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Original Research

Effects of Different Combined Passivators on Cadmium Availability in Contaminated Soils and Uptake by Pakchoi (*Brassica chinensis* L.)

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Abstract

To solve the problem of excessive heavy metals in farmland soil, there is a pressing need for research effort to screen for the soil passivator materials. The effects of combined passivators on cadmium (Cd) availability in soils and uptake by pakchoi have been investigated based on the passivator screening and pot experiment. The results indicated that sepiolite, calcined lime and polyacrylamide (PAM) could significantly decrease the available Cd content in soils among eight kinds of inorganic and organic passivators, which were declined by 28.64%, 40.06% and 74.55%, respectively. Therefore, sepiolite, calcined lime and PAM were identified as the components of the combined passivators to grow pakchoi. The pakchoi planting experiment results of combined passivators showed that the combination of "calcined lime+PAM+sepiolite" was the most effective in decreasing the available Cd content in soils, which can reduce it by 39.83% ($P<0.05$). Meanwhile, the increases in ratio of weak organic bound or iron and manganese oxidation fractions in soils were responsible for the transformation of soil available Cd to the more stabilized fraction after applying of combined passivators. The positive passivation responses of "calcined lime+PAM+sepiolite" for Cd transfer to the aboveground of pakchoi and "calcined lime+PAM" for Cd absorption by pakchoi root demonstrated that these combined passivators could reduce Cd uptake by pakchoi. Thus, application of combined passivator of "calcined lime+PAM+sepiolite" can effectively reduce the Cd availability and Cd uptake by pakchoi in this study. Based on the results of the present research would provide a useful reference to remediate Cd contaminated soils.

Keywords: combined passivator, Cd availability, Cd uptake, pakchoi, soil remediation

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Introduction

Heavy metal pollution in farmland soils is increasingly becoming a serious issue in China due to sewage irrigation, industrial development and fuel combustion [1]. A national soil pollution survey indicated that cadmium (Cd) is the most frequently detected inorganic pollutants in soils and 7% of the investigated sites are contaminated by Cd [2]. Cd is a highly toxic heavy metal with strong mobility and bioavailability that can be accumulated in the human body through food chain directly or indirectly and threaten human health [3]. Thus, it is the urgent problem to be solved how to effectively control Cd polluted soils. In-situ passivation of heavy metals in contaminated soils is based on the application of active passivation materials to change heavy metals fraction and further reduce the mobility and bioavailability of heavy metals in soils through chemical reactions such as dissolution-precipitation, ion exchange adsorption, oxidation-reduction, organic complexation and chelation [4]. In situ passivation has recently been gaining prominence in the remediation of heavy metal contaminated soils because of its cost-effectiveness, convenient operation and suitable for large-area popularization [5].

In *in-situ* passivation, there are various inorganic and organic materials used for remediation of heavy metal contaminated soils, including alkali substance [6], silicate [7], clay minerals [8], metallic oxide [9] and biochar [10]. The addition of alkali substance to contaminated soils is an extremely regarded passivator that can increase soil pH, enhance precipitation of metal carbonates and hydroxide and reduce metals bioavailability [11]. When quick lime of 300 $g \cdot m^{-2}$ applied into field soil, the available Cd content in soils decreased by 73.61%, and Cd contents in roots, stems and shells of rape were also significantly decreased [12]. Silicate passivators are recognized by forming the complex with Cd in soils, a decrease in the Cd uptake by plants was discovered [13]. Wu et al. demonstrated that the content of weak acid solution Cd fraction in soils decreased 19.8% after applying 0.5% silicate to Cd contaminated soil with 3.0 $mg \cdot kg^{-1}$ [14]. Clay minerals have been reported for their strong absorption of heavy metals due to their high stability, large surface area and ion exchange capacity [15]. It is reported that the Cd mobility in contaminated soil decreased after adding sepiolite to soil. Additionally, Cd uptake by aboveground and root of spinach decreased by 26.2% and 30.6% when the addition amount of sepiolite increased from 1% to 5% [16]. Metal oxides have the characteristics of strong reactivity, small particle size, high adsorption capacity and large relative specific surface area, which can reduce the mobility capacity of heavy metals [17]. Biochar added to soils has been considered an effective passivator, characterized by its well-developed pore structure and surface functional groups through adsorption, precipitation and ion exchange complexation [18]. Gao et al. investigated that acid soluble and reducible Cd fractions in soils were significantly decreased and residual fraction was dramatically improved after 3% rape straw charcoal was applied into soil [19]. Meanwhile, a recent research showed that the application of 0.5% slaughter waste biochar can promote the transformation of acid soluble Cd to more stable oxidizable fraction [20].

It is well known that organic passivators with active functional group can complex with water soluble and exchangeable heavy metal ions in soils. Some studies have reported that the content of residual Cd in soils increased 181.64% compared to the control, and the Cd content of maize grain decreased 62.20% [21]. Dhiman et al. investigated that the adsorption rate of heavy metals in soils can be significantly raised after applying 1% polyacrylamide (PAM) [22]. The application of PAM will improve soil physical and chemical properties; moreover, it can be used as a passivator for remediation of contaminated soils. As well, research has found that long-term extensive use of inorganic passivators will have adverse effects on soil properties and microbial diversity [23]. For example, lime as a passivator also can break the aggregated structure of the soil and affect microbial activity [24]. However, less information regarding how the combined passivatrs of inorganic and organic materials affect the Cd availability in contaminated soils and plant uptake is available. Therefore, the objectives of this study were to: (1) screen the effective combined passivators of inorganic and organic materials used in the remediation of Cd contaminated soil; (2) determine the effects of combined passivators application on Cd availability in soils; (3) assess the impacts of combined passivators on Cd adsorption and accumulation in pakchoi.

Materials and Methods

Experimental Materials

The soil used in the combined passivator screening experiment was collected from the top layer (0-20 cm) of farmland, located in Jiamusi, Heilongjiang, China. The Cd contaminated soils were artificially prepared by spraying $CdCl_2 \cdot 5H_2O$ solution into the collected soil at a level of 5.0 mg Cd $\cdot kg^{-1}$ soil. The Cd contaminated soil used in the pot experiment, which is characterized as brown soil, was obtained from the top layer of farmland in Shandong province, China. The soil pH, the content of organic matter and electrical conductivity (EC) were 4.92, 17.5$g \cdot kg^{-1}$ and 0.08 $mS \cdot cm^{-1}$ respectively. The content of total Cd was 4.34 $mg \cdot kg^{-1}$, which was significantly higher than the risk screening limit of 0.30 $mg \cdot kg^{-1}$ based on the Environmental Quality Standard for Soils of China (GB15618-2018). Soil samples were air dried at room temperature and ground to pass through 5 mm sieve.

The seeds of pakchoi (*Brassica chinensis*) were purchased from Taiyuan Jin-wu Seed Co., Ltd. of

Shanxi Province, China. The passivators used in the experiment included inorganic materials (zeolite, sepiolite, calcined lime, calcium hydroxide, calcium silicate and ferrous sulfide) and organic materials (sodium humate and PAM). Zeolite, sepiolite, calcined lime, calcium silicate, ferrous sulfide and PAM were purchased from Taiyuan Jiangyang Chemical Co., Ltd, and calcium hydroxide was purchased from Shanghai Sinopharm Reagent Co., Ltd. The content of Cd in these passivators was all undetected.

Experiment Design

Passivator materials were ground and passed through a 2 mm sieve prior to use in the passivator screening experiment. Eight passivators were selected for soil treatments and each passivator treatment was triplicate, and a total of 27 treatments was set up when carrying out the single passivator screening experiment. Five grams of passivator were mixed with prepared soil (one hundred grams of soils) and loaded into a pot (25 cm×20 cm×17 mm). The distilled water was added to each pot and kept for 7 days, during which 2-3 cm water was submerged at the soil surface. Then the samples were placed in an oven at 60ºC to dry and ground through a 2 mm nylon sieve to measure soil pH and the content of available Cd.

The effective passivators in the screening experiment were used as the components of combined passivator for pot experiment of pakchoi. A total of 15 treatments was conducted in the growing pakchoi experiment, with three replicates for each treatment. Four healthy seedlings were retained in each pot and a total of 60 plants was performed. The combined passivator was added in test group, while the control group (CK) was not. The added amount of calcined lime was 5.0 $g\cdot kg^{-1}$ in the T1 treatment, and the addition levels of calcined lime and PAM were 4.0 $g\cdot kg^{-1}$ and 1.0 $g\cdot kg^{-1}$ in the T2 treatment. In the T3 treatment group, 4.0 $g\cdot kg^{-1}$ calcined lime and 2.6 $g\cdot kg^{-1}$ sepiolite were successively applied into the soils. The addition amount of three passivators were 4.0 $g\cdot kg^{-1}$ calcined lime, 0.4 $g\cdot kg^{-1}$ PAM and 2.0 $g\cdot kg^{-1}$ sepiolite in the T4 treatment group. All pots were applied with the same amount of fertilizers (0.33 g $N\cdot kg^{-1}$ as $CO(NH_2)_2$, 0.10g $P_2O_5\cdot kg^{-1}$ as KH_2PO_4, and 0.09 g $K_2O\cdot kg^{-1}$ as KCl) to ensure the uniform nutrients input rates for proper pakchoi growth. Three kilograms of air-dried soils were mixed with the combined passivators in pots, and then deionized water was added along the pot wall to hold soil moisture within the proper range from 65% to 70%. After 1 week of equilibration, 16 seeds of pakchoi were planted in each pot and four uniform seedlings were kept per pot after germination from 7th April to 26th May 2021 (~50 days). Pots were arranged in a randomized design with three replicates. The pakchois were added with deionized water every 2 days for the growth need.

The aboveground and root of pakchoi were separated after the harvest, and the rhizosphere soils were collected. Pakchoi samples were washed with tap water and then rinsed 3 times with ultrapure water. The root of pakchoi was soaked with EDTA solution for 30 min to eluate he heavy metals adsorbed on the root surface. These pakchoi samples were green removed at 105ºC for 30 min and oven dried at 60ºC. Then the samples was crushed and ground through 2 mm nylon sieve to measure the Cd content of pakchoi. The rhizosphere soil was naturally air-dried and ground through 75 μm sieve for analysis.

Analystical Methods

Soil pH was determined in deionized water (soil to water ration of 1:2.5) using a glass electrode pH meter (PHS-3C, Leici, China) [25]. Soil Cd chemical fractions were obtained using the modified sequential extraction procedure [26]. The fractions of Cd were characterized as F1, F2, F3, F4, F5, F6 and F7, which represents water soluble, ion exchangeable, carbonate bound, weak organic bound, iron and manganese oxide bound, strong organic bound and residual Cd, respectively. The sum of water soluble, ion exchangeable and carbonate bound Cd in soils was taken as the available Cd directly absorbed and utilized by plants [27]. Soil samples were digested with HNO_3-HCl to measure total Cd contents in soils. Plant samples were digested with HNO_3-$HClO_4$ (v/v: 85/15) to determine Cd contents in pakchoi by graphite furnace atomic absorption meter (AA6880, GFAAS). Standard soil (GBW07445) and plant materials (GBW07603) from the National Institute of standards and Technology were used for the quality assurance and control. The Cd recovery rate of soil and pakchoi samples ranged from 85% to 115%.

Statistical Analysis

The bioconcentration factor of Cd (*BCF*) is calculated using the equation: *BCF* = Cd content in the aboveground part of pakchoi ($mg\cdot kg^{-1}$)/total Cd content in soils ($mg\cdot kg^{-1}$). Pakchoi transfer capability of Cd from root to aboveground part (*TF*) is calculated based on the formula: *TF* = Cd content in the aboveground part of pakchoi ($mg\cdot kg^{-1}$)/Cd content in root ($mg\cdot kg^{-1}$). All data were presented as mean±standard deviation and data analysis was performed using JMP11.The LSD was used to put up multiple comparison at the 0.05 significance level.

Results and Discussion

Screening of Combined Passivator

Effects of single passivator application on soil pH and available Cd content were shown in Table 1. Except for ferrous sulfide, application of inorganic passivators increased soil pH and calcined lime had the reinforcing effects on soil pH. Compared with the control (CK), sepiolite, calcined lime, calcium hydroxide and silicate significantly reduced the contents of available Cd in soils ($P<0.05$). Among organic passivators, application of sodium humate increased soil pH while PAM showed decreasing effects. Conversely, PAM had significantly decreasing impacts on soil available Cd content ($P<0.05$), and the effects of sodium humate on soil available Cd was not significant ($P>0.05$). Sepiolite, calcined lime, calcium hydroxide and PAM reduced the content of available Cd in soils by 28.89%, 40.00%, 42.22% and 74.81% respectively. Therefore, sepiolite, calcined lime and PAM were used as the combined passivators considering the decreasing effect and material cost.

Calcined lime and calcium hydroxide reduced soil Cd availability mainly by increasing soil pH. This is consistent with the conclusion that application of calcined lime and calcium hydroxide might be more effective in the nutrient elements supplement to achieve soil improvement because these alkaline substances can neutralize exchangeable and active acidis and improve soil pH [28]. Sepiolite and sodium humate could significantly reduce the content of available Cd in soils due to the strong natural cation exchange ability [29]. Moreover, sepiolite was decomposed into calcium carbonate to improve the soil pH and enhance its Cd adsorption capacity. Compared with CK, sepiote significantly reduced the available Cd content in soils in this research (P<0.05). The findings were consistent with the conclusion proposed by Zhan et al. that application of sepiolite could significantly increase soil pH and decrease soil available Cd content in contaminated maize fields [30]. It is believed that at lower soil pH, the competion between hydrogen and heavy mtal ions, which is responsible for the decrease of ion exchange capacity and affinity of humic acid on Cd^{2+} in soils. However, the effect of sodium humate on the content of available Cd in soils was not significant. This result is consistent with that of Yu et al. who proposed that the passivation effect of humic acid application on exchangeable Cd in soils was not persistent [31]. There have been many reports on the application of zeolite and silication for restoring heavy metal pollution of soils [32], however, the effects of zeolite and calcium silicate on soil Cd were not satisfactory in this study. The cationic Cd adsorbed on ferrous sulfide was converted into sulfides, the mechanism of which was similar to the substitution reaction [33]. The content of available Cd in soils was significantly decreased after applying PAM ($P<0.05$), which might result from the adsorption ability of PAM for Cd^{2+} in soils by complexation [34].

Effects of Combined Passivators on Soil Available Cd

After applying of different combined passivators, soil pH, TN, TP and SOM contents were significantly increased; while the content of soil TK had no significant change (Table 2). The effect of combined passivator of "lime+PAM+sepiolite" on soil physical and chemical properties was weaker than other treatments. Application of different combined passivators decreased the contents of available Cd in soils (P<0.05). It should be noted that the decreasing effects of the combined passivator of "calcined lime+PAM" and "calcined lime+PAM+sepiolit" on Cd availability in soils were more obvious than other treatments, which indicated that PAM showed remarkable decreasing effects on Cd availability in soils.

Compared with CK, the content of available Cd in soils was significantly decreased after applying of different combined passivators (Table 2). The combination of "calcined lime+PAM" had a stronger decreasing effect on soil Cd than that of calcined lime alone. In addition, the impacts of combined application of "calcined lime+PAM" and "calcined lime+PAM+sepiolite" on the content of soil available Cd was more obviously than the combined passivator of "calcined lime+sepiolite". This is probably because

Table 1. Effects of different passivators on soil pH and available Cd content.

Type of passivator	Passivator material	Soil pH	Soil available Cd content (mg kg^{-1})
Inorganic passivator	-	5.75±0.16d	1.35±0.09a
	Zeolite	7.73±0.19c	1.27±0.08a
	Sepiolite	7.47±0.19c	0.96±0.06b
	Calcined lime	11.43±0.21a	0.81±0.05c
	Calcium hydroxide	10.81±0.19b	0.78±0.04c
	Calcium silicate	7.22±0.17c	1.25±0.08a
	Ferrous sulfide	5.07±0.14f	1.28±0.08a
Organic passivator	Sodium humate	7.61±0.16c	1.48±0.10a
	PAM	5.45±0.14e	0.34±0.01d

Different lowercase letters indicate significant differences between treatments

Table 2. Effects of type and dosage of combined passivators on soil properties and available Cd content.

Treatments	Passivator type	Dosage (g kg^{-1})	pH	SOM (g kg^{-1})	TN (g kg^{-1})	TP (mg kg^{-1})	TK (g kg^{-1})	Soil available Cd content (mg kg^{-1})
CK	-	0	4.92±0.16c	17.50±1.26a	1.74±0.07a	311.34±13.67a	14.59±0.81a	1.18±0.09a
T1	Calcined lime	5.0	6.15±0.17a	14.22±0.86b	1.48±0.04b	296.22±14.74a	14.14±0.78a	1.01±0.07b
T2	Calcined lime+PAM	4.0+1.0	5.62±0.16b	12.75±0.81b	1.23±0.03d	227.95±10.45c	15.02±0.68a	0.87±0.06c
T3	Calcined lime+sepiolite	4.0+2.6	5.38±0.13b	13.83±0.78b	1.41±0.05c	274.17±12.44b	15.95±0.84a	0.99±0.06b
T4	Calcined lime+PAM + sepiolite	4.0+0.4+2.0	5.73±0.16b	14.79±0.87b	1.55±0.06b	202.69±10.70d	15.27±0.75a	0.71±0.05d

T1, calcined lime; T2, calcined lime+PAM; T3, calcined lime+sepiolite; T4, calcined lime+PAM + sepiolite. Different lowercase letters indicate significant differences between treatments

the passivation mechanism of the combination of "sepiolite+calcined lime" on soil Cd was attributed to the exchange and complexation of Cd^{2+} in soils and Ca^{2+} in calcined lime and sepiolite [35]. However, the complexation effect of PAM on Cd^{2+} was better than sepiolite and calcined lime.

The correlation between soil available Cd content and soil properties (pH, SOM, TN, TP and TK) was shown in Table 3. The content of available Cd in soils had a positive correlation with the contents of SOM, TN and TP ($P<0.05$), and negatively related to the content of TK ($P<0.05$). Although the available Cd content in soils applied of "calcined lime+PAM" was significantly lower than that of single calcined lime, combined passivators showed an inverse effect on soil pH. Meanwhile, there was no significant correlation between soil pH and available Cd content. These indicated that the complexing capacity of PAM with heavy metals was the key factor affecting Cd availability in soils.

The content of available Cd in soils was positively correlated with SOM, TN and TP ($P<0.05$). Soil pH was one of the important factors affecting the Cd availability in soils [1]. In this study, soil pH in T1 treatment was higher than that in T2 treatment, however, the content of soil available Cd in T2 treatment was significantly lower than T1 treatment and there was no distinct correlation between soil pH and available Cd content. Therefore, the complexation of PAM might be an important mechanism in reducing the Cd availability in soils. Meanwhile, the correlation coefficient between soil available Cd and TP content was the maximum (0.935). This was probably because water-soluble phosphate reacts with soil Cd^{2+} to form insoluble phosphate compounds and further stabilize Cd in soils [36]. In addition, application of combined passivators deceased the proportion of available Cd (F1+F2+F3), while increased the proportion of F4 and F5. As a result, combined passivators showed an adverse effect on the conversion of soil Cd to a more stable form and reduce soil Cd pollution risk. This is consistent with the conclusion that increased soil pH can facilitate the conversion of exchangeable Cd to a stable state [1]. When combined passivators were applied, soil pH and hydroxide ions in soil solution increased, which might be the reason that improved the binding ability of iron and manganese oxide and organic matter with soil Cd [37].

Effects of Combined Passivators on Soil Cd Fractions

The soil Cd fractions of water soluble (F1), ion exchangeable (F2) and carbonate bound (F3) were regarded as the available Cd that can be absorbed and utilized by plants directly [27]. After applying different combined passivators in soils, the proportion of available Cd (F1+F2+F3) in soils decreased by 25.93% on average (Fig. 1a). Among them, the proportion of available Cd in soils applied of "calcined lime+PAM+sepiolite" was the lowest (24.83%),

Table 3. Correlation analysis between soil properties and available Cd content.

	pH	SOM	TN	TP	TK	Soil available Cd content
pH	1.000					
SOM	-0.753**	1.000				
TN	-0.639*	0.910**	1.000			
TP	-0.561	0.644*	0.673*	1.000		
TK	-0.383	-0.442	-0.447	-0.539	1.000	
Soil available Cd content	-0.575	0.700**	0.641*	0.935**	-0.551	1.000

Single and double asterisks indicate significant correlations among soil properties and soil available Cd content at 0.05 and 0.01 levels.

which was 2.02%, 0.76% and 1.60% lower than that of other combined passivators. The application with combined passivators could decrease various fractions of Cd in soils (Fig. 1b). Similarly, the most obvious reduction was observed in T4 treatment of "calcined lime+PAM+sepiolite" for the Cd contents of weak organic bound (F4), iron and manganese oxide bound (F5) and strong organic bound (F6) that reduced by 0.081mg·kg^{-1}, 0.047 mg·kg^{-1} and 0.663 mg·kg^{-1} compared with the CK treatment. Application of single calcined lime and combination of "calcined lime+PAM+sepiolite" showed obviously decreasing effects on the content of residual Cd (F7). Compared with CK, the content of F7 in soils applied of calcined lime and combination of "calcined lime+PAM+sepiolite" reduced by 0.262 mg·kg^{-1}and 0.214 mg·kg^{-1}.

The correlation between soil properties and the content of soil fractions were shown in Table 4. Except for TK, there were significant correlations between the content of soil Cd fractions and soil pH, SOM, TN, TP after applying with combined passivatiors (P<0.05). Soil pH had a negative correlation with soil Cd fractions, particularly the content of F7. The contents of SOM, TN and TP in soils were positively correlated

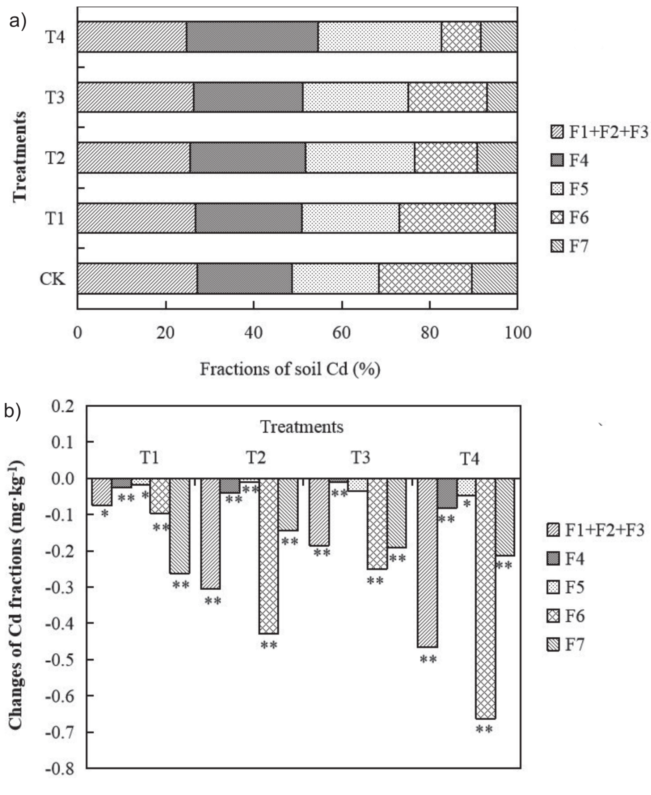

Fig. 1. Effects of combined passivator on Cd fraction distribution (a) and content (b) in soils. The fractions of Cd were characterized as F1, F2, F3, F4, F5, F6 and F7, which represents water soluble, ion exchangeable, carbonate bound, weak organic bound, iron and manganese oxide bound, strong organic bound and residual Cd, respectively. T1, calcined lime; T2, calcined lime+PAM; T3, calcined lime+sepiolite; T4, calcined lime+PAM+sepiolite. Single and double asterisks indicate significant differences among different passivator types at 0.05 and 0.01 levels.

Table 4. Correlation analysis between soil properties and Cd fractions.

	pH	SOM	TN	TP	TK
F1+F2+F3	-0.675*	0.706**	0.641*	0.935**	-0.304
F4	-0.720**	0.831**	0.792**	0.807**	-0.199
F5	-0.675*	0.701**	0.756**	0.720**	0.122
F6	-0.569	0.706**	0.704**	0.974**	-0.323
F7	-0.893**	0.846**	0.802**	0.591	-0.131

Single and double asterisks indicate significant correlations between soil properties and Cd fractions in soils at 0.05 and 0.01 levels.

with the content of soil Cd fractions. The correlations between SOM, TN and the content of F7 were the most significant, and the correlation coefficient were 0.846 and 0.802, respectively. Soil TP had the most obvious positive correlation with the content of F6 and the correlation coefficient was 0.974.

Effects of Combined Passivators on Cd Uptake and Accumulation of Pakchoi

The changes of Cd content in aboveground and root of pakchoi are shown in Fig. 2. After application of combined passivators in soils, the Cd content in aboveground and root of pakchoi were significantly reduced by 36.34-63.56% and 11.95-37.90%, respectively. The Cd content in aboveground part of pakchoi after applying single calcined and the combination of "calcined lime+PAM+sepiolite" was decreased significantly, but there was no noticeable difference between two application methods (P>0.05). On the contrary, the Cd content in root of pakchoi after applying of single calcined and combination of "calcined lime+PAM+sepiolite" was significantly higher than that of applying of combination of "calcined+PAM" (P<0.05).

Soil pH showed a significant negative correlation with the Cd content in aboveground part of pakchoi

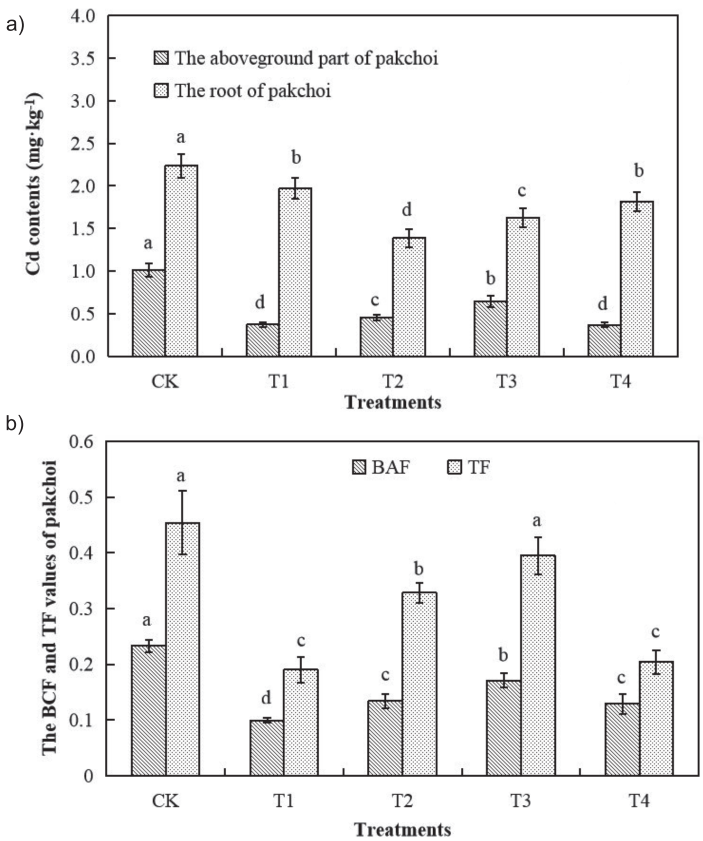

Fig. 2. Effects of different compound passivators on Cd content in aboveground and root of pakchoi, and Cd bio-concentration factors (*BCF*) and translocation factors (*TF*) of pakchoi.Different lowercase letters indicated significant differences among passivator treatments at 0.05 level.

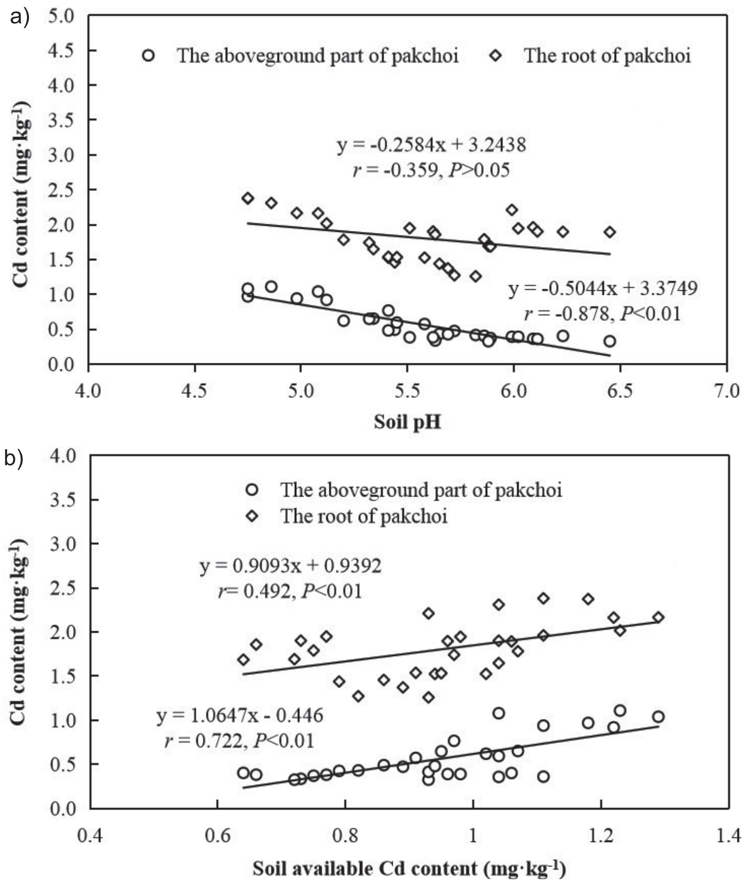

Fig. 3. The correlation between soil pH, available Cd content and Cd content in aboveground and root of pakchoi.

(Fig. 3). However, there was no significant correlation between soil pH and the Cd content in root of pakchoi. These indicated that the effects of combined passivator on Cd accumulation in pakchoi was not obvious, but combined passivators could contribute to the Cd migration of pakchoi. The available Cd content in soils had a significant positive correlation with the contents of Cd in aboveground part and root of pakchoi ($P<0.01$), which demonstated that combined passivators could reduce the Cd uptake ability of pakchoi by affecting the content of available Cd in soils.

The present study confirmed that applying of combined passivators greatly decreased the Cd uptake ability by the aboveground parts and roots of pakchoi. Meanwhile, the addition of combined passivators showed a prominent decrease in the Cd accumulation in roots and transfer ability to aboveground of pakchoi. It had been found that the Cd content in the aboveground parts of pakchoi were significantly decreased by 63.17%, 55.05%, 36.34% and 63.56% in T1, T2, T3 and T4 treatment compared to CK ($P<0.05$), and the Cd content in roots of pakchoi were reduced by 11.95%, 37.90%, 27.16% and 18.88% respectively ($P<0.05$). It can be demonstrated that the inhibitory effect of combined passivator of "calcined lime+PAM+sepiolite" on the Cd transfer from roots to aboveground parts was superior to other treatments, and the combined passivator of "calcined lime+PAM" had the considerable influence on the Cd uptake by pakchoi, indicating that PAM had an obvious effect on the uptake of heavy metals by plants. Hamid et al. revealed that the combination passivator of lime and sepiolite could reduce Cd adsorption by plants [29]. However, compared with the single application of calcined lime, Cd content in roots of pakchoi after applying with the combined passivator of "calcined lime+sepiolite" was remarkably improved ($P<0.05$), which showed that the decrease effect of combination of "calcined lime+sepiolite" was not apparent.

The Cd adsorption and enrichment by plants is related to the bioavailability of heavy metals in soils [38]. In this study, there was a significant negative correlation between the Cd content in aboveground parts of pakchoi and soil pH. This significant correlation might be due to the decline of soil pH and Cd bioavailability after applying of combined passivators [39]. Furthermore, the content of available Cd in soils had significant positive correlation with the Cd content in aboveground parts and roots of pakchoi. According to the present findlings, Cd availability in soils might be used to predict the actual Cd uptake by pakchoi. Nevertheless, Chen et al. reported that the availability of heavy metals in soils could not accurately predict the uptake of heavy metals by rice [40]. Therefore, it is suggested more studies need to be conducted to predict the relationship between Cd availability in soils and Cd uptake by plants after applying of combined passivators.

Conclusion

All the combined passivators significantly decreased the content of availability Cd in soils. The mechanism responsible for this decline could be the reactions of ion exchange and complexation. The combination of "calcined lime+PAM+sepiolite" was the most effective passivator for Cd content in soils. Application of different combined passivators could increase the proportion of weak organic bound and iron and manganese oxide bound Cd in soils. Combined passivators application was favourable the transformation from soil Cd to a more stable fractions. The Cd contents in aboveground parts and roots of pakchoi were significnatly declined in the treatment of various combined passivators. The combined passivator of "calcined lime+PAM+sepiolite" can effectively reduce the Cd transfer ability from roots to aboveground in pakchoi. "Calcined lime+PAM" is recommended to inhibit Cd uptake by roots of pakchoi in Cd contaminated agricultural soils. Finally, the effect of various combined passivators on Cd availability and plant uptake under field conditions remains to be further studied.

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Conflict of Interest

The authors declare no conflicts of interest.

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