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Innovative Practice of Heavy Metal Soil Remediation Technology under the Background of Rural Revitalization by Integrating Agriculture, Culture and Tourism

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Abstract

With the development and modernization of rural economies, the integration of agriculture, cultural tourism, and other fields has gradually become a new driving force for promoting rural revitalization. However, in recent years, the development of mines and the utilization of resources have led to severe heavy metal pollution of farmland soil, causing significant food safety risks and economic losses, which pose serious challenges to the integration of agriculture, culture, and tourism. Therefore, China has invested a lot of attention in addressing the issue of soil remediation in abandoned rural mining areas. The study focuses on an abandoned mining area polluted by heavy metals such as Cd, Zn, and Cu in a certain area. Two materials, biochar and compost, were added to the soil in the polluted area, and the weight ratios of biochar and compost were set to 0:100, 10:90, 20:80, 40:60, 60:40, and 100:0. A new type of biochar was prepared by mixing two materials at high temperatures, and its effects on the pH and organic carbon content of soil in heavy metal polluted rural abandoned mining areas were explored. The effective removal and adsorption of heavy metals in the soil were also investigated, as was the promotion of crop growth in the soil area. This indicates that the use of biochar and compost can significantly repair heavy metal contaminated soil in mining areas and improve soil availability. Meanwhile, research has found that the integration of agriculture, culture, and tourism provides a unique perspective on soil remediation technology, which may involve maintaining rural cultural traditions, enhancing the attractiveness of rural tourism, and ensuring food safety and agricultural sustainability. Therefore, the selection and implementation of repair technologies need to consider multiple factors to ensure the triple benefits to the economy, society, and environment.

Keywords: rural revitalization, composting, biochar, soil remediation, heavy metal pollution

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Introduction

Agriculture, culture, and tourism (ACT) integration is the integration of agriculture, cultural creativity, experience tourism, and other industries. Compared with traditional cultural tourism, it not only has more industrial roots, but also fulfills the responsibility of maintaining natural ecology. This is the inevitable trend of the current development of the tourism industry [1, 2]. In a broad sense, ACT integration is the only way to adapt to the market and plays an important role in the further implementation of the rural revitalization strategy. It has far-reaching significance in promoting economic benefits in rural areas and improving the rural ecological environment. With the deepening of ACT integration and rural revitalization, Heavy Metal pollution has gradually become an urgent problem in rural SR work [3, 4]. Heavy metals are one of the pollutants that are highly toxic, difficult to degrade, and easily amplified. After entering the soil, they gradually accumulate under the effects of adsorption, complexation, and sedimentation. This phenomenon greatly increases the content of heavy metals in soil sediments and poses a serious threat to the entire soil ecosystem. The content and types of heavy metals in abandoned mining areas are relatively high, and the soil is often affected by pollution from heavy metals such as Cd, Zn, Cu, etc. Heavy metal pollution in farmland near mining areas is a soil pollution phenomenon caused by excessive deposition of heavy metals in the soil [5, 6]. Heavy Metals will not decompose after entering the soil. But it will migrate and transform in the soil and inhibit the activity of soil enzymes through the biomagnification of the food chain. So the physical and chemical properties of soil are changed. Unlike organic pollutants, Heavy Metal pollution in soil will last for decades or even centuries. Biochar is an important soil Heavy Metal remediation agent that can fix Heavy Metal in soil. Therefore, the mobility of Heavy Metal organisms is reduced to a certain extent. So it can achieve the purpose of degrading organic pollutants and improving the quality of contaminated soil [7, 8]. Onmonya et al. used the adsorption of biochar to remove lead, chromium, mercury, and copper from soil and water. The results verified the effectiveness of this method [9]. Fayuan's team proposed to apply phytoremediation - biochar to soil remediation (SR) in view of the problem of Heavy Metal pollution caused by mining activities. It can effectively remove the contaminated biomass from the soil [10]. However, in the current research, there is a lack of utilization of the mechanism of biocarbon remediation. That is, the influence of soil characteristics, Heavy Metal

species, and other factors is ignored, resulting in poor remediation effects. Therefore, a new type of biochar was prepared by mixing biochar and compost at high temperatures. It is expected to improve the remediation capacity of Heavy Metal contaminated soil and provide new technical support for the sustainable use of soil.

Material and Methods

Selection and Measurement of Research Indicators

Selection and Physical and Chemical Properties of Test Soil

The Heavy Metal contaminated soil in the abandoned mining area selected by the research institute is located in the countryside, which makes it easy to have a great impact on the daily lives of rural people [11]. The experiment was carried out in the key laboratory for degraded ecosystem restoration and watershed eco hydrology built by the Nanchang Institute of Engineering. The laboratory is located in a subtropical monsoon climate. The annual average temperature remains around 18°C, and the annual relative humidity is 77.9%. The entire experiment lasted from April 11, 2020, to October 8, 2020, and the overall cycle was relatively long.

5 sampling points are set up in the selected abandoned mining area, and sampling was conducted on March 9, 2020. Each sampling point selects surface soil with a depth of 5-15 cm. After collecting each soil sample, plant roots and debris, such as sand and gravel, are removed. They are stored in a self sealing bag, and they are quickly transported back to the laboratory. The soil from 5 points is mixed evenly, and it is dried naturally in a ventilated indoor area for 4 weeks. The dried soil blocks are crushed, and they are passed through a 2 mm mesh sieve. These experiments are conducted to determine the physical and chemical properties of the selected soil and remediate heavy metal pollution in the soil. The specific physical and chemical properties covered by the selected test soil are shown in Table 1.

The basic soil properties are determined according to conventional methods, and the specific determination methods are as follows: To determine the pH value of the soil, 2 g of screened, air-dried mining area soil is put into a dried beaker (50 ml). Then deionized water is added according to the ratio of the soil sample: deionized water = 1:2.5 (w/v). Next, the sample is stirred violently with a clean glass rod for $1\sim2$ min and stands for half an hour. The liquid obtained after filtering with ordinary filter paper is used as the test sample, and the strictly

Table 1. Basic properties.

pН	TOC(g/kg)	Total nitrogen(g/kg)	Total phosphorus (g/kg)	Cu (mg/kg)	Cd (mg/kg)	Zn (mg/kg)
3.43	32.58	4.92	2.75	2915.41	15.66	365.89

calibrated precision pH meter is used for determination [12, 13]. The total organic carbon (TOC) in soil is determined by the loss on ignition method. The prepared soil samples are put into the oven; the temperature of the oven is set at $100 \pm 5^{\circ}$ C, and the samples are baked for 8-10 hours for weighing. The weighed sample is put into a muffle furnace for burning. The temperature is set at 550°C, and the sample is burned for 8 hours. The residual mass after burning is ash. The difference in sample quality before and after burning is the quality of total organic carbon [14, 15]. Formula (1) is the calculation of total organic carbon mass.

$$TOC(\%) = TOC / (TOC + Ash) \times 100\%$$
(1)

In Formula (1), TOC represents total organic carbon,

i.e., organic matter. Then the water soluble carbon (WEOC) of the soil is measured. 2.5 g of screened airdried mining soil is placed in a centrifuge tube, and 25 g of deionized water is added. Then it is placed on an oscillator to shake for 3.5 h, and centrifuged at 3000 r/min for 20 min. Finally, 0.45 µM of organic filter membrane filtration is used. The supernatant obtained by filtration is used to determine WEOC with a total organic carbon analyzer (TOC-VCPH) (Shimadzu, Tokyo, Japan). The cation exchange capacity (CEC) in soil is determined by the BaCl₂ forced exchange method. The main principle is that the cations in the soil can be equivalently exchanged by the positive divalent barium ion in the BaCl₂ solution. And it is combined with the sulfate ion to form the barium sulfate solution. The mass change of the sulfuric acid solution before and after the determination is determined by sodium hydroxide titration. Then the amount of sulfuric acid consumed can be obtained. Finally, the amount of cation exchange in the soil can be obtained [16-18]. Formula (2) is the calculation of CEC.

$$CEC = \left\lfloor \left(C \left(H_2 SO_4 \right) \times 50 - C \left(NaOH \right) \right. \\ \left. \times V \left(NaOH \right) \right) \times 100 \right\rceil / \left(W_0 \times K_2 \right)$$
(2)

In Formula (2), CEC means the cation exchange capacity. $C(H_2SO_4)$ is the concentration of standard sulfuric acid solution. V(NaOH) represents the volume of standard sodium hydroxide consumed by titration, in ml. W_0 is the weight of soil, in g. C(NaOH) is the concentration of standard sodium hydroxide solution, in mol/l. K, is the moisture conversion coefficient. Finally, NaHCO₃ is used to extract available P from the soil. In most soils, available P exists in the form of monocalcium phosphate and dicalcium phosphate. Extraction with NaHCO₃ can inhibit the activity of calcium ions and make the available P in soil combine with bicarbonate to form calcium carbonate precipitation. At the same time, calcium phosphate with high activity is fully extracted, and a certain amount of phosphate conjugate is leached through hydrolysis. Finally, P in the extracted solution was determined by molybdenum-antimony spectrophotometry. In the process, the yellow antimony phosphomolybdate heteropoly acid was reduced to phosphomolybdate blue, and the content was determined by colorimetry [19-21]. Formula (3) is the specific calculation.

$$W_{P} = (C \times t) / (m \times K \times 10^{3})$$
(3)

In Formula (3), W_p represents the content of available P (g/kg). C represents the content of the available P found on the record (μg). t represents the fractional multiple. m is the mass of athe ir-dried soil sample (g). K is the moisture conversion coefficient (i.e., an air-dried soil sample is converted to dry soil sample).

Determination of Heavy Metals in Soil

To determine the content of Heavy Metal in soil, 0.50 g of air-dried soil sample (through a 100 mesh sieve, accurate to 0.0001 g) is accurately weighed and put into a digestion tube with a capacity of 50 ml. Then, a little water is added to wet the sample. Next, 5 ml HNO₂, 5 ml HF, and 3 ml HC₁O₄ are added to the fume hood and mixed evenly. The graphite digestion instrument is used to decompose the organic matter according to the set procedures and parameters to obtain a clear sample solution [22-24]. After completion, it is necessary to transfer all the sample solution obtained into a 50 ml volumetric flask, wash it, fix the volume, and shake it well. Finally, the content of Heavy Metal in the soil (Cd, Cu, and Zn) can be obtained by measuring the content of Heavy Metal in the sample with a flame atomic absorption spectrophotometer (AA700, Perkin Elmer Inc., USA). There are three conditions for the digestion process and temperature setting: the temperature is 100°C, and the digestion takes 30 minutes. The temperature is 170°C, and the digestion time is 90 min. The temperature is 150°C, and the digestion time is 60 min.

Then the availability of Heavy Metal is determined. The specific method is as follows: 3.0 g (accurate to 0.0001 g) of air-dried mining soil is weighed and put into 50 ml of a clean and dry conical flask. Then 30 ml of 0.01 M CaCl₂ solution is added. The conical flask is put into the oscillator together, and the oscillation is continued for 24 h at 60 rpm. After mixing evenly, centrifugation is conducted at 3500 r/min for 20 min. 0.45 μ m organic membrane is used to filter the clear liquid. And 2 drops of 1 mol/L nitric acid (HNO₃) solution are dropped into the sample solution to avoid Heavy Metal precipitation and reduce the activity of microorganisms in the solution [25-27]. Finally, the availability of Heavy Metals is determined by an ion emission spectrometer (ICP-AES).

Samples are taken from the soil of the rural abandoned mining area to be repaired, and the morphological distribution of Heavy Metal (Cd, Cu, and Zn) in the soil is determined. The study plans to use Tessier technology to extract different forms of Heavy

Different forms of heavy metals	Experimental reagent	Oscillation shaking time	
Commutative state	1 M MgCl ₂	1 h at 25°C	
Carbonate bound state	1 M CH ₃ COONa	5 h at25°C	
Fe-Mn oxide bound state	$0.04 \text{ MNH}_2\text{OH} \cdot \text{HC}_1 \text{ in } 25\% \text{ (v/v)CH3COOH}$	6 h at 96°C	
Organically bound state	$30\% \text{ H}_{2}\text{O}_{2}/0.02 \text{ M HNO}_{3} \text{ (pH = 2),followed by } 3.2 \text{ M} \text{ CH}_{3}\text{COONH}_{4}/20\% \text{ (v/v) HNO}_{3}$	2 h at 85°C/3 h at 85°C	
Residual state	HNO ₃ -HF-HClO ₄	Clear up	

Table 2. Continuous extraction method steps for different morphological distributions of heavy metals.

Table 3. Experimental design of soil remediation.

Description of the experiments	Abbreviation
400 g soil (Control)	S+C
400 g soil + 40 g compost (0% w/w biochar)	S+B/C (10/90)
400 g soil + 36 gcompost + 4 g biochar (10%w/w biochar)	S+B/C (20/80)
400 g soil + 32 g compost + 8 g biochar (20% w/w biochar)	S+B/C (40/60)
400 g soil + 24 g compost + 16 g biochar (40% w/w biochar)	S+B/C (60/40)
400 g soil + 16 g compost + 24 g bioc har (60% w/w biochar)	S+B
400 g soil + 40 g biochar (100% w/w biochar)	S+C

Metal step by step. The main forms are exchangeable, nitrate bound, iron manganese oxide bound, organic bound, and residue [28-30]. Table 2 shows the extraction steps for each form of Heavy Metal.

Preparation of a Biocarbon-Compost Remediation Agent

The main materials of the remediation agent used in the study are biochar, organic compost, and a mixture of biochar and compost. Biochar (B) is prepared from rice husk and straw as raw materials, which are crushed and screened after pyrolysis at 500°C at a high temperature and slow speed in a continuously flowing vacuum nitrogen environment. The specific preparation process for biochar is as follows: the weighed raw materials are mixed evenly. Then they are loaded into the vacuum tube type high-temperature furnace tube. The temperature in the tube is set at 4000 w and gradually rises to 500°C at a rate of 25°C/min. The overall temperature rise and pyrolysis time last for 2 hours. Then, after the temperature is reduced to room temperature, the obtained materials are stored in a drying dish for standby. Compost (C) is prepared by combining 85% fresh weight pig manure and 25% fresh weight sawdust under aerobic conditions after 2 months of accumulation and fermentation [31, 32]. The effect of biochar and compost combined (B+C) and their different proportions on the adsorptiondesorption behavior of Heavy Metal contaminated soil is studied. The biochar mixture, compost, and biochar are applied to rural Heavy Metal contaminated soil in different proportions (w/w = remediation agent/soil)

[33-35]. Biochar and compost are mixed evenly into the soil to be repaired at the weight ratios of 0:100, 10:90, 20:80, 40:60, 60:40, and 100:0, respectively. Soil remediation was conducted at 25°C for two months, during which irrigation was conducted regularly to keep 60% water in the soil [36, 37]. Table 3 shows the specific design of the SR experiment.

Determination of Biomass Carbon Index

For the effective determination of biochar yield, it is necessary to weigh the dry weight of the selected sample materials before and after pyrolysis. The effective yield of biochar is calculated in different proportions. Equation (4) is the calculation method.

$$Productivity(\%) = \frac{Dry \text{ weight of sample after pyrolysis}}{Dry \text{ weight of prepared material}} \times 100$$
(4)

In Formula (4), productivity (%) represents the biomass carbon yield. The dry weight of the sample after pyrolysis is the dry weight of the sample after pyrolysis. The dry weight of the prepared material is the dry weight of the prepared material. Then the determination process of the EC value of biochar is analyzed. First, deionized water is used for extraction. The ratio of biochar to deionized water was 1:10 (m/v), and the supernatant was determined by an EC electrode. The ash content of biochar is determined according to the national standard GB/T17664-1999. After grinding different biochar, it needs to make it through

Index	Soil	Compost	Biochar
pH	5.74	6.23	7.50
CEC (cmol/kg)	17.84	135.22	40.93
TOC (%)	7.48	70.56	45.10
WEOC (mg/kg)	241.22	4837.65	278.89
Available P (mg/kg)	17.09	1024.32	143.57
Cd (mg/kg)	5.59	ND	ND
Cu (mg/kg)	53.90	241.07	0.20
Zn (mg/kg)	210.82	260.03	56.11
Available Cd (mg/kg)	0.35	ND	ND
Available Cu (mg/kg)	0.15	2.25	0.02
Available Zn (mg/kg)	3.06	1.71	0.11

Table 4. Related physicochemical properties of the test soil, biochar and compost.

the 100-mesh sieve and weigh 1 $g\pm0.02$ g of the prepared biochar. Then the ash content is put into a drying muffle furnace. The temperature is set at 750°C, and it is continuously ashed for 6 hours. After cooling to room temperature, the ash content is weighed to obtain the ash mass, as shown in Formula (5).

$$Ash(\%) = (m_2 - m_1) / m \times 100$$
(5)

Ash means ash content in Formula (5). m_2 stands for the mass of the sample after burning. m_1 represents the quality of the vessel carrying the sample. m is the initial mass of the sample. Finally, all data need to be preprocessed and counted. Generally speaking, the concentration of Heavy Metal adsorbed by the soil is often the difference between the concentration of Heavy Metal in the blank treatment and that in the water phase. Formula (6) is the specific calculation.

$$Q_e = (C_o - C_e) \times V / m \tag{6}$$

In Formula (6), Q_e refers to the content of Heavy Metal adsorbed by the soil of each experimental group (mg/g). C_o means the initial concentration of different Heavy Metal solutions added (mg/L). C_e stands for the concentration of each Heavy Metal in the aqueous phase after equilibrium (mg/L). V is the added solution volume of each Heavy Metal (mL). m is the soil mass in each experimental group (g). To evaluate the adsorption capacity of the repaired soil to Heavy Metal, the Langmuir and Freundlich models are used to fit the isothermal adsorption characteristics of the repaired soil for Heavy Metal. Formula (7) is the specific calculation.

$$\begin{cases} Langmuir: Q_e = (K_L Q_m C_e) / (1 + K_L C_e) \\ Freundlich: Q_e = K_F C_e^{1/n} \end{cases}$$
(7)

In Formula (7), Q_m stands for the maximum adsorption amount of Heavy Metal (mg/g) by the soil of

each experimental group. K_L represents the constant of the Langmuir equation (L/g). K_F is the soil adsorption capacity for Heavy Metal in the Freundlich equation. *n* refers to the general constant, reaction and adsorption reaction strength. Based on the above formula, the relevant physical and chemical properties of the soil, biochar and compost in Table 4 are obtained.

Results and Discussion

Analysis of the Remediation Effect of Different Proportions of Biochar and Compost on Heavy Metal Contaminated Soil in a Mining Area

The study used SPSS24.0 software to continue the statistical analysis of all experimental data. The Tukey test (s) was used to test different soil samples' basic properties and Heavy Metal 's availability. It can be used to evaluate the significance of the differences between these experimental data (P<0.05). For experimental data and parameters' correlation analysis and evaluation, Pearson correlation is used. The drawing software is Origin V9 [38-40]. Firstly, the impact of different proportions of remediation agents on soil physical and chemical properties was analyzed. Table 5 shows the specific results.

Table 5 shows the basic properties of Heavy Metal contaminated soil after remediation with different proportions of remediation agents. The pH value, CEC, total organic carbon, WEOC, and available P content of the contaminated soil increased significantly. With the increase in the proportion of biochar, the soil pH value also increased gradually. When the specific gravity of biochar is 20% and 40%, the pH value is 6.87 and 6.80 respectively. When the proportion of biochar is increased, the soil pH value begins to decrease, which indicates that the soil is affected by the biochar and compost proportion changes. The reason

=		-		
Treatments	pH	CEC	TOC (%)	WEOC (mg/kg)
S	5.74	17.84	8.21	241.11.
S + C	6.64	26.75	11.56	293.54
S + B + C (10/90)	6.77	24.91	11.23	276.97
S + B + C (20/80)	6.87	24.18.	11.14	266.96
S + B +C (40/60)	6.80	23.52	11.03	249.72
S + B + C (60/40)	6.48	21.37	10.93	220.65
S + B	6.26	19.23	10.59	183.14
Treatments	Available P (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Zn (mg/kg)
S	17.07	592	52.89	212.16
S + C	85.86	5.66	71.90	22251.
S + B + C (10/90)	72.16	4.97	67.43.	210.40
S + B + C (20/80)	66.29	5.14	65.15	210.78
S + B + C (40/60)	54.32.	5.17	61.73	209.54.
S + B + C (60/40)	38.64	5.08	57.55	199.06
S + B	28.37	4.73	51.57	194.59

Table 6. The Pearson correlation coefficient between different indicators.

Variables	pН	TOC	WEOC	Cd	Cu	Zn
pH	1.000	-	-	-	-	-
TOC	0.865**	1.000	-	-	-	-
WEOC	0.478**	0.215**	1.000	-	-	-
Cd	-0.472**	-0.641**	0.380**	1.000	-	-
Cu	0.680**	0.534**	0.930**	0.105**	1.000	-
Zn	0.176**	-0.037**	0.904**	0.642**	0.782*	1.000
T1-Cd	-0.946**	-0.877**	-0.627**	0.317**	-0.835**	-0.361**
T1-Cu	0.843**	0.652**	0.835**	-0.029**	0.939**	0.635**
T1-Zn	-0.919**	-0.729**	-0.762*	0.233**	-0.894**	-0.498**
T8-Cd	-0.934**	-0.978**	-0.374**	0.539**	-0.659**	-0.103**
T8-Cu	0.857**	0.831*	0.709*	-0.240**	0.895**	0.496**
T8-Zn	-0.948**	-0.815*	-0.658**	0.355**	-0.828*	-0.371**
Variables	T1-Cd	T1-Cu	T1-Zn	T8-Cd	T8-Cu	T8-Zn
T1-Cd	1.000	-	-	-	-	-
T1-Cu	-0.929**	1.000	-	-	-	-
T1-Zn	0.951**	-0.971**	1.000	-	-	-
T8-Cd	0.954**	-0.787**	0.844**	1.000	-	-
T8-Cu	-0.956**	0.909**	0.924**	-0.891**	1.000	-
T8-Zn	0.969**	-0.938**	0.982**	0.906**	-0.932**	1.000*

Note: (1) T1-Heavy Metal: availability of Heavy Metal after applying different SR agents to soil for one week. (2) T8-Heavy Metal: availability of Heavy Metal after two months of application of different SR agents to soil. (3) *, **, and *** refer to P<0.10, P<0.05, and P<0.01, respectively.



Fig. 1. Utilization of heavy metals in soil after different proportions.

may be biochar and compost's interaction during the remediation process. That is, compost can accelerate the oxidation of the surface of biochar, promote biochar's basic oxygen-containing functional group formation, and promote SR. In addition, due to the high content of CEC, WEOC, and available P in compost, the CEC of the soil also increases when the compost proportion increases. However, biochar contains insoluble stable carbon, so its water soluble carbon (WEOC) content is low. Heavy Metals (Cd, Cu, and Zn) in soil decreased with the increase in the proportion of remediation agents. However, the use of different proportions of repair agents increases the content of available P, and there is a strong affinity between available P and Heavy Metal. This will increase the mobility and leachability risk of Heavy Metals. Therefore, the increase in the availability of P may increase the potential risk.

Analysis of The Availability and Distribution of Heavy Metals in Soil After Remediation with Different Proportions

In soil remediation with different proportions of remediation agents, the availability and form of distribution of Heavy Metals have a great impact on the actual effect of remediation agents. Fig. 1 shows the specific effect.

In Fig. 1, CaCl, is used to extract and determine Heavy Metals in soil. The availability of Heavy Metals Cd, Zn, and Cu) in soil decreased significantly after the addition of remediation agents. In Fig. 1a), after adding the remediation agent, the availability of Cd in the soil has been declining and is lower than 0.12 mg/kg. When the proportion of biochar is less than 20%, the ratio of biochar to compost has little effect on the availability of Cd. However, when the proportion of biochar exceeds 20%, the availability concentration of Cd will gradually increase with the increase in the proportion of biochar to compost. Fig. 1b) shows that the ratio change of biochar to compost has a great impact on the availability of Zn in soil. With the increase in biochar content, the availability of Zn gradually decreased. When the proportion of biochar is between 10% and 20%, the availability of Zn is the lowest. After that, the availability of Zn increased with the proportion increase in biochar. The change in Zn availability may be caused by a change in soil pH. In Fig. 1c), unlike Cd and Zn, the bioavailability of Cu increases with the increase in compost proportion under the effect of different proportions of remediation agents. The overall comparison shows that the availability of Zn is significantly higher. Table 6 shows the Pearson correlation coefficient between different indicators.

Table 6 shows the Pearson correlation among indicators. The mobility of Heavy Metal and soil pH



Fig. 2. Morphological distribution of heavy metals in the soil after applying different proportions of remediation agents.

have a negative correlation (r<-0.91, P<0.01). This indicates that the availability and mobility of Cd and Zn in soil are closely related to pH value (pH value changes with the proportion of biochar and compost). In addition, Heavy Metal ions are not easy to move and absorb under high pH changes. The use of SR agents increases the pH value and reduces the mobility and availability of Heavy Metal extracted from CaCl2, which is beneficial to the stabilization of Heavy Metal in soil. In addition, the availability and mobility of Heavy Metal-Cd are significantly related to TOC, which means that the increase in organic carbon content in soil is beneficial to increase the retention of Cd and reduce its potential harm to soil organisms.

In addition, remediation agents promoted the availability and mobility of Cu, and its availability increased when the compost proportion increased. Available Cu concentration in soil has a positive correlation with WEOC (r>0.70, P<0.05) and total Cu content (r>0.89, P<0.01). This indicates that the increase in Cu availability and mobility is related to the increase in WEOC and total Cu content. And the increase in compost proportion directly affects the change in WEOC and Cu concentrations in the soil. Fig. 2 shows the morphological distribution of Heavy Metals in soil.

In Fig. 2a), when the compost proportion increased, the exchangeable content of Cd decreased significantly. When the compost proportion increased, the residue content of Cd increased significantly. In each group of soil experiments, the exchangeable content of Cd accounted for 37% and 63% of the total Cd content. This indicates that Cd has strong mobility in soil, and the combination of Cd with soil colloid and the SR agent is weak. However, the SR agent does not affect the carbonate bound state, iron manganese oxide bound state, or organic bound state of Cd, obviously. In Fig. 2b), for Zn, the exchangeable content gradually decreases with the increase in compost. But the carbonate bound content of Zn increases when compost content increases. The residual state increases when the proportion of biochar increases. In Fig. 2c), about 80% of Cu exists in the iron manganese oxide bound state, organic bound state, and residual state. This means that, compared with Cd, the mobility and migration abilities of Cu in soil are relatively small. The application of different proportions of SR agents has no obvious effect on the exchangeable state and nitrate binding state of Heavy Metals in soil. However, the Fe-Mn oxide bound state of Cu decreases when the biochar proportion increases. And the content of organically bound states increases significantly.

8

	5	1 0	2	0	1		
	Langmuir				Freundlich		
Treatments	K_L (L/g)	$Q_m (mg/g)$	Maximum buffer capacity	R^2	$K_{F}(\mathrm{L/g})$	n^{-I}	R^2
			Cd adsorption				
S	0.0372	2.4212	0.09007	0.9680	0.2230	0.4532	0.9919
S + C	0.0473	5.4971	0.2600	0.9820	0.7668	0.3805	0.9610
S + B + C (10/90)	0.0528	5.2625	0.2779	0.9687	0.7860	0.3734	0.9880
S + B + C (20/80)	0.0547	3.8755	0.2120	0.9424	0.6608	0.3495	0.9916
S + B + C (40/60)	0.0750	3.5133	0.2635	0.9701	0.6503	0.3387	0.9806
S + B + C (60/40)	0.0836	3.3310	0.2785	0.9516	0.6398	0.3326	0.9790
S + B	0.0320	3.2535	0.1041	0.9708	0.3379	0.4222	0.9903
			Cu adsorption				
S	0.1115	2.8239	0.3149	0.9467	0.7313	0.2613	0.9777
S + C	0.7530	3.9549	2.9780	0.9433	1.2860	0.2744	0.8656
S + B + C (10/90)	1.0466	3.9761	4.1614	0.9038	1.4281	0.2590	0.8260
S + B + C (20/80)	0.9378	4.0533	3.8012	0.9335.	1.3833	0.2763	O.8704
S + B + C (40/60)	0.8385	3.7487	3.1433	0.9532	1.2851	0.2552	0.8882
S + B + C (60/40)	0.3812	3.7607	1.4336	0.9319	1.2080	0.2579	0.9150
S + B	0.1807	3.2658	0.5901	0.8996	1.0255	0.2397	0.9594
			Zn adsorption				
S	0.0262	2.7451	0.0719	0.9843	0.2672	0.4132	0.9914
S + C	0.0790	3.1522	0.2490	0.9531	0.5663	0.3407	0.9812
S + B + C (10/90)	0.0854	3.0758	0.2627	0.9644	0.5857	0.3285	0.9801
S + B + C (20/80)	0.0716	3.0146	0.2158	0.9736	0.5570	0.3256	0.9795
S + B + C (40/60)	0.0713	2.9126	0.2077	0.9801	0.5304	0.3271	0.9762
S + B + C (60/40)	0.0692	2.8066	0.1942	0.9791	0.5025	0.3317	0.9706
S + B	0.0422	2.7827	0.1174	0.9717	0.3655	0.3765	0.9895

Table 7. Results of thermod	vnamic adsorption	fitting of heavy metals	s in the Langmuir and Fi	reundlich equations.
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Note: (1) Parameters K_L and K_F in the two equations are the adsorption affinity and stability of soil to Heavy Metal respectively. (2) Parameter Q_m means the maximum adsorption capacity in soil to Heavy Metals.

The content of the residual state increases when the compost proportion increases. The increase in the organic bound state of Cu is mainly due to the decrease in the content of the bound state and residual state of Fe-Mn oxide. This indicates that the SR agent can effectively promote the transformation of the Fe-Mn oxide bound state and the residue state of Cu to an organically bound state.

Adsorption and Desorption of Soil Heavy Metal by Different Proportions of Remediation Agents

Table 7 shows the thermodynamic adsorption fitting results of the Langmuir and Freundlich equations for Heavy Metal.

From Table 7, the fitting effects of the two equations for Heavy Metal in soil are significantly different.

The fitting effect of the two equations on Cd and Zn is good (R2>0.94), which means that the two equation models can better show the thermodynamic adsorption behavior of Cd and Zn. For the soil experiment of different combinations, the fitting effect R2 of the model shows that the fitting effect of the Langmuir equation ($0.8996 \le R2 \le 0.9532$) on Cu is better than that of the Freundlich equation (0.8260 ≤ R2 ≤ 0.9777). After adding SR agent, the parameters K_{I} and K_{F} increased significantly, indicating that the use of SR agent can improve the adsorption capacity of soil for Heavy Metals. In the Langmuir equation model, different proportions of remediation agents have high adsorption affinity for Heavy Metals. The use of remediation agents can significantly promote soil adsorption of Heavy Metals, and increase the soil's maximum adsorption capacity Q_m



Fig. 3. The Langmuir adsorption isotherm of heavy metals in soil after the application of different remediation agents.



Fig. 4. Desorption rate of heavy metals in soil after applying different proportions of remediation agents.

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and adsorption affinity parameters for Heavy Metals. This promotion will increase with an increase in F the proportion of compost in the remediation agent. Fig. 3 shows the adsorption isotherm of Heavy Metals after soil remediation with different proportions of remediation agents.

Fig. 3 shows the adsorption isotherm of soil to Heavy Metal under the concentration gradient of different remediation agents. From the adsorption isotherms of each Heavy Metal, the use of SR agents significantly increased the amount of Heavy Metal adsorption by soil. When the concentration of Heavy Metal is low, the adsorption capacity shows an obvious linear increase with the increase in concentration, and Heavy Metal is almost completely adsorbed. When the concentration of Heavy Metal is high, the adsorption of different SR agents on Heavy Metal gradually reaches an equilibrium trend, and the adsorption isotherm curve gradually tends to be flat. This is because of the heterogeneity and heterogeneity of the soil surface. The soil surface contains both high-energy adsorption sites and low-energy adsorption sites. When the concentration of Heavy Metal in the soil is low, Heavy Metal in the soil preferentially adsorbs at highenergy binding sites. In addition, when the concentration of Heavy Metal gradually increases, the ions contained in Heavy Metal can combine with the low-energy adsorption sites, finally causing the adsorption of Heavy Metal in soil to reach saturation. In Fig. 3b), when the proportion of biochar in the remediation agent is 10% and 20%, respectively, the soil has the maximum adsorption capacity for Cu. This means that biochar application is conducive to enhancing the adsorption capacity of soil and the maximum buffer capacity for Cu.

According to the comprehensive adsorption isotherm and fitting adsorption parameters, the use of different proportions of remediation agents significantly affects the soil adsorption of Heavy Metal. The study uses Cd and Zn as examples. When compost increases, the maximum adsorption capacity of soil and the maximum buffer capacity for Cd and Zn increase. Because the organic matter content, and available P and CEC in compost are higher compared with biomass carbon. The application of compost can significantly improve the physical and chemical properties of soil, increase the content of organic matter, and increase theavailable P and CEC, thus improving the adsorption capacity of soil for Heavy Metals. The study shows that after a terrific amount of Cd and Zn entering the soil in a short time, the adsorption effect of compost on Cd and Zn in the soil is very obvious, but the effect of biochar is small. Because of the slight acidity before and after SR (pH<6.9). In acid soil, the adsorption of Heavy Metal is reversible, so the desorption of Heavy Metal becomes particularly important. Fig. 4 shows the desorption of Heavy Metal.

Conclusions

The integration of agriculture, culture, and tourism into rural revitalization has brought new development opportunities to rural China, but it also faces the challenge of how to deal with and repair soil problems caused by heavy metal pollution. Traditional soil remediation techniques may not be suitable for complex rural contexts and require some innovative practices. In view of this, the study used biochar and compost as soil remediation agents to explore the role and impact of different ratios of biochar and compost on heavy metals (Cd, Zn, and Cu) in the soil of rural abandoned mining areas and analyze the effects of applying different ratios of biochar and compost. Change the characteristics of soil physical and chemical properties, heavy metal bioavailability and mobility, heavy metal form distribution, and adsorption-desorption reactions in rural abandoned mining areas, and explore the causes and mechanisms of the changes. The experiment first prepared a new type of biochar under high-temperature conditions and finally verified the remediation effect of this method in an abandoned mining area contaminated by Heavy Metals in a certain area. Different from traditional remediation methods, all soil remediation agents prepared in the experiment effectively reduced the bioavailability of Cd and Zn in the soil; they had a significant effect on the form distribution of heavy metals in the soil. After applying different ratios of biochar and compost mixtures to wetland soil contaminated by multiple heavy metals, the pH, TOC, WEOC, available phosphorus, and CEC of the wetland soil increased significantly. The above results all show that the addition of a certain amount of biochar can effectively reduce the release of adsorbed Cd and Cu. The resolution rate of Zn gradually decreased with the increase in compost ratio. The proposed method can promote soil remediation and has certain effectiveness. However, this research was conducted under laboratory control conditions, but the complexity of the actual environment and the diversity of external environmental factors will also have an impact on the remediation of soil heavy metals, so it is necessary to conduct relevant field experiments and onsite experimental research.

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Conflict of Interest

The authors declare no conflict of interests.

References

- YOTSUMOTO Y., VAFADARI K. Comparing cultural world heritage sites and globally important agricultural heritage systems and their potential for tourism. Journal of Heritage Tourism. 16 (1), 43, 2021.
- 2. RA I. Cultural tourism as a possible driver of rural development in Czechia. Wine tourism in Moravia as a case study. European Countryside. **12** (3), 292, **2020**.
- SURUP G., VEHUS T., EIDEM P.A., TRUBETSKAYA A., NIELSEN H.K. Characterization of renewable reductants and charcoal-based pellets for the use in ferroalloy industries. Energy. 167 (15), 337, 2019.
- PENIDO E.S., MARTINS G.C., MENDES T.M., MELO L.A., GUIMARAES I., GUILHERME L.G. Combining biochar and sewage sludge for immobilization of heavy metals in mining soils. Ecotoxicology and Environmental Safety. 172, 326, 2019.
- LIANG M., LU L., HE H., LI J., ZHU Z., ZHU Y. Applications of biochar and modified biochar in heavy metal contaminated soil: A descriptive review. Sustainability. 13 (24), 14041, 2021.
- GHOSH D., MAITI S.K. Biochar assisted phytoremediation and biomass disposal in heavy metal contaminated mine soils: a review. International journal of phytoremediation. 23 (6), 559, 2021.
- MAZARJI M., BAYERO M.T., MINKINA T., SUSHKOVA S., MANDZHIEVA S., TERESHCHENKO A., KESWANI C. Realizing united nations sustainable development goals for greener remediation of heavy metals-contaminated soils by biochar: Emerging trends and future directions. Sustainability. 13 (24), 13825, 2021.
- RAHEEM A., HE Q., MANGI F.H., AREEPRASERT C., DING L., YU G. Roles of heavy metals during pyrolysis and gasification of metal-contaminated waste biomass: a review. Energy & Fuels. 36 (5), 2351, 2022.
- ONMONYA Y.A., ADAMU S.G., SADIQ M. Potential of biochar for clean-up of heavy metal contaminated soil and water. African Journal of Environmental Science and Technology. 16 (4), 146, 2022.
- FAYUAN W., CHENG P., ZHANG S., ZHANG S., YUHUAN S.U.N. Contribution of arbuscular mycorrhizal fungi and soil amendments to remediation of a heavy metal-contaminated soil using sweet sorghum. Pedosphere. 32 (6), 844, 2022.
- WANG L., RINKLEBE J., TACK F.M., HOU D. A review of green remediation strategies for heavy metal contaminated soil. Soil Use and Management. 37 (4), 936, 2021.
- LI F., JI W., CHEN Y., GUI X., LI J., ZHAO J., ZHOU C. Effect of temperature on the properties of liquid product from hydrothermal carbonization of animal manure and function as a heavy metal leaching agent in soil. Water, Air, & Soil Pollution. 232 (5), 189, 2021.
- CARVALHO R.L., LINDGREN R., GARCIA-LOPEZ N., NYAMBANE A., NYBERG G., DIAZ-CHAVEZ R. Household air pollution mitigation with integrated biomass/cookstove strategies in western Kenya. Energy Policy. 131 (8), 168, 2019.
- HAO Y., WU X., GUO Y. Study on test and detection method of mechanical properties of heavy metal contaminated soil. Soil and Sediment Contamination. 29 (5), 1, 2020.
- ZHU J., GAO W., ZHAO W., GE L., NIU Y. Wood vinegar enhances humic acid-based remediation material to

solidify pb(ii) for metal-contaminated soil. Environmental Science and Pollution Research. **28** (5), 1, **2021**.

- KOSIOREK M., WYSZKOWSKI M. Macroelement content in plants after amendment application to cobaltcontaminated soil. Journal of Soils and Sediments. 21 (3), 1, 2021.
- 17. NEMETHY S., SZEMETHY L. Adverse and beneficial effects of woody biomass feedstock plantations on biodiversity and wildlife habitats. Acta Regionalia et Environmentalica. **16** (2), 25, **2019**.
- MORAGASPITIYA C., RAJAPAKSE J., MILLAR G.J. Effect of struvite and organic acids on immobilization of copper and zinc in contaminated bio-retention filter media. Journal of Environmental Sciences. 97, 35, 2020.
- ZHAO T., ZHANG K., CHEN J., SHI X., LI X., MA Y. Changes in heavy metal mobility and availability in contaminated wet-land soil remediated using lignin-based poly (acrylic acid). Journal of Hazardous Materials. 368 (15), 459, 2019.
- DHALIWAL S.S., SINGH J., TANEJA P.K., MANDAL A. Remediation techniques for removal of heavy metals from the soil contaminated through different sources: a review. Environmental Science and Pollution Research. 27 (2), 1319, 2020.
- ZHANG J., ZHU Y., WANG M., HAN Y., GE J. Remediation of heavy-metal-contaminated soil by EGTA washing enhanced with reduction solubilization. Huan jing ke xue= Huanjing kexue. 41 (5), 2390, 2020.
- DW A., AN B., JM A., AM A. Ecological restoration of heavy metal-contaminated soil using na-bentonite and green compost coupled with the cultivation of the grass festuca arundinacea. Ecological Engineering. 138, 420, 2019.
- 23. LI F., LI Z., MAO P., LI Y., LI Y., MCBRIDE M. Heavy metal availability, bioaccessibility, and leachability in contaminated soil: effects of pig manure and earthworms. Environmental science and pollution research international. 26 (20), 20030, 2019.
- 24. FANG X., PENG B., SONG Z., WU S., TU X. Geochemistry of heavy metal-contaminated sediments from the four river inlets of dongting lake, china. Environmental Science and Pollution Research, (10), 1, 2021.
- 25. RANNA A., SINDHU M., KUMAR A., DHAKA R.K., CHAHAR M., SINGH S., NAIN L. Restoration of heavy metal-contaminated soil and water through biosorbents: A review of current understanding and future challenges. Physiologia Plantarum. 173 (1), 394, 2021.
- KHATAWKAR D.S., JAMES P.S., DHALIN D.R. Energy self-sufficient farmstead: design analysis. International Journal of Current Microbiology and Applied Sciences. 9 (4), 3006, 2020.
- JLC A., GVPM A., JTV A., EJ B., DCRE A., JAST A. Kinetic investigation of self-reduction basic oxygen furnace dust briquettes using charcoals from different biomass. Journal of Materials Research and Technology. 9 (6), 13282, 2020.
- ROMAN M., HALINA B., ADAM K. Virginia fanpetals (sida) biomass can be used to produce high - quality bioenergy. Agronomy Journal. 111 (1), 24, 2019.
- 29. DANU D., SUDRAJAT D.J. Improving of degraded soil quality for ficus variegata nursery media by adding organic matters and npk fertilizer. Jurnal Wasian. 6 (2), 101, 2019.
- 30. GHANBARY E., KOUCHAKSARAEI M.T., ZARAFSHAR M., BADER K., MIRABOLFATHY M.,

ZIAEI M. Differential physiological and biochemical responses of quercus infectoria and q. libani to drought and charcoal disease. Physiologia Plantarum. **168** (4), 876, **2020**.

- CHAN N.I., RITTMANN B.E., ELSER J. Suitability of an algal biofuel species, scenedesmus acutus, as a fertilizer for growth of conventional and genetically modified lettuce. HortScience: a publication of the American Society for Horticultural Science. 56 (5), 1, 2021.
- 32. ABDUH M.Y., TARIGAN N.B., HIDAYAT A., MANURUNG R. Valorization of rice straw and tofu residue using hermetia illucens to produce protein rich biomass and organic fertilizer. Research Journal of Applied Sciences, Engineering and Technology. 18 (1), 26, 2021.
- BASTA A.H., LOTFY V.F., SALEM A. Valorization of biomass pulping waste as effective additive for enhancing the performance of liquid crystal hydroxypropyl cellulose nanocomposite film. Waste and Biomass Valorization. 13 (4), 2217, 2021.
- 34. EJESIEME V.O., RIAZA J., VORSTER N., DUGMORE G., Zeelie B. Reclamation of ultra-fine coal with scenedesmus microalgae and comprehensive combustion property of the coalgae composite. Journal of Energy in Southern Africa. **31** (1), 14, **2020**.
- 35. BAPAT S., JASPAL D., MALVIYA A. Efficacy of parthenium hysterophorus waste biomass compared with

activated charcoal for the removal of ci reactive red 239 textile dye from wastewater. Coloration Technology. **137** (3), 234, **2021**.

- 36. SVETLANA P., MARTIN J., JUSSI H. Global biomass trade for energy – part 2: production and trade streams of wood pellets, liquid biofuels, charcoal, industrial roundwood and emerging energy biomass. Biofuels, Bioproducts and Biorefining. 13 (2), 371, 2019.
- 37. MOHANTA S., SAHU M.K., MISHRA P.C., GIRI A.K. Removal of cr (vi) from aqueous solution by activated charcoal derived from sapindus trifoliate 1 fruit biomass using continuous fixed bed column studies. Water Science and Technology. **84** (1), 55, **2021**.
- CAI J., RAHMAN M.M., ZHANG S., SARKER M., ZHANG X., ZHANG Y., FINI E.H. Review on aging of bio-oil from biomass pyrolysis and strategy to slowing aging. Energy & Fuels. 35 (15), 11665, 2021.
- KPELOU P., KONGNINE D.M., KOMBATE S., MOUZOU E., NAPO K. Energy efficiency of briquettes derived from three agricultural waste's charcoal using two organic binders. Journal of Sustainable Bioenergy Systems. 9 (2), 79, 2019.
- KANG Y., LIU C., ZHANG Y.Z., XING H.W., ZHAO K. Flue gas circulating sintering based on biomass fuel on reduction of NO_x and SO₂ emission. ISIJ International. 60 (8), 1633, 2020.