

Effects of Mixed Application of Wood Vinegar and Biochar on Cadmium Absorption of Pakchoi under Different Concentrations of Cadmium Stress

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ABSTRACT

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Because of its characteristics, wood vinegar is widely used in agricultural production processes. Wood vinegar can be used as a strong antioxidant, antibacteria, plant growth agent, an insecticide, and currently shows superiority in the treatment of heavy metals. Wood vinegar contains organic acids, organic compounds, and phenol, which can effectively adsorb heavy metals. A large number of studies have been conducted on the adsorption of heavy metals by biochar, but few studies have analyzed the effects of biochar and wood vinegar fertilization on the growth of cadmium soil genus plants and changes in soil heavy metal forms. This article analyzed the effects of wood vinegar and biochar mixed fertilizer on the growth and plant efficacy of pakchoi from the properties of wood vinegar, and confirmed that 0.75% wood vinegar liquid treatment is the most effective concentration. By analyzing the effectiveness of 0.75% wood vinegar and biochar mixture and single fertilization, the combined application of biochar + wood vinegar reduced the absorption rate of cadmium by pakchoi leaves and roots by 12.8% and 13.1% compared with the single treatment group. The yield of crops increased by 111.9~150.1%. The results of evaluating the enrichment coefficient and single-factor index are 0.17~0.67%, 0.005-0.008, and the ranking is D> E> C> B> A> CK.

When observing the changes in soil morphology, the content of residual cadmium, carbonate-bound cadmium, and iron-manganese oxide-bound cadmium increased by $0.3^{2}33.7$ times, and the exchangeable cadmium content and the content of organic and sulfide-bound cadmium were reduced to $1.0^{6.6}$ times.

It can be seen that under different cadmium stress conditions, the mixed fertilization of wood vinegar and biochar will reduce the growth of pakchoi and the plant availability of cadmium, and it has a higher mitigation effect on

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cadmium soil pollution.

Keywords : Wood vinegar, Biochar, Cadmium, Pakchoi, Passivation of heavy metals, Plant availability

I. INTRODUCTION

At present, the cause of heavy metal (HML) pollution is caused by human activities and is mainly aggravated by mining, fertilizers, pesticides, waste, and wastewater irrigation. Soil is the main source of absorption of heavy metals released into the environment by human activities [1-4]. Soil heavy metal pollution can not only cause the decrease of soil fertility and grain yield and pollute surface water and underground water but also threaten human health through the food chain. [5, 6].

Heavy metals are toxic to soil microorganisms and will change the diversity, population size, and overall activities of soil microbial communities. In addition, if it accumulates in the human body along the food chain, certain essential nutrients in the body may be exhausted, and the defense capabilities of immunity will also be reduced. Heavy metals are not necessary for plant growth because they do not perform known physiological functions in plants. Plants that absorb heavy metals and accumulate along the food chain are a potential threat to humans, and plant roots are the main way. [7]. Many studies demonstrated that Cd(II) was the main predominant contaminants in soil[8]. Cadmium (Cd) is one of the most toxic elements to plants [9]. It can inhibit the hydrolysis of carbonwater compounds and sugar conversion, resulting in slower growth of seedlings [10], reducing the biomass and stem length of seedlings [11-18]. Of primary concern is its transfer from vegetable products of agriculture to the human diet. It is widely concluded that vegetable foods contribute \geq 70% of cadmium intake in humans [19]. As a result, the amendment and remediation of heavy-metal-contaminated soil have been a research hotspot in agriculture and the environment [20]. In particular, choosing low-cost and ecologically sustainable materials and using them for soil remediation is the most reasonable choice. Secondly, the researchers studied the heavy metal passivation of biochar. Biochar is a safe carbonized solid product of high-temperature pyrolysis of biological materials produced by plants or animals. It can improve soil, store charcoal, and repair the environment, and is widely recognized [21]. In addition, biochar can be used to improve soil cadmium form changes. The effect of combined BC and Fe0was better than that of using them alone. Using BC alone decreased significantly the content of exchangeable Cd and enhanced the formation of carbonate-bound Cd, organic-bound Cd, and residual form of Cd [22]. Biomass charcoal is mainly composed of monocyclic and polycyclic aromatic compounds. This structural feature makes it have higher chemical and biological stability than the source parent charcoal and has stronger anti-microbial degradation ability. Under certain conditions, it can exist stably in the soil for thousands of years. Biomass charcoal has a high adsorption capacity for heavy metals. When placed in the soil, it can reduce the bioavailability of heavy metal elements. It is a low-cost and effective method to reduce the absorption of heavy metals by plants in the soil [23-26]. Studies have shown that adding biochar to heavy metal contaminated soil can reduce the absorption of cadmium by pakchoi, and reducethe concentration of cadmium in the soil leaching solution by about one-tenth. 3% RHB can effectively hold Cd [27]. The use of biochar can increase soil pH, increase the immobilization of heavy metals, increase the maintenance of soil nutrients, improve the microbial community structure, and increase the growth and decline of crops [21]. However, the effect of biochar on plant growth depends on the specific types of soil and plants and the interaction between them. It is necessary to use biochar in conjunction with other soil amendments to improve the effect. Second, the researchers researched the effect of wood vinegar on plant growth and the passivation of heavy metals. Wood vinegar is a brown liquid obtained by condensing and separating the gas mixture produced during the dry distillation of wood. It contains [28] acetic acid, alcohol esters, phenols, aldehydes, ketones, amino acids, etc[29]. Using WV can promote plant growth, improve seed germination and increase yield. The joint action of PWV and PBC can correspondingly promote the growth of tomatoes [30]. The addition of biochar and bamboo vinegar reduced the mobility of copper and zinc in pig manure composts [31]. Wood vinegar or biochar is a prospective soil amendment to promote soil improvement and crop growth [27-30, 32-34]. However, there is a lack of research and understanding on the effect of its combined use, the inactivation of heavy metals in the soil, and the improvement of the effect of heavy metal stress on plants. In this experiment, pakchoi was planted in 90 divisions, and wood vinegar and Biochar were mixed. The effect of wood vinegar on the cadmium uptake status of the plant's above-ground and roots, the growth of crops, and the change of cadmium form in the soil was investigated to determine the effect and its concentration on the adsorption of heavy metals.

II. MATERIALS AND METHODS

2.1. Research materials and physical and chemical properties

2.1.1. Materials

- Pakchoi, the variety is Changfeng Four Seasons pakchoi, harvested 30 days later, the suitable growth temperature is 20~28°C.
- Biochar is a rice husk biochar that is pyrolyzed at 700°C provided by Wuchang Runnong Company.
- Wood vinegar is obtained from the production of rice husk pyrolysis biochar provided by Wuchang Runnong Company, with a pH of 3.20.
- National standard reagent: CdCl₂·2.5 H₂O, environmental standard reference standard material: GBT 1286-1994)

(National standard sample cadmium standard solution GSB 04-1721-2004, standard value: 1000ug/mL)

2.1.2. The physical and chemical properties of biochar and wood vinegar

Table1. Physical and chemical indexes of wood vinegar.

Moi	pН	Acidit	Acid	Aceti	Organ	Den
stur	valu	у	(wt %	с	ic	sity
e	e	(mg/g))	acid	matte	(mg
(wt		а		(wt	r	m-3)
%)				%)	(wt %	
)	
74.8	3.20	12.68	11.02	9.49	5.83	1.03
8						

Acid-free degree was calculated by acetic acid content.

Table 2. Physical and chemical properties of biochar

pН	CEC	Spe	Orga	Electr	Micro	Cad
		cific	nic	ical	pore	miu
	(cmo	surf	carb	Cond		m
	l/kg)	ace	on	uctivi	struct	Con
		area	(g/k	ty	ure	tent
		(m ²	g)	(mS/c	(%)	(mg
		/ g)		m)		kg ⁻¹)
9.65	18.39	185.	277.2	0.69	large	0.16
		69	0		apertu	3
					re	
					38%	
					`	
					small-	
					bore	
					43%	

The test soil was black soil of Northeast China, and the cadmium reagent added was national standard cadmium.

2.2. Methods

2.2.1. Experiment design and preparation

This experiment was carried out in the form of potted plants, with a total of 25 treatment groups and 5 control groups, and each group was repeated 3 times for a total of 90 pots. The specific processing settings are shown in Table 3.

Dispose			Balanc	Number of
Cadmium	Bioch	Wood	ed	pots (90)
mg kg-1	ar	vinega	array	
	(%	r	(Repe	
)	(%)	at 3	
			groups	
)	
Cd	0.0	0.0	Check	15 pots
(0.0 ,			plot	
0.5 ,			(5Gro	
2.0 ,			up)	
3.5 ,	5.0	0.0	Labora	75 pots
5.0)	5.0	0.25	tory	
	5.0	0.5	area	
	5.0	0.75	5*5	
	5.0	1.0	(25Gr	
			oup)	

Table 3. Processing Settings Table

The Cd concentration in the soil was adjusted to 0, 0.5, 2.0, 3.5, 5.0 mg·kg⁻¹ by adding the prepared CdCl₂ solution to the soil sample, and it was equilibrated for 30 days under constant temperature conditions.

After the soil is balanced for 30 days, the rice husk biomass charcoal that has passed through a 2 mm sieve is applied to the soil. The addition amount per pot is 5.0%, and the addition amount of wood vinegar per pot is 0.0%, 0.25%, 0.5%, 0.75%, 1.0%, stir evenly, equilibrate for 30 days under constant and temperature conditions. All treatment settings were repeated three times. Seed disinfection treatment before sowing: The seeds are first immersed in 100% hydrogen peroxide for 20 minutes, and then thoroughly washed with distilled water. Plant 15 cabbage seeds per pot with 1 kg of soil. During the whole growth period, the soil temperature is controlled to 18±5°C, and the soil humidity is 60%~70%.



Figure 1. Effect of mixed fertilization of wood vinegar and biochar on growth of pakchoi under different cadmium stress

2.2.2. Method for determination of cadmium in plants and soil

During the digestion, attention should be paid to observe. The number of various acids can be increased or decreased according to the digestion situation. The soil digestion solution should be white or light yellow (soil with high iron content), and there should be no obvious sediments. Exchangeable cadmium: Take 1.0 g of the dried and sieved soil sample in a 50 mL plastic centrifuge tube, add 10.0 mL of 1.0 mol·L-1 MgCl2 solution, and shake and extract for 1 h at (25±1) °C, then Centrifuge for 30 min, and filter the supernatant with a 0.22µm microporous membrane. Carbonatebound cadmium: Transfer all the residues obtained from the above centrifugal separation to a 50 mL plastic centrifuge tube, add 10.0 mL of 1.0 mol·L-¹CH₃COONa solution, shake and centrifuge, and filter supernatant with a 0.22µm microporous the membrane. Iron-manganese oxide-bound cadmium: Transfer all the residues obtained from the above centrifugal separation into a 50 mL plastic centrifuge tube, add 0.004 mol·L-1NH2OH·HCl solution 20.0mL, water bath heat preservation, and extraction for 6 hours, shake centrifugation with 0.22µm micro The supernatant is filtered through a pore filter membrane. Organic matter and sulfide-bound cadmium: Transfer all the residues obtained from the above centrifugal

separation to a 50 mL plastic centrifuge tube, add 0.02 mol·L⁻¹HNO₃ 3.0 mL and 30% H₂O₂ 5.0 mL and shake and extract for 2 hours. Then add 3.0mL 30% H₂O₂, shake and extract for 3h. After cooling, add 3.2 mol·L⁻¹ 5.0mL, continue to shake for 30 minutes, centrifuge and filter the supernatant with a 0.22 μ m microporous membrane.

Calculate the content of cadmium in the sample according to "Determination of Soil Quality Lead and Cadmium Graphite Furnace Atomic Absorption Spectrophotometry" GB/T 17141-1997"

Exchangeable cadmium: Take 1.0 g of the dried and sieved soil sample in a 50 mL plastic centrifuge tube, add 10.0 mL of 1.0 mol·L⁻¹ MgCl₂ solution, and shake and extract for 1 h at (25±1) °C, then Centrifuge for 30 min, and filter the supernatant with a $0.22\mu m$ microporous membrane. Carbonate-bound cadmium: Transfer all the residues obtained from the above centrifugal separation to a 50 mL plastic centrifuge tube, add 10.0 mL of 1.0 mol·L⁻¹CH₃COONa solution, shake and centrifuge, and filter the supernatant with a 0.22µm microporous membrane. Iron-manganese oxide-bound cadmium: Transfer all the residues obtained from the above centrifugal separation into a 50 mL plastic centrifuge tube, add 0.004 mol·L⁻¹ NH2OH·HCl solution 20.0mL, water bath heat preservation, and extraction for 6 hours, shake centrifugation with 0.22µm micro The supernatant is filtered through a pore filter membrane. Organic matter and sulfide-bound cadmium: Transfer all the residues obtained from the above centrifugal separation to a 50 mL plastic centrifuge tube, add 0.02 mol·L-1HNO3 3.0 mL and 30% H2O2 5.0 mL and shake and extract for 2 hours. Then add 3.0mL 30% H₂O2, shake and extract for 3h. After cooling, add 3.2 mol·L-¹ 5.0mL, continue to shake for 30 minutes, centrifuge and filter the supernatant with a $0.22\mu m$ microporous membrane. Residual cadmium: Subtract the cadmium content of the first 4 forms from the total cadmium content to get the residual cadmium content.

2.2.3. Heavy metal Cd bioaccumulation coefficient and calculation of agricultural product safety evaluation index

The enrichment capacity of vegetables for soil heavy metal Cd can be expressed by the bioconcentration factor (BCF), and its calculation formula is:

$$BCF(\%) = CV/CS \times 100$$
(1)

Where, CV is the content of Cd in the edible parts of vegetables (mg $\cdot kg^{-1}$),

CS is the content of Cd in the soil $(mg \cdot kg^{-1})$.

The calculation formula of the single factor index method for agricultural product safety evaluation is:

Ei=Ci/Li (2)

Where, Ei is the Cd single factor exceeding index; i is the type of agricultural products;

Ci is the heavy metal Cd content of agricultural products (mg kg^{-1});

Li is the limit value of the national food safety standard for heavy metal Cd in i agricultural products (GB 2762-2017). Tomato, cabbage, and cowpea were 0.05, 0.2, and 0.1 mg·kg⁻¹, respectively.

According to the Ei value, the degree of over-standard agricultural products is divided into 3 levels (Table 4).

Table4. Classificationofagriculturalproductsexceeding standards

Over- standard level	Ei
INot exceeded	Ei≤1.0
IISlightly exceeded	$1.0 < E_i \le 2.0$
IIISeverely exceeded	Ei> 2.0

2.2.4. Statistical analysis

All experiments were triplicated. Analysis of variance (ANOVA) of the results was performed using Design-Expert version 11. All data is processed by using SPSS 26.0 and GraphPad Prism 8.0.1 software.

III. RESULTS

3.1. The effect of WV + BC combined application on the overground part and root cd absorption of pakchoi

Table J. Experimental design	Table 5.	Experimental	design
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Process gradient	Code		
Cadmium	Biochar	Wood	
concentration(mg	(wt %)	vinegar(w	
$\cdot \mathbf{kg}^{-1}$)		t %)	
Cd (0.0, 0.5,	0.0	0.0	CK
2.0, 3.5, 5.0)	5.0	0.0	А
	5.0	0.25	В
	5.0	0.5	С
	5.0	0.75	D
	5.0	1.0	Е

3.1.1. The effect of WV + BC combined application on cadmium absorption in the overground part of pakchoi

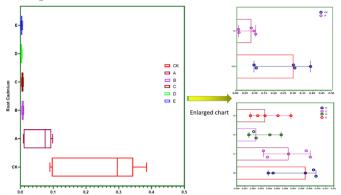


Figure 2. The effect of WV + BC combined application on cadmium absorption in the overground part of pakchoi

*((WV-0.0, 0.25, 0.5, 0.75, 1.0% diluted 200 times + 5.0% biochar), CK-BC0.0%+WV0.0%+cd))

Figure 2 shows the effect of combined application of biochar and wood vinegar in heavy metal soil on cadmium uptake in the aerial parts and roots of pakchoi. As shown in Figure 2, under different concentrations of cadmium stress, without the addition of biochar and wood vinegar, the cadmium content of the above-ground part of pakchoi in the soil was significantly higher than that of BC and BC + WV treatments. The above-ground part of pakchoi is 0.23~0.31mg·kg⁻¹, and the standard value of pollutionfree vegetables exceeds 1.17~1.58 times. According to the standard of pollution-free vegetables (GB 2762-2017), BC, BC + WV meet the requirement of Cd content (cd0.2 mg·kg⁻¹). However, under the same biochar addition conditions, with the increase of the concentration of wood vinegar, the Cd content in the shoots of pakchoi decreases. When the wood vinegar is 0.75%, the Cd content is the lowest, which is 0.001-0.0018 mg·kg⁻¹, the trend is a slight increase to 1.0%. Only the Cd content of the aboveground part of the biochar fertilization area was 11.8-25.2 times lower than that of the control. Depending on the concentration of wood vinegar (B, C, D, E), the combined application of biochar and wood vinegar 37.6~125.7, 38.9~137.1, 77.4~231.1, was and 50.3~153.0 times lower than the control, respectively. In addition, when mixed with wood vinegar and biochar, the above-ground cadmium content is 2.4~6.7 times, 2.5~7.9 times, 6.1~11.7 times, and $3.2^{9.6}$ times lower than that of biochar alone.

3.1.2. Effect of WV + BC combined application on cadmium uptake by pakchoi roots

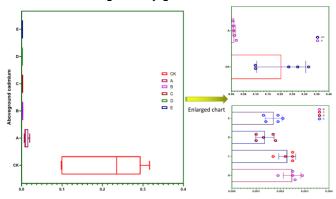


Figure 3. Effects of biochar and wood vinegar mixed fertilization and individual fertilization on the fresh weight of pakchoi under different cadmium stress conditions

* ((BC-Biocha 5.0%) , (WV-Wood vinegar fluid 0.25, 0.5, 0.75, 1.0%) , (Fresh weight Unit:g))

Figure 3 is the result of measuring the cadmium content of pakchoi root after adding wood vinegar and biochar. As shown in the figure, the root content of cabbage in the soil without adding biochar and wood vinegar solution under Cd stress is significantly higher than that in the soil treated with biochar alone and wood vinegar mixed with biochar. Except for the Cd0.0mg·kg⁻¹ and cd0.5mg·kg⁻¹ treatments of cabbage root, the Cd content of all other treatments is $0.29^{-0.38}$ mg·kg⁻¹, which is $1.47^{-1.92}$ times higher than the standard value of pollution-free vegetables. The separate biochar treatment area and the biochar + vinegar solution combined wood application treatment area meet the requirements of the Cd content (cd0.2 mg·kg⁻¹) in the pollution-free vegetable standard (GB 2762-2017). However, under the same biochar addition conditions, the Cd content in the roots of pakchoi decreased with the increase of the concentration of wood vinegar, and the Cd content in 0.75% wood vinegar was the lowest, which was 0.0015 to 0.0055 mg·kg⁻¹. Compared with the control group, the cadmium content of the biochar fertilization area alone was 3.0~25.7 times lower. Depending on the concentration of wood vinegar (B, C, D, E), the mixed treatment area of biochar and wood vinegar was 10.3~67.9, 11.2~78.8, 18.4~182.5, and 15.2~145.6 times lower than the control, respectively. In addition, the mixed treatment of wood vinegar and biochar is 1.34~22.1, 1.7~25.6, 2.7~40.8 2.2~28.5 times lower than that of the single biochar treatment. The average Cd content of pakchoi root is 1.1~4.9 times higher than that of leaves, and the higher the amount of Cd added, the higher its content. This indicates that the cadmium accumulation capacity of roots is stronger than that of leaves. The combined treatment of biochar and wood vinegar can reduce the absorption of pakchoi by the upper part and root of the plant. It is related to the ability of biochar and wood vinegar. After adding biochar, the amount of cation exchange in the soil, the content of organic matter, and the pH of the soil are significantly increased. By including the abundant carbon of the biochar itself, the pores of the soil are improved and the hydrolysis of Cd is affected. So Cd is reduced by chemical precipitation because it is fixed. [35, 36] The addition of wood vinegar promotes the activity of hydrolytic enzymes, increases the metabolism of microorganisms and the utilization of carbon sources, and increases the activity of soil enzymes through the propagation of microorganisms. In addition, heavy metals are adsorbed by the action of acetic acid, which is the main component of wood vinegar. It is important to note that, as shown in several studies, treating wood vinegar after adding biochar will make the surface of biochar dense and rough, making it more effective in adsorbing heavy metals.

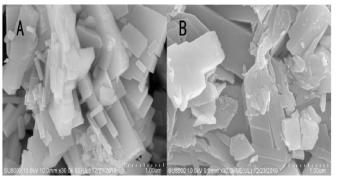


Figure 4. The surface morphology and structure changes of PR materials after wood vinegar treatment were observed by SEM.

Using SEM, it was observed that the surface morphology and structure of the PR material changed after the wood vinegar solution treatment. The surface of WV-PR is significantly rougher than that of PR[37]

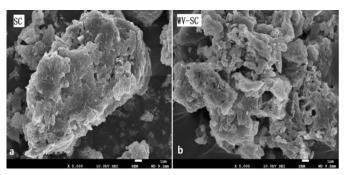


Figure 5. SEM micrographs of the SC and WV-SC The WV-SC showed more uneven and rougher surface compared to the SC. [38]



3.2. The effect of WV + BC combined application on the enrichment coefficient

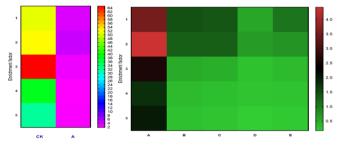


Figure 6. The effect of WV + BC combined application on the enrichment coefficient

The concentration of many pollutants in organisms is much higher than that in the environment. As long as these pollutants continue to exist, the concentration of pollutants in organisms will increase with the increase of growth and development time. As shown in the figure, if you look at the enrichment factor, the area with the lowest cadmium content is the D area, which is 0.17~0.67%. In this order, D (0.17~0.67%)> E $(0.20^{-1}.08\%)$ > C $(0.25^{-1}.4\%)$ > B $(0.29^{-1}.44\%)$ > A (1.8~4.4%)> CK (32.0~65.0%))become. CK was 11.8~25.2% higher than the BC treatment area, which was 37.6~125.7%, 38.9~137.1%, 77.4~231.1%, and 50.3~153.1%, respectively. As a result, if you mix vinegar biochar under wood and different concentrations of cadmium stress, the toxicity of the edible parts of plants under cadmium stress can be reduced below the national standard, and its effectiveness is highest when BC + WV (0.75%).

3.3. Evaluation of agricultural product safety based on single-factor index method

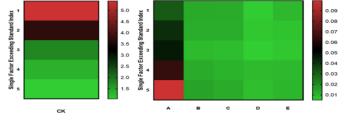


Figure 7. Evaluation of agricultural product safety based on single-factor index method

The single factor index method was used to evaluate the pollution degree of the above-ground parts of pakchoi grown under different cadmium stresses as follows. As shown in Figure 5, the area with the smallest Ei value is D, which is 0.005-0.008. The ranking is D> E> C> B> A> CK. CK was 15.8%, 107.7%, 126.5%, 185.7% and 153.0% higher than BC and BC + WV treatment groups, respectively. As a result, if wood vinegar and biochar are mixed under different cadmium conditions, the higher the concentration, the better the effect. The best concentration is BC + WV (0.75%).

3.4. Effects of WV + BC fertilization on the growth of pakchoi crops under different cadmium stresses

deal	Growth index				
with	Fresh leaf	Root	Leaf	Root	
	weight	fresh	length	length	
	(g)	weight	(cm)	(cm)	
		(g)			
CK	11.95±0.01	0.23 ± 0.02	22.39±0.	11.09±	
	а	а	02a	0.01a	
А	15.51±0.04	0.33 ± 0.03	25.07±0.	12.57±	
	а	а	05Ъ	0.03ab	
В	16.27±0.04	0.37±0.05	26.03±0.	14.77±	
	b	bc	04a	0.06bc	
С	15.63±0.02	0.39 ± 0.03	24.19±0.	12.68±	
	а	а	02a	0.08c	
D	17.37±0.01	0.49 ± 0.05	27.56±0.	15.78±	
	а	b	03a	0.07bc	
Е	16.91±0.03	0.42 ± 0.03	26.88±0.	15.38±	
	а	а	01a	0.02a	

Table 6. Changes of Pakchoi Crop Growth Indexunder Different Concentrations of Cadmium Stress

As shown in Table 6, according to the BC treatment and the WV + BC combined treatment, the fresh weight of pakchoi and the length of leaves and roots showed significant changes. The fresh weight, leaf, and root length of the control without BC treatment and WV + BC treatment were very small. After biochar treatment, the fresh weight of leaves and roots increased to 129.8% and 142.3%, and the lengths of leaves and roots increased to 111.9 and 113.3%, respectively. Compared with the control, the fresh weight of aerial parts and roots increased by 130.7~213.7%, and the length of leaves and roots increased by 108~142%. Compared with the treatment with biochar alone, except for the treatment with cd2.0mg·kg⁻¹ In addition, the increase of wood vinegar concentration in all treatments increased the growth to $0.9^{-25.3\%}$. Especially in the D treatment group, all valuesshowed the highest value, while the E treatment showed a slight downward trend. This is because biochar and wood vinegar have a positive effect on changes in soil composition. Biochar has its own physical and chemical properties, which will affect the changes in soil volume and density, water retention capacity, pH, nitrogen, phosphorus, and potassium, and have a great impact on changes in shape. This is because in this process, the organic carbon content in the soil increases, the ability to absorb heat and light is enhanced, and root activity is promoted, thereby increasing the nutrient absorption capacity.

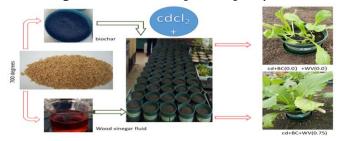
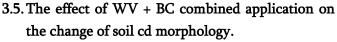
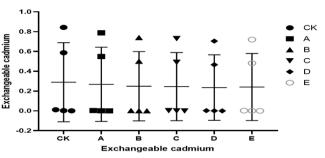
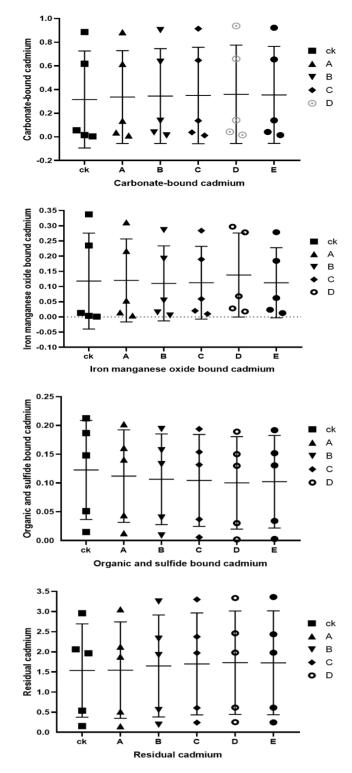


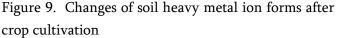
Figure 8. Wood vinegar and biochar addition and crop growth changes

* ((CK treatment: Cd + BC (0.0%) + WV (0.0%), (D treatment: Cd + BC (5.0%) + WV (0.75%))









* ((BC-Biochar 5.0%) , (WV-Wood vinegar fluid 0.25 , 0.5 , 0.75 , 1.0%) , (Fresh weight Unit:mg·kg⁻¹)

As shown in Figure 9, after harvesting pakchoi, in the soil added with biochar and wood vinegar, the

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average cadmium form changes at different concentrations are as follows. Among the various forms of cadmium in the soil, the content of exchangeable cadmium and cadmium combined with organic and sulfide was significantly reduced by $1.1^{4.5}$ times in all regions compared with the control. The ranking is BC + WV> BC> CK, specifically, BC + WV (0.75%)> BC + WV (1.0%)> BC + WV (0.5%)> BC + WV (0.25%)> BC + WV(0.0%)> CK. In other words, as the concentration of the wood vinegar solution increases after the addition of biochar, the amount of adsorbent decreases, and the maximum value decreases to 0.75% of the wood vinegar solution, and 1.0% tends to increase slightly. At BC + WV (0.75%), compared with the single treatment group and the control group, the exchangeable cadmium content and the combined organic and sulfide cadmium content were reduced by 4.5 times, 2.4 times, 1.6 times, and 2.16 times, respectively. The concentration of carbonate-bound cadmium increased by 184.0% compared with the control in the single biochar treatment, and the concentration of wood vinegar in the mixed treatment of biochar and wood vinegar gradually increased, the change was 194.3~223.1%, the largest The value is 0.75% at this time, compared with the control group, it increased by 223.1%, followed by 1.0%, reaching 213.7%. The iron-manganese oxide-bound cadmium gradually increases with the concentration of wood vinegar at a Cd concentration of 0.0mg·kg⁻¹~2.0mg·kg⁻¹, BC, BC + WV combined treatment conditions, however the concentration of Cd increased gradually under the condition of 3.5mg·kg^{-1~}5.0mg·kg⁻¹. This is because the addition of biochar and wood vinegar at high Cd concentrations will increase the solubility of Cd by increasing the content of water-soluble organic matter in the soil solution. When the cadmium concentration is 0.0mg·kg^{-1~}2.0mg·kg⁻¹, the residual cadmium gradually decreases according to the concentration of wood vinegar in the BC and BC + WV treatments, but at 3.5-5.0mg·kg⁻¹. The cadmium concentration gradually increased. In addition, when

biochar is added, the soil pH, organic matter, and CEC content all increase, and the adsorption capacity for Cd are stronger [27, 29]. The addition of wood vinegar increases the activity of microorganisms in the decomposition process. The higher the concentration, the faster the decomposition rate of soil organic carbon, and promotes the change of the chemical form of heavy metals. As a result, under different cadmium stresses, the fertilization of biochar alone and the combined application of biochar and wood vinegar will reduce the exchangeable cadmium and the combined organic and sulfide cadmium content. It can be seen that the content of carbonatecadmium, bound iron-manganese oxide-bound cadmium, and residual cadmium is increased to immobilize it. At this time, the most effective wood vinegar concentration is 0.75%>1.0%. In addition, the comparison between the application of biochar alone and the fertilization mixed with biochar and wood vinegar is obvious. Compared with the application of biochar alone, the fixation effect of cadmium exceeds 10%.

IV. DISCUSSION

At present, heavy metal pollution is becoming more and more serious. Among them, preventing the transfer of highly toxic cadmium plants and ensuring the safe production of plants have become important issues. Although it has been proven in many studies, materials that fix soil cadmium and reduce plant efficacy have been introduced, and it has been revealed that biochar and wood vinegar are effective in this process. Based on the characteristics of these two materials, the effects of combined treatment on the absorption of pakchoi and soil morphology changes under different cadmium stresses were analyzed.

As shown in Figure 1, in 0.75% wood vinegar, the Cd content is the lowest, 0.001~0.0018mg·kg⁻¹, and there is a slight increase trend at 1.0%. Compared with the single treatment and the control, the above-ground cadmium content was reduced to 6.1~11.7 times and

77.4~231.1 times, respectively, reaching the pollution-free standard value. As shown in Figure 2, compared with the biochar treatment and the control, the cadmium content in the roots was reduced to 2.7~40.8 times and 18.4~182.5, respectively. The average Cd content of pakchoi root is 1.1~4.9 times higher than that of leaves, and the higher the amount of Cd added, the higher its content. This indicates that the cadmium accumulation capacity of roots is stronger than that of leaves. As shown in Figure 6, by analyzing the accumulation factor, the area with the lowest cd content is the D area, ranking as D (0.29~1.44%)> A (1.8~4.4%)> CK (32.0~65.0%). As shown in Figure 7, the single-factor index method was used to evaluate the pollution degree of the above-ground parts of pakchoi grown under different cadmium threats. The area with the lowest singlefactor index is Area D, 0.005~0.008, ranking D> E> C> B > A > CK. As shown in Table 6, by analyzing the growth of crops, compared with the treatment using biochar alone, the fresh weight of the combined treatment of wood vinegar liquor and biochar increased by 130.7~213.7%, and the length increased by 108~142%. In contrast, the growth rate increased to 0.9~25.3%. The combined treatment of biochar and wood vinegar reduces the absorption of cadmium by the upper and roots of plants and ensures the safe production of crops. The addition of biochar will increase the pH, CEC, and organic content in the soil, and affect the hydrolysis of Cd, thereby fixing Cd through chemical precipitation, thereby reducing the absorption of heavy metals by plants [21, 35, 36]. In the secondary decomposition process after wood vinegar solution treatment, the hydrolytic enzyme activity and microorganisms doubled, and the metabolic capacity was enhanced. In addition, in this process, carbon source utilization capacity and soil enzyme activity increase, heavy metals are converted into compounds, and the plant effectiveness of cd decreases [24]. As shown in Figure 9, compared with a single treatment, 0.75% wood vinegar treatment can reduce the content of acid-converted cadmium and organic and sulfide combined cadmium to 1.1~3.3 times and 1.0~6.3 times. Increase cadmium and residual cadmium by 1.1~92.7 times, 3.2~233.7 times, and 0.3-6.6 times respectively. This is related to the role of organic acids and organic compounds. Organic acids and organic compounds are the main components of wood vinegar. As mentioned in several studies, the treatment of wood vinegar after adding biochar will make the surface of biochar dense and rough, making it more effective in adsorbing heavy metals [37, 38]. This theoretically proves that the positive effect produced from the SEM image results of [37, 38] is combined with the material effect produced by the wood vinegar in the full fermentation process, which makes the heavy metal passivation effect greater. In other words, this is because compounds such as organic acids and phenols in wood vinegar dilute and neutralize heavy metals and their derivatives, and promote the conversion of heavy metals. Under the continuous threat of cadmium, the combined treatment of wood vinegar and biochar is more effective than using biochar alone. The fixing effect of cadmium exceeds 10%.

V. CONCLUSION

In this experiment, the effects of wood vinegar and biochar fertilization on the absorption of cadmium in pakchoi under different cadmium stress conditions were studied. At present, biochar and wood vinegar are considered to be very active materials for adsorbing heavy metals and have been widely used in agricultural production, so the scope of research is expanding. In particular, the efficacy of wood vinegar is improving day by day, and its superiority is also reflected in the reduction of heavy metals. This study, the purpose of this study is to determine whether the fertilization of biochar and wood vinegar is more effective than the use of biochar alone and to determine the most appropriate concentration required to meet environmental standards and ensure safe production. As a result, the concentration of wood vinegar that maximizes the cadmium absorption of pakchoi is 0.75%, which is the most effective in terms of aerial parts, roots, crop growth, and soil cadmium fixation. In other words, if 0.75% wood vinegar is used to dilute 200 times in 5% biochar, the plant potency of cd can be reduced to the lower limit of the pollution-free vegetable standard, the yield can be increased, and safe production can be ensured. The data can be reasonably used to provide agricultural ecology and environmental data.

VI. REFERENCES

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