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Article

Investigation into the passivating efficacy of various passivators on cadmium (Cd)-contaminated soil in Enshi

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Abstract: To address the issue of cadmium (CD) contamination in the Enshi Mountain vegetable-growing soil, a pot experiment was conducted to assess the impact of various passivators (including biochar, hydroxyapatite, lime powder, fly ash, and a blend of organic passivators) on the passivation of Cd in the test soil, as well as on the yield, quality, and Cd content of Chinese cabbage. The findings revealed that while lime powder treatment hindered the growth of Chinese cabbage, all other treatments enhanced the fresh weight and height of the plants, with the fly ash treatment increasing the fresh weight of Chinese cabbage by 109.72%. Hydroxyapatite, lime powder, and the mixed passivator raised the soil pH by 25.18%, 36.61%, and 28.21% respectively. None of the treatments significantly affected the activities of soil urease, cellulase, and sugarcane enzyme, but biochar and mixed passivator treatments significantly boosted phosphatase activity by 52.85% and 69.82%, respectively, while lime powder treatment significantly suppressed it. All five passivator treatments decreased the Cd content in Chinese cabbage, with biochar, hydroxyapatite, lime powder, and mixed passivator treatments showing significant suppression, with lime powder being the most effective at reducing Cd by 73.80%. None of the treatments significantly impacted the quality of Chinese cabbage. Biochar and mixed passivator treatments lowered the total Cd content in the soil by 27.21% and 46.98% respectively, while lime powder and mixed passivator treatments reduced soil ion-exchangeable Cd by 67% and 47.35% respectively. The application of these five passivators was effective in reducing the Cd content in Chinese cabbage. Specifically, the mixed passivator treatment not only maintained the yield and quality of Chinese cabbage but also enhanced soil enzyme activity and decreased the proportion of total and effective Cd (ionic and water-soluble) in the soil.

Keywords: Enshi; Cd; heavy metals in soil; passivator; a variety of Chinese cabbage; enzyme activity; biomass

1. Introduction

Cadmium (CD) is a non essential element for human body and one of the most toxic heavy metal elements [1]. After long-term physical, chemical and biological effects in the soil, it is transformed into an effective component available to plants, which affects the biological ecological environment effect [2], agricultural product quality and human health through active migration [3,4]. Excessive Cd intake in food will lead to cardiovascular system damage and metabolic diseases [5]. With the economic development, people's dietary structure has also changed. Vegetables play an important role in residents' dietary structure and provide people with rich vitamins, mineral elements, dietary fiber and other nutrients [6]. According to statistics, in 2019, the vegetable planting area in Hubei Province reached 145,400

Hm2, with a total output of nearly 4.1604 million tons and an output value of about 6.471 billion yuan, of which Enshi area accounted for a high proportion in vegetable planting area, total output and output value [7]. How to ensure the safe production of vegetables is very important to the health of Enshi residentsenshi is located in the southwest of Hubei Province and is known as the "selenium capital of the world". It is rich in selenium resources and abundant organic fertilizer. With an average altitude of about 1000 m, Enshi has good ecology and abundant rainfall. It is the preferred place for Alpine vegetable planting. The survey results of the "golden land" project in Hubei Province show that in addition to rich selenium content, the soil in Enshi Prefecture is also enriched with a variety of heavy metal elements, of which CD is the most serious [8]. The research shows that selenium and CD are associated, which is controlled by the soil forming parent material of Permian black rock series and organic matter and sulfide in the soil [9]. There have been many researches on remediation methods of soil heavy metal pollution, mainly including physical remediation, chemical remediation and bioremediation common methods such as physical repair, soil replacement and electrophoresis are expensive and are not suitable for large-scale promotion. Bioremediation mainly includes phytoremediation, microbial remediation, low animal remediation and other methods [10]. It is easy to bring secondary pollution risk, so it is not recommended to promote its use Chemical remediation refers to the application of passivator to polluted soil to change the form and activity of heavy metals in the soil, reduce the absorption and transformation of heavy metals by plants, and achieve the effect of soil remediation [11–13]. At present, passivators mainly include phosphate, lime, clay minerals, industrial waste residue, organic waste, biochar, etc. [14–16]. In this study, the passivating agent is locally obtained. The planting area of corn is large in Enshi, and the straw is easy to obtain; Lime powder is commonly used by local farmers to improve soil acidification; Fly ash, biochar [17] and hydroxyapatite are effective in the remediation of reported soil heavy metalsin the early stage, plant (17), soil (8) and water (3) samples were collected from Enshi heavy metal polluted area (Mufu). The results showed that according to the requirements of the standard for risk control of soil pollution on agricultural land [18], Pb (< 70 mg/kg) and as (< 30 mg/kg) in the sample soil did not exceed the risk control value, while the content of Cd in the soil was between 3.5~23.6 mg/kg, which seriously exceeded the risk control value of 0.6 mg/kg, Bring harm to farmland production, rural life and farmers' health in this area. Through pot experiment, simulate the acid Cd Polluted Soil in Enshi, study the effects of different passivators on CD content, yield, quality, soil pH, enzyme activity and CD form distribution of Alpine vegetables (Chinese cabbage), and then put forward the technical scheme of soil remediation, in order to provide guidance for the safe planting of vegetables in mountainous areas.

2. Materials and methods

2.1. Test materials

The tested crop is Chinese cabbage, and the variety is Lv bao fast food. The tested soil is the tea garden of Enshi Academy of Agricultural Sciences. Stones and weeds are removed. The soil is naturally air dried and screened for 2 mm. The basic physical and chemical properties are shown in **Table 1**. The soil passivator biochar, hydroxyl lime powder, lime powder, fly ash and mixed organic passivator (straw + fly ash + phosphorous minerals, etc.). Were purchased from Jiangxi Jiedi environmental treatment Ecological Technology Co., Ltd.

Table 1. Physical and chemical properties of soil and passivator.

Handle	**Ph**	**Cd/(mg/kg)**	**Alkali hydrolyzable nitrogen/(mg/kg)**	**Available phosphorus/(mg/kg)**	**Available potassium/(mg/kg)**	**Organic matter/(g/kg)**
Soil	5.96	0.59				
Biochar	11.06	0.57				
Fly ash	5.64	1.17	231.0	50.17	269.0	16.08
Hydroxyapatite	10.71	0.22				
Lime powder	13.67	0.38				
Mixed passivator	12.54	2.42				

2.2. Test scheme

The test site is in the greenhouse of Enshi Academy of Agricultural Sciences, which is a pot experiment. According to the analysis of soil samples collected around the Mufu office in Enshi City in the early stage, the average value of CD is 5 mg/kg. The potted soil was contaminated with CD. The source of CD was cdcl2, so that the soil Cd concentration was 5 mg/kg. After mixing evenly, it was balanced at room temperature for 1 month. Six treatments are set in this test, namely CK, biochar, hydroxyapatite, lime powder, fly ash and mixed organic passivator. The passivator is added according to 5% of the soil quality. Compared with the treatment without passivator, it is mixed and stirred evenly, watered and matured for 4 weeks. Put the matured soil into pots, with each pot containing 5 kg of soil, and repeat each treatment for 3 times Sow Chinese cabbage, grow 3 real leaves for intercropping, leave 4 plants in each pot, and pour the same amount of deionized water every 2 days until the materials are collected.

2.3. Sample collection and item detection

After the Chinese cabbage seedlings grow for 5 weeks, collect plant and soil samples plant samples shall be washed with tap water, then with deionized water and dried with paper towels. Measure the plant height and fresh weight with a ruler and balance, put it into an envelope, kill and dry it to constant weight, smash it and bag it for storage.

For the determination of soil pH, shake and stand at the soil liquid ratio of 1:5 to determine the supernatant $K_2Cr_2O_7$ external heating method is used for soil organic matter detection. The contents of alkali hydrolyzable nitrogen, available phosphorus and available potassium are determined according to the method of soil agrochemical analysis (Lu rukun 2000 version). The total amount of Cd in soil is determined by HNO_3, HF and $HClO_3$ digestion method (GB/T 17141-1997). The extracts of seven forms of Cd in soil are water, magnesium chloride, acetic acid sodium acetate, sodium pyrophosphate, hydroxylamine hydrochloride, hydrogen peroxide and hydrofluoric acid. The determination is in accordance with the technical standard for geological survey of China Geological Survey (dd200503). The content of Cd in plants is determined by HNO_3 and $HClO_3$ digestion. The content of Cd in solution is determined by ICP-OES optima 7000dv inductively coupled plasma mass spectrometer. The determination methods of soluble sugar, nitrate, VC and total chlorophyll refer to the principles and techniques of plant physiological and biochemical experiments. The determination of soil urease refers to the sodium phenol sodium hypochlorite colorimetry, the determination of soil phosphatase activity refers to the sodium diphenyl phosphate colorimetry, the determination of soil sucrase activity refers to the 3,5-Dinitrosalicylic acid colorimetry, and the determination of soil cellulase activity refers to the 3,5-Dinitrosalicylic acid colorimetry [19-21].

2.4. Data analysis

Excel, SPSS 20.0, sigma plot and other software are used for data processing, statistical analysis and drawing respectively.

3. Results and analysis

3.1. Effect of Passivator on fresh weight and plant height of Chinese Cabbage

It can be seen from **Table 2** that lime powder treatment can inhibit the fresh weight and plant height of Chinese cabbage, which are reduced by 40.40% and 13.67% respectively compared with the control Fly ash and hydroxyapatite treatment significantly increased the fresh weight and plant height of Chinese cabbage, reaching 109.72% and 23.90% respectively. Other treatments can promote plant fresh weight and plant height, but can not achieve significant effect.

Table 2. Effects of Passivator on fresh weight and plant height of Chinese Cabbage.

Handle	Fresh weight/g	Plant height/cm
Contrast	27.87 ± 6.91ab	20.75 ± 0.25ab
Biochar	54.84 ± 16.58ab	22.42 ± 1.9ab
Fly ash	58.45 ± 19.74a	23.51 ± 4.33ab
Hydroxyapatite	56.36 ± 15.04a	25.71 ± 3.48a
Lime powder	16.61 ± 6.14c	17.92 ± 4.0b
Mixed passivator	38.71 ± 22.67ab	22.15 ± 6.4ab

Note: the data is the mean ± standard deviation of three repetitions. Different lowercase letters after the data in the same column indicate significant difference ($P < 0.05$).

3.2. Effect of passivator application on soil pH

The soil ph is acidic or alkaline, which directly affects the mobility of soil heavy metals and the absorption and utilization of mineral elements. Hydroxyapatite, lime powder and mixed passivator treatment can significantly increase the ph of the test soil (**Figure 1**), with an increase of 25.18%, 36.61% and 28.21% respectively, and lime powder has the most significant effect There was no significant difference among other treatments.

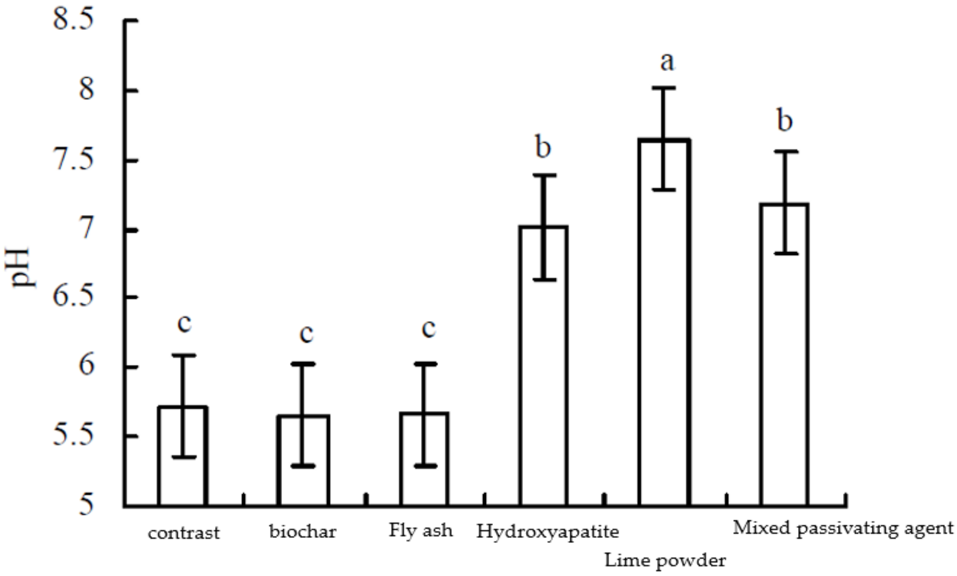


Figure 1. Effect of Passivator on soil ph.

3.3. Effect of passivator application on soil enzyme activity

Soil enzyme is an important indicator of ecosystem function and soil fertility, which promotes the decomposition of organic matter and nutrient circulation. Among them, urease, cellulase, phosphatase and sugarcane enzyme activities are important references compared with the control, the treatment of five passivators had no significant effect on urease, cellulase and sucrase (**Figure 2**); Lime powder treatment inhibited phosphatase activity, which decreased by 62.91% compared with the control; Biochar and mixed passivator treatment significantly increased phosphatase activity by 52.85% and 69.82% respectively.

3.4. Effects of passivator application on CD content and quality of Chinese Cabbage

It can be seen from **Figure 3** that the application of five passivators reduced the absorption of heavy metal Cd in soil by Chinese cabbage respectively. Among them, biochar, hydroxyapatite, lime powder and mixed passivator treatment had significant inhibitory.

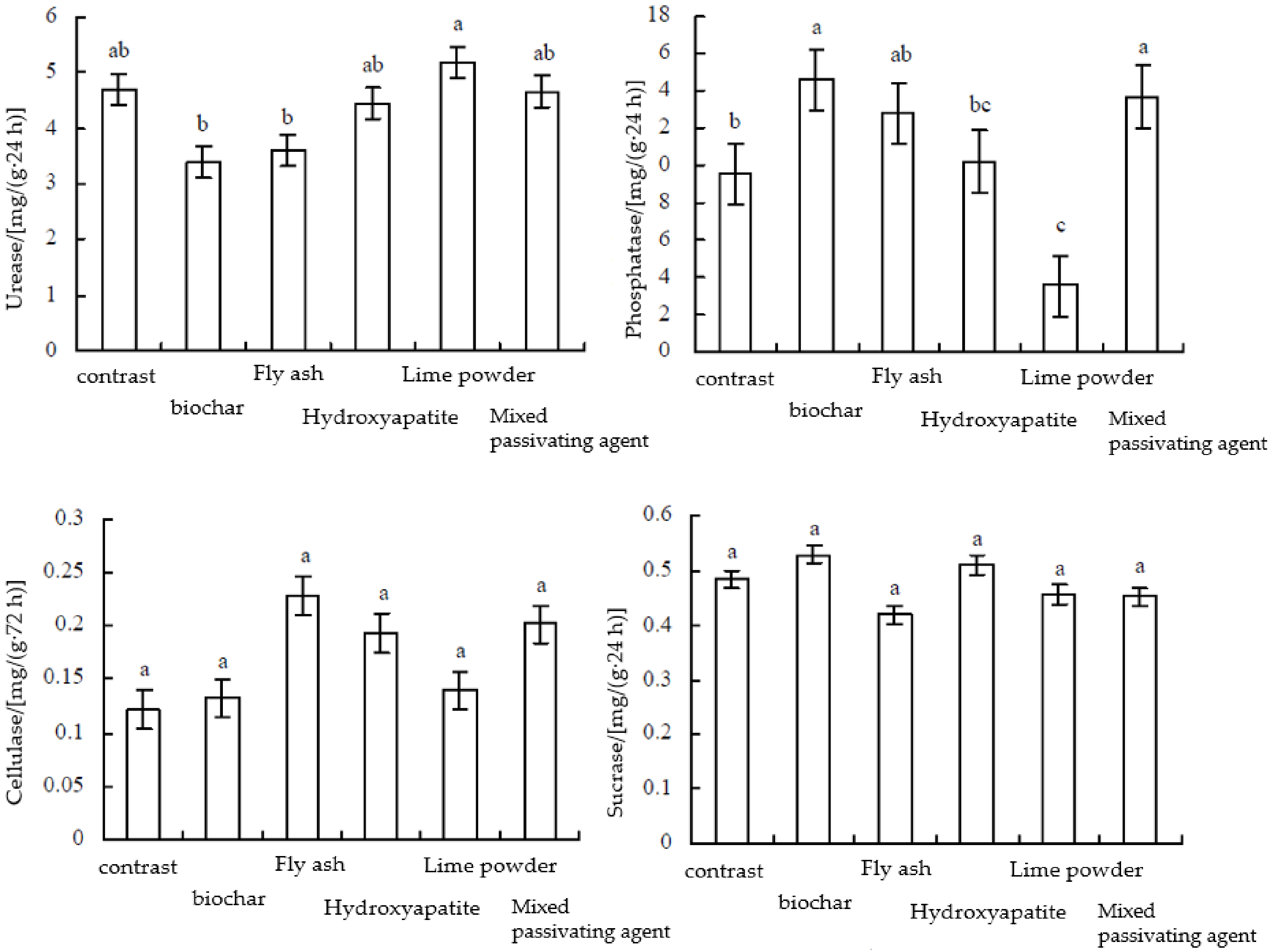


Figure 2. Effect of Passivator on soil enzyme activity 60.00.

effect on absorption, and lime powder was the best, which decreased by 73.80% compared with the control It can be seen from **Figure 4** that compared with the control, the application of five passivators had no significant effect on the contents of soluble sugar, nitrate and VC in Chinese cabbage, and the mixed passivators promoted the increase of total chlorophyll content in leaves by 32.22%.

3.5. Effects of passivator application on the occurrence forms of Cd in soil

The occurrence forms of Cd in soil are mainly ion-exchange state (including water-soluble state), ion-exchange state > carbonate binding state > humic acid binding state > iron manganese oxide > strong organic binding state>residue state>water-soluble state. It can be seen from **Figure 5** that the treatment of biochar and mixed passivator reduced the total Cd content in soil by 27.21% and 46.98% respectively compared with the control Lime powder and mixed passivator treatment significantly inhibited the existence of ion-exchange CD in soil, reducing 43.67% and 47.35% respectively.

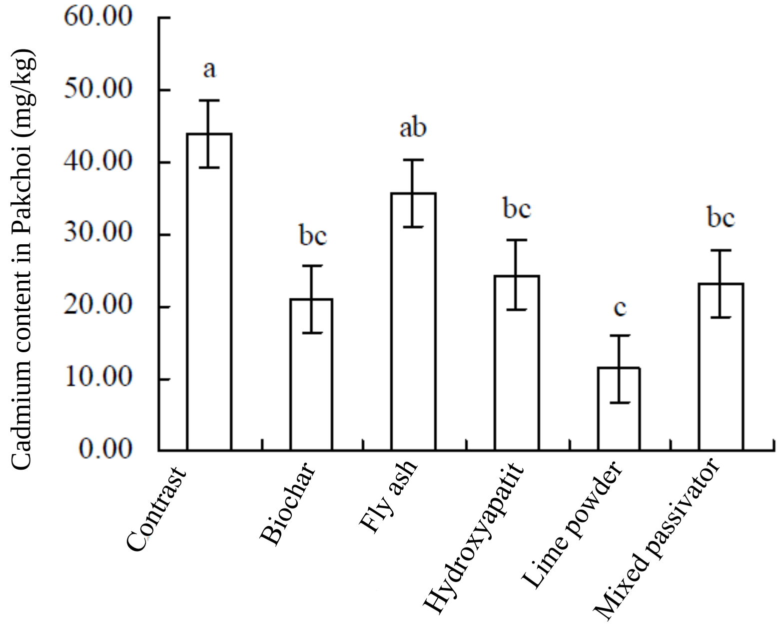
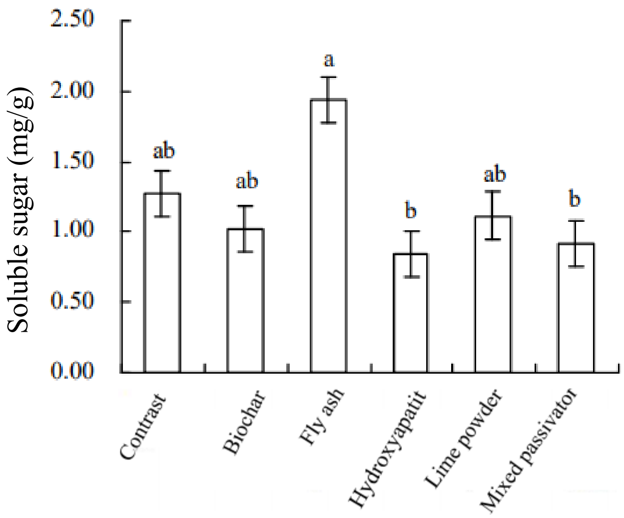
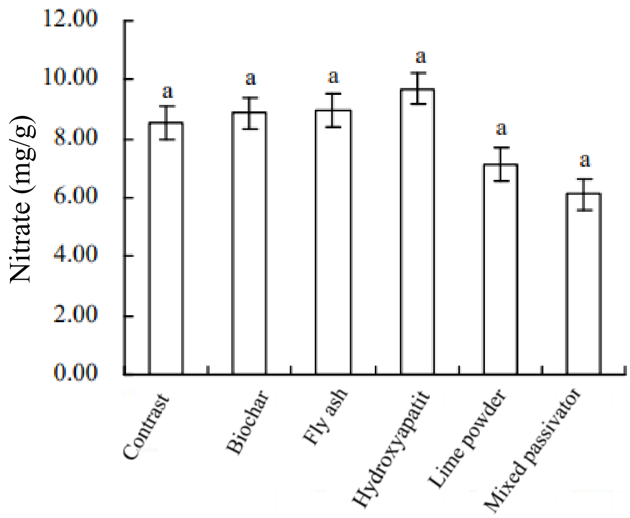


Figure 3. Effect of Passivator on absorption of heavy metal CD by Pakchoi.

4. Discussion

Common soil heavy metal passivators include calcareous materials, carbon materials, clay minerals, phosphorus containing substances, organic fertilizers, etc. [15–16]. Their passivation principles mainly include chemical adsorption and ion exchange, redox, organic complexation and precipitation. By changing the chemical form of heavy metals in the soil, the ion exchange state and water-soluble state are transformed into other forms for fixation, such as organic binding state and residue state, Reduce its solubility and biotransformation effectiveness [22–24], and then affect plant absorption. Soil enzymes are mainly urease, cellulase, phosphatase and sugarcane enzyme. They are important participants in soil biochemical processes. They come from soil microorganisms, animals and plant secretions. They are important indicators of soil fertility level, soil pollution and environmental change [25]. Yang Ningning et al. [26] found that the effect of Cd on soil urease and catalase activity is higher than that of Pb and Zn, and is related to the degree of heavy metal pollution. Feng Dan et al. [27] found that the combined pollution of heavy metals inhibited the activities of soil invertase, urease and alkaline phosphatase. In this study, the application of five passivators has no significant effect on urease, cellulase and sucrase. Lime powder treatment inhibits the activity of phosphatase, which may be related to the hydrolysis of phosphate esters (glycerol phosphate, sugar phosphate, etc.). In alkaline environment to produce orthophosphate [28]. It has been reported that the application of biochar [17], lime powder [30,31], hydroxyapatite, fly ash [32] and other passivators on heavy metal contaminated soil will reduce the toxic effect of heavy metals in the soil on crops, inhibit the absorption of CD by crops [33], and improve crop products and quality. In this study, the application of hydroxyapatite, lime powder and mixed passivator increased the soil ph by 25.18%, 36.61% and 28.21% (**Figure 1**), inhibited the effective transfer of CD by Chinese Cabbage (**Figure 3**), and the CD content in plants was the lowest when treated with lime powder, but seriously affected the yield and quality of Chinese Cabbage (**Table 2**) (**Figure 4**) Hydroxyapatite, lime powder and mixed passivator are alkaline substances, which can effectively improve soil ph and fix heavy metal ions[34-35] through chemical precipitation, chelation and adsorption, so as to reduce the bioavailability of soil Cd. The application of lime powder is the main method of improving soil acidification [36,37] and repairing Cd pollution [38] in Enshi Prefecture, which will make the soil calcareous, cause the concentration of heavy metal ions in the soil to remain high for a long time, and reduce the yield and quality of farmland crops. In the test, the mixed passivator can improve the soil ph, inhibit the absorption of heavy metal CD by Chinese cabbage, reduce the content of total Cd in the soil (**Figure. 5**), and do not reduce the crop yield and quality (**Table 2**, **Figure. 4**). This may be related to its composition its main components are straw, fly ash, phosphorus containing minerals, etc. Straw produces a large number of organic acids during the process of decomposition, which react with metal oxides, hydroxides and metal ions of minerals to form metal organic complexes and reduce metal transfer efficiency. At the same time, hydroxyapatite improves soil ph, increases the surface negative charge of soil particles [39], and phosphate induces the adsorption of heavy metals to form coprecipitation, so as to inhibit the absorption and accumulation of heavy metals by plants[40] Guo Jibin [41] revealed in his research that fly ash, as a passivator, changes the occurrence state of heavy metals in soil, transforms available heavy metals into iron manganese oxidation bound state, organic bound state and residue state, and reduces soil heavy metal pollution. In the experiment, biochar reduced the content of Cd in Chinese Cabbage by 52.32% and enhanced the activity of phosphatase, which may be related to the large specific surface area and high surface energy of biochar, which can organically combine heavy metal ions [42] and reduce its mobility in soil.





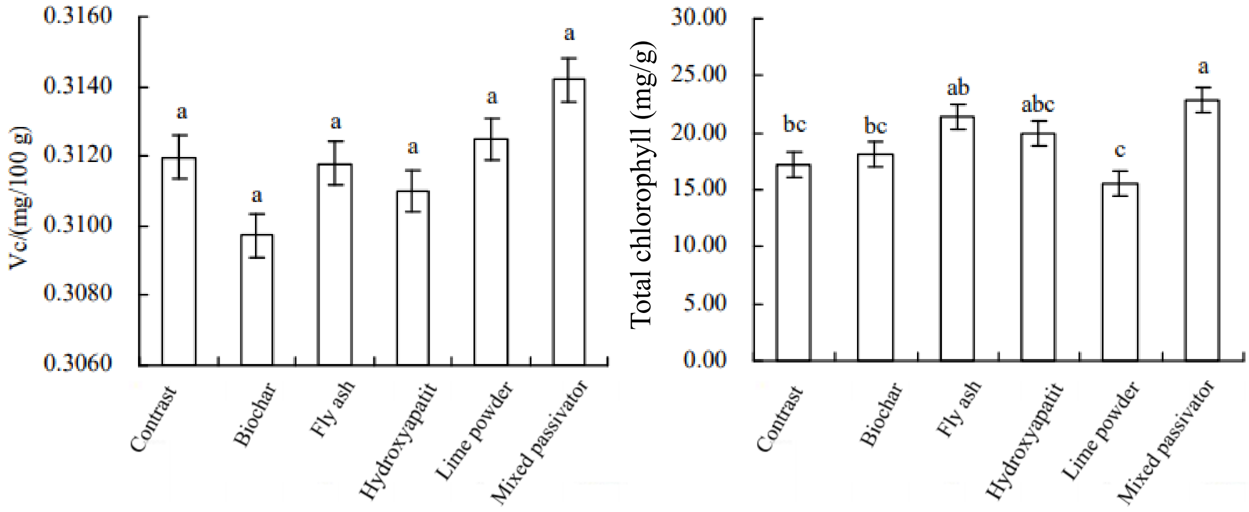


Figure 4. Effect of Passivator on the quality of Chinese.

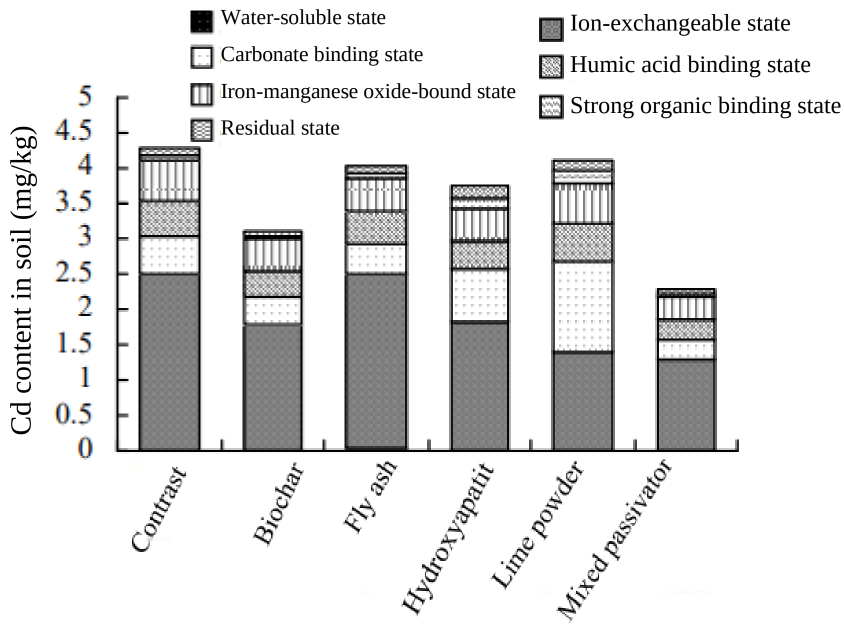


Figure 5. Effect of Passivator on the occurrence form of Cd in soil.

5. Conclusions

The results of this study show that the application of five passivators can reduce the CD content of Chinese cabbage. The mixed passivator treatment can not affect the product and quality of Chinese cabbage, enhance the soil enzyme activity, and reduce the total Cd content and the proportion of effective CD (ionic and water-soluble) in the soil The CD content of different vegetables with different passivator materials is also very different, and the physiological reasons for the difference need to be further discussed.

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