]. This is consistent with our research findings to some extent. In this study, biochar combined with phosphogypsum increased the soluble sugar and vitamin C content of Chinese cabbage, possibly because some of the biochemical processes in Chinese cabbage plants were affected after biochar application [48].

In summary, biochar combined with phosphogypsum shows a good application prospect in agricultural production. The results of this experiment showed that biochar combined with phosphogypsum could effectively improve and repair Cd-contaminated soil and improve the yield and quality of Chinese cabbage. This provides an effective solution for the sustainable recovery of heavy metal-contaminated soil and provides a new way to use phosphate fertilizer production by-products.

5. Conclusions

In this study, it was found that the use of biochar in combination with phosphogypsum effectively improves the Cd-contaminated soil and increases the yield and quality of Chinese cabbage through potting experiments. Specifically, the combined use of biochar and phosphogypsum significantly increases soil pH and soil nutrient content, reduces the available Cd content in soil, and blocks the transfer of Cd to Chinese cabbage, reducing the ecological risk of Cd. With the increase in phosphogypsum dosage, this remediation effect is first enhanced and then weakens, in which the use of 3000 kg/hm^2 biochar with 3000 kg/hm^2 phosphogypsum has the best effect. In addition, the porous structure of biochar helps to increase soil aeration and water retention, while phosphogypsum provides essential nutrients and alkalinity, and the combined use of the two helps to improve soil fertility, promote crop growth, and reduce the use of chemical fertilizers, reducing the risk of agricultural surface pollution. However, biochar and phosphogypsum are more expensive to produce and transport and may be more suitable for areas close to the source of raw materials. The technology is still in the experimental stage, and more technical support and research and development investment are needed to ensure its effectiveness and safety.

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References

1. Sakshi; Singh, S.K.; Haritash, A.K. Polycyclic aromatic hydrocarbons: Soil pollution and remediation. *Int. J. Environ. Sci. Technol.* **2019**, *16*, 6489–6512. [CrossRef]
2. Liu, Y.R.; Van der Heijden, M.G.; Riedo, J.; Sanz-Lazaro, C.; Eldridge, D.J.; Bastida, F.; Delgado-Baquerizo, M. Soil contamination in nearby natural areas mirrors that in urban greenspaces worldwide. *Nat. Commun.* **2023**, *14*, 1706. [CrossRef] [PubMed]
3. Liu, Z.; Yin, Y.; Zhang, Y.; Shi, S. Legal system of soil pollution remediation in China and its regulation and guidance to soil pollution remediation. *Sustainability* **2023**, *15*, 11504. [CrossRef]
4. Lin, H.; Wang, Z.; Liu, C.; Dong, Y. Technologies for removing heavy metal from contaminated soils on farmland: A review. *Chemosphere* **2022**, *305*, 135457. [CrossRef]
5. Lu, Z.; Su, H. Employing gene chip technology for monitoring and assessing soil heavy metal pollution. *Environ. Monit. Assess.* **2022**, *194*, 2. [CrossRef]
6. Zheng, X.J.; Li, Q.; Peng, H.; Zhang, J.X.; Chen, W.J.; Zhou, B.C.; Chen, M. Remediation of heavy metal-contaminated soils with soil washing: A review. *Sustainability* **2022**, *14*, 13058. [CrossRef]
7. Ciaramella, B.R.; Corinzia, S.A.; Cosentino, S.L.; Testa, G. Phytoremediation of heavy metal contaminated soils using safflower. *Agronomy* **2022**, *12*, 2302. [CrossRef]
8. Zheng, X.; Lin, H.; Du, D.; Li, G.; Alam, O.; Cheng, Z.; Li, J. Remediation of heavy metals polluted soil environment: A critical review on biological approaches. *Ecotoxicol. Environ. Saf.* **2024**, *284*, 116883. [CrossRef] [PubMed]
9. Khalid, S.; Shahid, M.; Niazi, N.K.; Murtaza, B.; Bibi, I.; Dumat, C. A comparison of technologies for remediation of heavy metal contaminated soils. *J. Geochem. Explor.* **2017**, *182*, 247–268. [CrossRef]

10. Wang, L.; Rinklebe, J.; Tack, F.M.; Hou, D. A review of green remediation strategies for heavy metal contaminated soil. *Soil Use Manag.* **2021**, *37*, 936–963. [CrossRef]
11. Azhar, U.; Ahmad, H.; Shafqat, H.; Babar, M.; Munir, H.M.S.; Sagir, M.; Khoo, K.S. Remediation techniques for elimination of heavy metal pollutants from soil: A review. *Environ. Res.* **2022**, *214*, 113918. [CrossRef] [PubMed]
12. Sánchez-Castro, I.; Molina, L.; Prieto-Fernández, M.Á.; Segura, A. Past, present and future trends in the remediation of heavy-metal contaminated soil-Remediation techniques applied in real soil-contamination events. *Heliyon* **2023**, *9*, e16692. [CrossRef]
13. Wang, J.; Huang, F.; You, X.; Hou, X. Molecular cloning, characterization and expression analysis of $BcHHP_3$ under abiotic stress in Pak-choi (*Brassica rapa* ssp. Chinensis). *J. Plant Interact.* **2019**, *14*, 1–9. [CrossRef]
14. Kiran, Y.K.; Barkat, A.; CUI, X.Q.; Ying, F.E.N.G.; PAN, F.S.; Lin, T.A.N.G.; YANG, X.E. Cow manure and cow manure-derived biochar application as a soil amendment for reducing cadmium availability and accumulation by *Brassica chinensis* L. in acidic red soil. *J. Integr. Agric.* **2017**, *16*, 725–734. [CrossRef]
15. Xiang, L.; Liu, S.; Ye, S.; Yang, H.; Song, B.; Qin, F.; Tan, X. Potential hazards of biochar: The negative environmental impacts of biochar applications. *J. Hazard. Mater.* **2021**, *420*, 126611. [CrossRef] [PubMed]
16. Marcińczyk, M.; Oleszczuk, P. Biochar and engineered biochar as slow-and controlled-release fertilizers. *J. Clean. Prod.* **2022**, *339*, 130685. [CrossRef]
17. Huang, H.; Ge, L.; Zhang, X.; Chen, H.; Shen, Y.; Xiao, J.; Li, R. Rice straw biochar and lime regulate the availability of heavy metals by managing colloid-associated-but dissolved-heavy metals. *Chemosphere* **2024**, *349*, 140813. [CrossRef]
18. Lu, W.H.; Wang, Y.F.; Liu, J.; Ren, L.J.; Zhang, N.M. Research progress on harmless modification of phosphogypsum and its application in farmland soil improvement. *Soil* **2023**, *55*, 699–707.
19. Samet, M.; Charfeddine, M.; Kamoun, L.; Nouri-Ellouze, O.; Gargouri-Bouzid, R. Effect of compost tea containing phosphogypsum on potato plant growth and protection against Fusarium solani infection. *Environ. Sci. Pollut. Res.* **2018**, *25*, 18921–18937. [CrossRef]
20. Peng, X.; Deng, Y.; Liu, L.; Tian, X.; Gang, S.; Wei, Z.; Yue, K. The addition of biochar as a fertilizer supplement for the attenuation of potentially toxic elements in phosphogypsum-amended soil. *J. Clean. Prod.* **2020**, *277*, 124052. [CrossRef]
21. Awad, M.; El-Sayed, M.M.; Li, X.; Liu, Z.; Mustafa, S.K.; Ditta, A.; Hessini, K. Diminishing heavy metal hazards of contaminated soil via biochar supplementation. *Sustainability* **2021**, *13*, 12742. [CrossRef]
22. Chaudhary, H.; Dinakaran, J.; Notup, T.; Vikram, K.; Rao, K.S. Comparison of adsorption performance of biochar derived from urban biowaste materials for removal of heavy metals. *Environ. Manag.* **2024**, *73*, 408–424. [CrossRef]
23. Michalovicz, L.; Müller, M.M.L.; Tormena, C.A.; Dick, W.A.; Vicensi, M.; Meert, L. Soil chemical attributes, nutrient uptake and yield of no-till crops as affected by phosphogypsum doses and parceling in southern Brazil. *Arch. Agron. Soil Sci.* **2019**, *65*, 385–399. [CrossRef]
24. Chi, W.; Nan, Q.; Liu, Y.; Dong, D.; Qin, Y.; Li, S.; Wu, W. Stress resistance enhancing with biochar application and promotion on crop growth. *Biochar* **2024**, *6*, 43. [CrossRef]
25. Qi, J.; Zhu, H.; Zhou, P.; Wang, X.; Wang, Z.; Yang, S.; Li, B. Application of phosphogypsum in soilization: A review. *Int. J. Environ. Sci. Technol.* **2023**, *20*, 10449–10464. [CrossRef]
26. Qin, X.; Luo, J.; Liu, Z.; Fu, Y. Preparation and characterization of MgO-modified rice straw biochars. *Molecules* **2022**, *25*, 5730. [CrossRef]
27. Xie, Y.F.; Cheng, D.Y.; Shi, J.Q.; Zhu, X.; Li, Z.L.; Wang, L. Study on the adsorption of Cd^{2+} by potassium permanganate modified wheat straw. *J. Ecol. Rural Environ.* **2019**, *35*, 668–674.
28. Zhou, H.Y.; Li, J.Q.; Bao, L.; Xia, Y.S.; Wang, S.; Wu, L.H.; Zhang, N.M. Effects of different control measures on the accumulation of Cd and lead in lettuce and its quality. *Environ. Sci.* **2023**, *9*, 5196–5203.
29. Bao, S.D. *Soil and Agricultural Chemistry Analysis*, 3rd ed.; China Agriculture Press: Beijing, China, 2000.
30. *GB/T 17141-1997*; Determination of Soil Quality Lead and Cadmium. Standardization Administration of the People's Republic of China: Beijing, China, 1997.
31. *GB/T 3739-2009*; Determination of Heavy Metals in Soil. Standardization Administration of the People's Republic of China: Beijing, China, 2009.
32. *GB 5009.15-2014*; Determination of Heavy Metals in Food. Standardization Administration of the People's Republic of China: Beijing, China, 2014.
33. Liu, Q.; Wang, S.; Zhao, X.Y.; Chen, W.; Bao, L.; Zhang, N.M. Study on the difference of Cd and Pb accumulation and transport in maize by different foliar inhibitors. *J. Agric. Environ. Sci.* **2023**, *42*, 1247–1256.
34. Ahmad, M.; Rajapaksha, A.U.; Lim, J.E.; Zhang, M.; Bolan, N.; Mohan, D.; Ok, Y.S. Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere* **2014**, *99*, 19–33. [CrossRef]
35. Guo, B.Y.; Yang, K.P.; Zhang, J.; Dai, J.C.; Cheng, Z.Y.; Zhang, Y.P. Study on passivation remediation of lead and Cd contaminated soil by manganese dioxide/amino modified biochar. *J. Ecol. Rural Environ.* **2023**, *39*, 422–428.
36. Wang, X.B.; Ruan, S.L.; Zhu, X.L.; Qian, L.H.; Tong, C.M.; Yan, J.L. Effects of passivators on soil available Cd, Pb and their accumulation in the roots of Tetrastigma hemsleyanum. *J. Ecol. Rural. Environ.* **2024**, *40*, 565–571.
37. Wang, X.; Wang, T.; Huang, Y.; Liu, A.; Li, Q.; Wang, Y.; Tang, Z. Effect of biochars on the immobilization and form of Cd (Cd) in simulated Cd deposition of iron rich soils. *Ecotoxicol. Environ. Saf.* **2024**, *272*, 116045. [CrossRef]

38. Jiao, Z.Q.; Ge, S.J.; Zheng, W.X.; Liu, J.H.; Chen, M.; Kong, Y.K.; Wang, Y.Y. Passivation remediation of Cd-contaminated soil by thiol-modified biochar and soil microbial response. *Environ. Sci.* **2024**, *45*, 5570–5577.
39. Dai, C.X.; Hu, Y.; Ma, L.P.; Yang, J.; Guo, Z.Y.; Ao, R.; Xie, L.G. The influence mechanism of modified phosphogypsum on the migration and change of heavy metals in sludge. *China Environ. Sci.* **2024**, *9*, 5063–5076.
40. de la Rosa, J.M.; Rosado, M.; Paneque, M.; Miller, A.Z.; Knicker, H. Effects of aging under field conditions on biochar structure and composition: Implications for biochar stability in soils. *Sci. Total Environ.* **2018**, *613*, 969–976. [CrossRef] [PubMed]
41. Wang, K.; Wei, Y.W.; Ji, X.M.; Yun, F.; Zou, K.; Long, Z. Effects of combined application of biochar-based fertilizer and Trichoderma harzianum agent on the quality of flue-cured tobacco and tobacco-planting soil. *J. Crops* **2021**, *3*, 106–113.
42. Chen, F.J.; Xia, H.J.; Liu, F.D.; Kong, W.J.; Lu, S.Y. Biochar characteristics and their effects on soil properties and mechanisms. *J. Environ. Eng. Technol.* **2022**, *12*, 161–172.
43. Yu, D.; Feng, M.Y.; Li, Y.; Luo, Y.J. Effects of straw biochar on the growth and development of Chinese cabbage and soil properties. *South. Agric.* **2019**, *13*, 45–47.
44. Zhang, C.G.; Bai, L.H.; Yue, X.R.; Xia, Y.S.; Hong, C.Q.; Zhu, J. Analysis of chemical characteristics of main phosphogypsum in Yunnan Province. *J. Yunnan Agric. Univ. Nat. Sci.* **2012**, *5*, 756–762.
45. Luo, Y.; Liu, F.; Luo, X.; Ren, J.; Guo, J.; Zhang, J. Influence of EMR–Phosphogypsum–Biochar Mixtures on Sudan Grass: Growth Dynamics and Heavy Metal Immobilization. *Agronomy* **2024**, *14*, 945. [CrossRef]
46. Wang, P.; Liu, Q.; Fan, S.; Wang, J.; Mu, S.; Zhu, C. Combined Application of Desulfurization Gypsum and Biochar for Improving Saline-Alkali Soils: A Strategy to Improve Newly Reclaimed Cropland in Coastal Mudflats. *Land* **2023**, *12*, 1717. [CrossRef]
47. Li, J.; Wu, H.S.; Gao, Z.Q.; Shang, X.S.; Zheng, P.H.; Yin, J.; Ma, S.J. The effects of phosphogypsum on CO_2 emission and wheat yield in wheat field and its economic and environmental benefits were analyzed. *Environ. Sci.* **2015**, *36*, 3099–3105.
48. Wang, W.; Li, M.; Zhang, W.H.; Han, Y.Q.; Liu, M.M.; Du, J.D. Effects of different improvement measures on the growth and yield of kidney bean in saline-alkali land. *J. Heilongjiang Bayi Agric. Univ.* **2018**, *30*, 1–7+16.