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The cooperative application of oyster shell and biochar efficiently enhanced in-situ remediation of cadmium contaminated soil around intensive industry

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Abstract

Biochar has been widely used for the in-situ remediation in the cadmium (Cd) contaminated soil, while the high-cost of biochar limited its application in farmland. In this study, we firstly investigated the possibility of cooperative application of oyster shell and biochar to enhance Cd immobilization efficiency and reduce the cost in field experiments under rice-oilseed rape rotation. Treatments were comprised of: rice planting without amendments (R-PA0); followed with 15000 kg/ha biochar (R-PA1); followed with 15000 kg/ha oyster shell (R-PA2); followed with 7500 kg/ha biochar and 7500 kg/ha oyster shell (R-PA3); rice-oilseed rape rotation without amendments (RT-PA0); rotation with 15000 kg/ha biochar (RT-PA1); rotation with 15000 kg/ha oyster shell (RT-PA2); rotation with 7500 kg/ha biochar and 7500 kg/ha oyster shell (RT-PA3). Results revealed that HOAc-extractable Cd was significantly decreased by 38.46% in R-PA2. Cd contents in brown rice and oilseed were reduced by 29.67% in R-PA3 and 19.74% in RT-PA3 compared with control. Meanwhile, Hazard Quotient of brown rice and oilseed significantly decreased in RT-PA3. The Olsen-P in R-PA3 and RT-PA3 was markedly increased by 187.46% and 184.73%, respectively. In addition, activities of urease, catalase, and β-galactosidase in RT-PA3 were significantly increased by 268.88%, 30.44% and 245.28%, respectively. Furthermore, the jiont application of biochar with oyster shell significantly decreased the cost of soil remediation at least 9600 RMB/ha. These results demonstrated that the joint utilization of biochar with oyster shell might be an economical and effective pathway to achieve in-situ remediation of Cd contaminated farmland.

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

Keywords: Biochar; Oyster shell; Rice-oilseed rape rotation; In-situ remediation; Enzyme activities; Cadmium

1. Introduction

Heavy metals have been considered as hazardous materials for human health, and among which cadmium (Cd) is one of the most toxic heavy metals (Yang et al., 2021). The excessive intake of Cd could cause serious damages to bones, thyroid, and kidneys (Ma et al., 2021a). According to the latest national survey on the status of soil environmental quality in China, Cd has ranked as the highest contaminants (7%) among all heavy metals (Mou et al., 2020). In southwest China, a large amount of farmlands were contaminated with Cd owing to the intensive industrialization (Chen et al., 2018a). In addition, soil acidification also aggravated the bioavailability and solubility of Cd, thus enhancing Cd uptake by crops (Feng et al., 2020). Therefore, the development of cost-effective and eco-friendly remediation technologies is crucial for food safety and soil quality.

In recent years, in-situ immobilization as an effective technology has raised wide attentions in the remediation of Cd contaminated farmlands, which can reduce the Cd uptake by plants without delaying agricultural production (Palansooriya et al., 2020; Wang et al., 2021). In recent years, biochar derived from bio-wastes is widely recommended as a soil amendment (Zong et al., 2021). Amounts of nutrients (such as C, N, P, K, and Mg etc.) in biochar could improve soil fertility and promote plant growth (Lu et al., 2015). Moreover, biochar has a large surface area and plenty of functional groups, which are reactive to immobilize heavy metals, including Cd, Pb,

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

and Ni (Wang et al., 2021). However, the high price of biochar limited its large application. In addition, the soil pH regulation by biochar in acid fields was not very significant, while the soil pH values were negatively related to Cd availability (Liu et al., 2018). Therefore, it is vital to decrease the remediation cost of biochar without reducing immobilization efficiency of Cd. Oyster shell is a low-cost and largely available bio-waste product from oyster farming (Li et al., 2020). Previous studies found that oyster shell as a promising slow-release alkaloid has outstanding effects on pH adjustment and Cd immobilization in soils (Chen et al., 2018b; Peng et al., 2020). In this sense, we think that the joint use of biochar and oyster shell might be a low-cost and effective pathway to decrease Cd uptake by crops and improve soil biochemical quality in acidic fields. However, there was little known about the joint effects of biochar and oyster shell on the in-situ remediation in Cd contaminated soil.

Rice and oilseed rape were the main food and economic crops in southwest China, and rice-oilseed rape rotation is the dominant production model (Liu et al., 2014). Previous studies mainly focused on the effects of amendments on reducing the Cd uptake by rice, while the remediation efficiency of passivators under the rice-rape rotation was little known. Based on above opinions, a filed experiment under rice-oilseed rape rotation was designed: (1) to investigate the cooperative effects of biochar and oyster shell on Cd immobilization; (2) to evaluate the effects of biochar and oyster shell on decreasing human health risk of Cd; (3) to reveal the effects of biochar and oyster shell on soil biochemical properties including pH, CEC, total organic carbon, organic matter, Olsen-P, Olsen-K, Alkeline-N, and the activities of

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

soil enzymes, so as to estimate the pearson correlation analysis (PCA) model of main parameters in the moderately polluted farmland.

2. Material and methods

2.1. Experimental site and soil properties

A field trial was conducted during 2019-2020 in a rice-oilseed rape rotation cultivated site where the soil was moderately contaminated by Cd. The field site was located in a dominant agricultural cultivation region round industrial parks in Chengdu plain, Sichuan province, China (104°18′N, 31°81′E). This region belongs to a subtropical monsoon humid climate with an average temperature of 16.1 ℃ and annual rainfall of about 1000 mm. The main properties of the topsoil (0 - 20 cm) collected from the site in 2019 and 2020 were shown in Table S1.

2.2. Characteristics of experimental materials

Biochar was purchased from Zhenjiang Zedi agricultural and biological Co., Ltd., which was produced from rice straw in a reactor with N_2 and 500 ℃ for about 4 h. Oyster shell was purchased from Fujian Mata Co., Ltd (< 0.3 mm mesh). The surface structures of biochar and oyster shell were analyzed by Scanning Electron Microscope (SEM, JSM-7500F). The functional groups of biochar and oyster shell were measured by Fourier Transform Infrared Spectra (Nicolet 6700). The seeds of rice “Yixiang 2115” and seeds of oilseed rape “Yiyou 15” were obtained from Rice Research Institute, Sichuan Academy of Agricultural Science.

2.3. Experimental setup

The field experiment was conducted during 2019 - 2020 as following treatments:

- R-PA0: Rice planting without passivators;
- R-PA1: Rice planting with 15 t/ha biochar;
- R-PA2: Rice planting with 15 t/ha oyster shell;
- R-PA3: Rice planting with 7.5 t/ha biochar and 7.5 t/ha oyster shell;
- RT-PA0: Rice-oilseed rape rotation without passivators;
- RT-PA1: Rice-oilseed rape rotation with 15 t/ha biochar;
- RT-PA2: Rice-oilseed rape rotation with 15 t/h oyster shell;
- RT-PA3: Rice-oilseed rape rotation with 7.5 t/ha biochar and 7.5 t/ha oyster shell.

The concentrations of biochar and oyster shell used in this study were referred to previous reports (Ameloot et al., 2014). Each experimental plot was 56 m^2 (7 x 8 m) and arranged in a randomized design with three replicates. Before rice planting, the passivators were sufficiently mixed with topsoil. After the harvest of rice, the oilseed rape was planted following the conventional tillage pattern without any passivator.

2.4. Plant analysis

The rice grain and rapeseed were dried and ground to powder. Then, 0.2 g samples were digested with HNO_3:$HClO_4$:HF in a mixture of 5:4:3 (v/v) and the mixture was then diluted to 10 mL with 1% HNO_3 (Wu et al., 2019b). The Cd concentrations in the mixture were determined by AAS.

2.5. Soil analysis

Soil pH was determined by a pH meter (METTLER-S220) with a soil/water ratio of 5 g/25 mL. The bioavailable Cd of soil was measured by the TCLP method (Xu et

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

al., 2020). Briefly, 2 g of soil sample was mixed with 40 mL 0.11 M acetic acid and shaken at 25 ℃, 150 rpm for 16 h. Then, the mixture was centrifuged for 5 min at 8000 rpm and the supernatant was collected to determine Cd content by atomic absorption spectroscopy (AAS; VARIAN, SpecterAA-220Fs). Olsen-P, Olsen-K, and Alkeline-N were measured according to the method ascribed by (Liu et al., 2017). Soil TOC and OM were determined by the method ascribed by (Walz et al., 2017).

In addition, activities of soil enzyme were analyzed to reflect the biological quality in this study. Dehydrogenase activity was evaluated by the production of triphenylfornazan (TPF) at OD_{492nm} and expressed as μg TPF/g soil/24 h (Benefield et al., 1977). Acid phosphate activity was assayed by the *p*-nitrophenol (pNP) release at OD_{400nm} and expressed as μg pNP/g soil/24 h (van Aarle and Plassard, 2010). Urease activity was determined by the NH_4-complex at OD_{578nm} and expressed as μg NH_4-N/g soil/24 h (Yan et al., 2013). Catalase activity was measured by back titration of H_2O_2 added to soil with 0.1 M $KMnO_4$ and expressed as by mL 0.1 M $KMnO_4$/g soil/h (Zhang et al., 2011). Invertase activity was assayed by the amount of glucose production at OD_{508nm} and expressed as μg glucose/g soil/24 h (Wu et al., 2019b). β-galactosidase activity was measured by the released 4-methylumbelliferone (MUF) and expressed as μg MUF μmol/g soil/h (Martínez-Iñigo et al., 2009).

2.6. Human risk assessment of Cd

The health risks of Cd to adults and children in the crops were separately assessed by the Hazard Quotient (HQ) according to the method introduced by Environmental Protection Agency (EPA) in the US (Wei et al., 2020). HQ values were

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

calculated as the following formula:

HQ = (*EF* x *ED* x *C* x *IR*)/(*BW* x *AT* x *RfD*) (1)

EF (Exposure Frequency): 365 days/year.

ED (Exposure Duration): 70 years for adult, 7 years for children.

C: Cd concentrations in the rice grain and oilseed (mg/kg).

IR (Ingestion Rate): For rice grain, 0.3892 kg/day for adult and 0.1984 kg/day for children, respectively. For rape oil, 0.025 kg/day for adult and 0.0125 kg/days for children, respectively.

BW (Body Weight): 62.71 kg for adult male, 55.1 kg for adult female and 25.6 kg for children.

AT (Averaging Time): 25550 days for adult and 2555 days for children.

RfD (Reference of Dose): 0.001 mg/kg for Cd.

2.7. Statistical analysis

In this study, statistical significance was analyzed using SPSS 18.0 package, and means values were considered to be different when $P < 0.05$ using least significant difference (LSD). All statistics were performed using Origin 8.0 (USA).

3. Results and discussion

3.1. Characteristics of soil and amendments

The main characteristics of soil, biochar and oyster shell were shown in Table S1. The soil in the field was acidic soil with pH values of 5.27 - 5.51. The biochar and oyster shell used in the field study were alkaline materials and their pH values were 8.22 and 8.52, respectively. The OM of biochar (541.53 mg/kg) was significantly

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

higher than that of soil (39.32 mg/kg) and oyster shell (12.60 mg/kg). The carbon percentage of biochar also reached 92.50%.

The surface of oyster shell (Figure 1a) was a regular filamentary layer with some disordered deposition, which might be calcium compounds. The structure of biochar (Figure 1b) was lamellar and polyporous, which was in favor of Cd absorption. In addition, FTIR was operated to detect functional groups of oyster shell and biochar (Figure 1c). The characteristic peaks of calcium carbonate in oyster shell were observed at 1427 cm^{-1} and 879 cm^{-1} (Lu et al., 2021). Biochar showed obvious peaks at 1089 cm^{-1} and 790 cm^{-1}, which were related to C-O, and C-H bending vibration, respectively (Wu et al., 2019a). In addition, an obvious feature at 3436 cm^{-1} corresponding to -OH was loaded on oyster shell and biochar (Lian et al., 2021).

3.2. Analysis of soil Cd bioavailability

To evaluate the effect of different amendments on Cd bioavailability, the concentrations of AcOH-extractable Cd in soils were determined by TCLP method (Halim, 2003). Figure 2 showed the variations of AcOH-extractable Cd with different amendments in rice-oilseed rape rotation. Compared to rice planting, the concentrations of AcOH-extractable Cd increased in the oilseed rape planting, which was mainly related to the different irrigation methods. In this study, rice planting was performed by flooding irrigation during the whole physiological period whereas dry-land cultivation was used in oilseed rape planting. In general, flooding irrigation is beneficial to reduce Cd bioavailability due to the precipitation of Cd compounds under low-redox status (Eh < 0 mV) (Mou et al., 2020). In addition, treatments with

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

biochar and oyster shell resulted in the reduction of AcOH-extractable Cd in soils. Compared to R-PA0, the AcOH-extractable Cd was significantly decreased by 20.79% and 40.59% in R-PA1 and R-PA2, respectively. Compared to RT-PA0, the AcOH-extractable Cd was also reduced by 5.76% and 17.85% in RT-PA1 and RT-PA2, respectively. Moreover, the Cd immobilization efficiency in R-PA3 and RT-PA3 was higher than that in R-PA1 and RT-PA1. These results demonstrated that oyster shell gave a better Cd immobilization than biochar and the addition of oyster shell could strength the Cd immobilization capacity of biochar.

3.3. Analysis of Cd contents in brown rice and oilseed

As shown in Figure 3, the application of biochar and oyster shell significantly reduced Cd contents in brown rice and oilseed. Treatments without amendments, the contents of Cd in brown rice reached 0.88 mg/kg. Compared to control (R-PA0), the Cd contents in brown rice was decreased by 20.88% in R-PA1 and 30.77% in R-PA2, indicating that oyster shell has the superior of Cd immobilization capacity than biochar. Obviously, the cooperative addition of biochar and oyster shell (R-PA3) contributed to higher Cd reduction (29.67%) in brown rice than that in sole biochar (R-PA1, 20.88%). In addition, Cd contents in oilseed were significantly reduced in the RT-PA1 and RT-PA3, about 27.63% and 19.74% lower than that in RT-PA0, respectively. The results indicated that biochar and oyster shell application could efficiently decrease Cd accumulation in brown rice and oilseed.

3.4. Health risk assessment of cadmium

HQ values of Cd for brown rice and oilseed intake in different treatments were

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

presented in Figure 4. The order of HQ for consuming rice and oilseed was children > adult female > adult male, indicating that children were more sensitive than adults under Cd exposure. Without amendments (R-PA0), HQ values of consuming brown rice for adult male, adult female and children reached 5.46, 6.21 and 6.82, respectively. After the application of amendments, HQ values of brown rice intake were significantly decreased by 20.87%, 31.11% and 29.76% in R-PA1, R-PA2 and R-PA3, respectively. Although HQ values of oilseed were significantly lower than that of rice grain, but the values also decreased by 17.27 - 28.14% in the oyster shell and biochar treatments.

3.5. Analysis of soil biochemical properties

3.5.1. Analysis of soil pH and CEC

It was observed that soil pH was weakly increased by biochar, but significantly increased by oyster shell (Figure 2a). After the oyster shell application, the soil pH increased to neutral (6.9 - 7.3) from acidity (5.2 - 5.5). Compared with control (R-PA0), the soil pH was increased by 1.8, 1.6, 1.4 and 1.7 pionts in R-PA2, R-PA3, RT-PA2 and RT-PA3, respectively. The application of oyster shell slight increased the CEC in the rice planting, while oyster shell and biochar had no significant effects on CEC in the rice-oilseed rotation (Figure 2b).

3.5.2. Analysis of soil nutrients

It is important for in-situ remediation of Cd contaminated soil by bio-wastes without inhibiting the soil available nutrients. To analyze the effects of amendments on soil bioavailable nutrients, the contents of TOC, OM, Olsen-P, Olsen-K, and

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

Alkeline-N were determined during the rice-oilseed rape rotation (Table S2). Biochar application slightly increased TOC and OM in rice planting and rice-oilseed rotation. In rice planting, TOC and OM in R-PA3 were increased by 10.09% and 9.92% compared with R-PA0, respectively. In rice-oilseed rape rotation, soil TOC in RT-PA1 was enhanced by 11.06% and 11.32% compared with RT-PA0, respectively. More obviously, Olsen-P was significantly increased by the addition of oyster shell. Compared with R-PA0, the Olsen-P in R-PA2 and R-PA3 significantly increased by 200.96% and 187.46%, respectively. Compared with RT-PA0, the Olsen-P in RT-PA2 and RT-PA3 significantly increased by 295.92% and 184.73%, respectively.

3.5.3. Analysis of soil enzyme activities

As shown in Figure 6, adding amendments variously changed the activities of soil enzyme. In the rice planting, biochar application increased the dehydrogenase activity, about 20.12% (R-PA1) and 25.49% (RT-PA1) higher than that of control (R-PA0). However, oyster shell significantly increased the dehydrogenase activity in rice-oilseed rotation, which was markedly increased by 59.75% and 53.39% in the RT-PA2 and RT-PA3 compared with control, respectively. Urease activity was no obvious variation in the biochar treatment whereas markedly enhanced in the oyster shell treatment. Compared with RT-PA0, urease activity was significantly increased by 268.88% in RT-PA3. However, oyster shell and biochar had no obvious impacts on acid phosphate activity, except for a reduction of 43.30% in R-PA2. In addition, the application of biochar has no negative effects on invertase activity, while oyster shell slightly decreased the invertase activity on rice-oilseed rape rotation. In the RT-PA3

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

treatment, catalase activity was significantly increased by the application of biochar and oyster shell. Moreover, β-galactosidase activity was significantly increased by 245.28% in RT-PA0 with the maximum of 12.29 μg MUF μmol/g soil/h.

3.6. Analysis of correlation coefficient

To analyze and confirm the relationship among different parameters, the Pearson correlation analysis was used to experimental data. As shown in Figure 7a, Cd content in brown rice was positively correlated to Cd bioavailability (R^2 = 0.90) but negatively correlated to soil pH (R^2 = -0.83). Meanwhile, the activities of soil enzymes except acid phosphate were positively connected to alkaline-N, Olsen-P, Olsen-K, and TOC. Figure 7b showed a weak correlation between Cd uptake of rape and Cd bioavailability. In addition, soil pH was positively correlated to Olsen-P and β-galactosidase activity (R^2 > 0.95), which further demonstrated that alkaline substances could increase Olsen-P content and β-galactosidase activity by adjusting soil pH in acid fields.

3.7. Cost approach for amendments

Considering the large scale remediation of the contaminated agricultural soil, the cost of amendments is a key parameter in the practical application. The market price of biochar (> 1200 RMB/t) was much higher than that of oyster shell (500 RMB/t) (detailed information see Supplementary Information). In this study, the dosage of amendments was 12000 kg/ha. The market price for biochar amendment was at least 14400 RMB/ha, while the jiont use of biochar and oyster shell significantly decreased the cost of amendments at least 9600 RMB/h. Furthermore, the jiont application of

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

biochar and oyster shell is more effective to improve soil biochemical properties compared to biochar. Based on these consideration, the collaborative passivation of biochar and oyster shell might be a economical pathway for the safe-use of Cd contaminated soil.

4. Discussion

Rice and oilseed rape were the most important crops over the globe. Simultaneously, rice and oilseed rape rotation was the main cultivated model in China. However, the Cd contamination in agricultural lands, especially in acidic soils, has severely threatened food safety production and human health. Cd accumulation in the plants poses a gereat human health risk. Cd uptake by crops may result in kidney damage and adverse effects on lung, cardiovascular, musculoskeletal systems (Wei et al., 2020).

In-situ immobilization was an effective pathway to decrease Cd uptake by crops by the application of amendments. Biochar is originated from bio-wastes, such as straw, coconut shell and animal manure. Previous studies has revealed that biochar has a great potential on Cd immobilization by surface absorption and co-precipitation. However, the high price of biochar and weak Cd binding in acidic soil was limited its large application in agricultural lands. In this study, our results showed that the cooperative application of oyster shell and biochar could contribute to the reduction of AcOH-extractable Cd in soils (Figure 2) and Cd uptake by crops (Figure 3). Furthermore, the non-cancer risk description methodology of HQ was widely applied to assess the possibility of health risk of Cd in different plants (Ma et al., 2021b). The

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

decreased HQ values demonstrated the human health risk of Cd decreased by the application of oyster shell and biochar.

AcOH-extractable Cd has widely used to evaluate Cd bioavailability in soils, and the reduction of Cd bioavailability was main mechanism of in-situ immobilization (Liu et al., 2021). Soil pH was the main factor influencing the Cd bioavailability in soils. It has been widely verified that soil pH determined solid-solution equilibria of heavy metals in soils (Zhao and Masaihiko, 2007). Comparatively, soil pH in the oyster shell treatment was higher that in biochar treatment (Figure 5). Although the pH values of oyster shell (8.52) and biochar (8.22) were similar, oyster shell was regarded as a low-release alkaloid in soils due to it is composed of CaO and $CaCO_3$. The dissolution of CaO and $CaCO_3$ from oyster shell in water could produce hydroxyl ion (OH^-) as the following chemical reactions (Ok et al., 2010):

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \quad (2)$$

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^- \quad (3)$$

An increase in soil pH can cause an increase in the negative soil surface charge, which easily causes an increased capacity of cationic metal adsorption (Ok et al., 2010). The precipitants of metal oxy/hydroxides could be formed due to increased hydroxyl ions (Bolan et al., 2014). In addition, previous studies also found that functional groups such as -OH and C-O loaded on the surface of oyster shell and biochar can decrease the Cd solubility by surface adsorption and precipitation (Ok et al., 2010; Tang et al., 2020). Therefore, the cation exchange, surface complexation and co-precipitation might be mechanisms for the Cd immobilization of biochar and oyster shell in acidic

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

filed.

Olsen-P, Olsen-K and Alkeline-N play an important role on soil biochemical quality and plant growth. P fractions are mainly dependent on soil pH, soil mineralogy and phosphate fertilizer application (Lee et al., 2008). Fe-P and Al-P are the predominant forms in acidic soils while calcium bound-P is the predominant form in alkaline soils (Dean, 1949). In acidic soils, the loosely bound phosphates are converted into Fe-P and Al-P fractions gradually owing to the re-precipitation process. Previous studies found that Olsen-P content reaches the maximum at neutral pH soils (Lee et al., 2008). Our results showed that the addition of oyster shell markedly increased the content of Olsen-P in soils, which might be resulted from the enhancement of soil pH (Table S2). PCA analysis (Figure 7) further demonstrated that Olsen-P was highly correlated with changes of soil pH ($R^2 > 0.99$). The contents of Olsen-K and Alkeline-N also slightly increased with the application of biochar and oyster shell, indicating an improvement of soil fertility.

Activities of soil enzyme have been widely used to reflect soil biological quality (Lin et al., 2021). In this study, activities of dehydrogenase, urease, acid phosphate, invertase, catalase and β-galactosidase were determined, and most of which were increased by the application of biochar and oyster shell (Figure 6). Especially, the increase of activities of dehydrogenase, urease, catalase and β-galactosidase was obvious under the stimulation of biochar and oyster shell. The increase of soil enzyme activities might be explained from the following aspects. The addition of oyster shell increased the soil pH, which usually caused the enhancement of dehydrogenase and urease activities (Wen et al., 2021). Abd El-Azeem et al reported that dehydrogenase activity was positively correlated with soil pH (Abd El-Azeem et al., 2013). Oyster shell could raise the urease activity, thus catalyzing the hydrolysis of urea to CO_2 and NH_3 with an optimum pH around 7.4 (Lee et al., 2008). In addition, the porous structure and rich nutrients of biochar and oyster shell can contribute to the growth of soil microorganisms, and thus might increase the soil enzyme activities (Azadi and Raiesi, 2021; Wu et al., 2019a). Moreover, the enhancement of enzyme activities in biochar and oyster shell treatments could also be related to the decrease of Cd toxicity in soils (Zhang et al., 2021). In conclusion, the cooperative application of biochar and oyster shell was the most effective pathway in the in-situ remediation of Cd contaminated farmlands.

5. Conclusions

The current study revealed the effects of oyster shell and biochar on Cd bioavailability, Cd uptake by crops, and human health risk of Cd as well as soil biochemical properties during rice-oilseed rape rotation. The application of oyster shell showed an extraordinary potential to increase soil pH for a duration, which significantly decreased the Cd bioavailability in soils. The cooperative application significantly reduced Cd contents and human health risk of brown rice and oilseed. In addition, biochar application increased OM and TOC, while the addition of oyster shell was suitable to improve Olsen-P, Olsen-K, and Alkeline-N. Furthermore, the activities of soil enzyme were markedly enhanced by the cooperative application of oyster shell and biochar. In addtion, Our results suggested that the joint application of biochar and cheap oyster shell was a low-cost pathway to effectively reduce Cd uptake of crops and improve soil biochemical properties.

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Figure captions:

Figure 1 SEM images of oyster shell (a) and biochar (b) and FTIR spectra (c) of oyster shell and biochar.

Figure 2 The effects of passivators on Cd bioavailability in soil. Dots represent the value of each sample. Bars followed with different lowercase letters (a - c) and capital letters (A, B) indicated significant ($p \leq 0.05$) difference among different treatments in rice planting and oilseed rape planting according to the LSD test. Values represent means ± standard deviation.

Figure 3 The effects of passivators on Cd contents in brown rice (a) and oilseed (b). Dots represent the value of each sample. Bars with different lowercase letters indicated significant ($p < 0.05$) difference among different treatments according to the LSD test. Values represent means ± standard deviation.

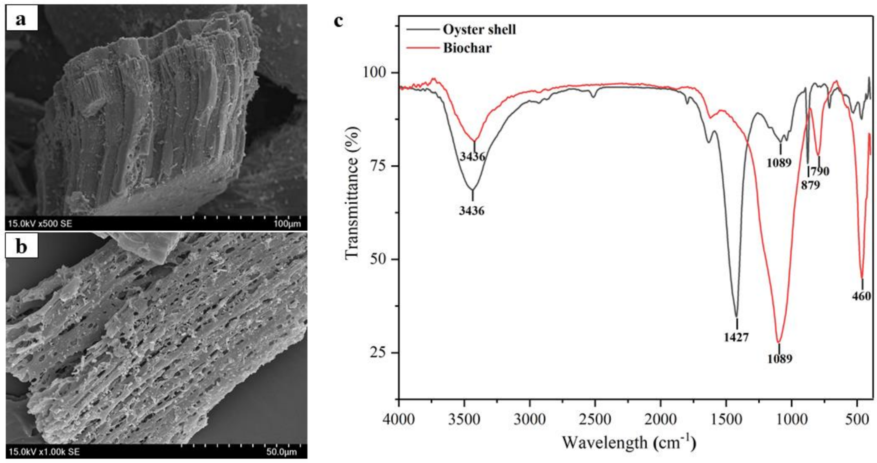
Figure 4 The effects of different passivators on the HQ of grown rice and oilseed. Mean with different lowercase letter indicated significant ($p < 0.05$) difference from each other according to the LSD test. Values represent means ± standard deviation.

Figure 5 The effects of different passivators on soil pH (a) and CEC (b). Dots represent the value of each sample. Bars followed with different lowercase letters (a - c) and capital letters (A, B) indicated significant ($p \leq 0.05$) difference among different treatments in rice planting and oilseed rape planting according to the LSD test. Values represent means ± standard deviation.

Figure 6 The effects of different passivators on the activities of soil enzyme. Dots represent the value of each sample. Bars followed with different lowercase letters (a - c) and capital letters (A-C) indicated significant ($p \leq 0.05$) difference among different treatments in rice planting and oilseed rape planting according to the LSD test. Values represent means ± standard deviation.

Figure 7 The correlation of investigated parameters in rice planting (a) and rice-oilseed rape rotation (b)

https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022



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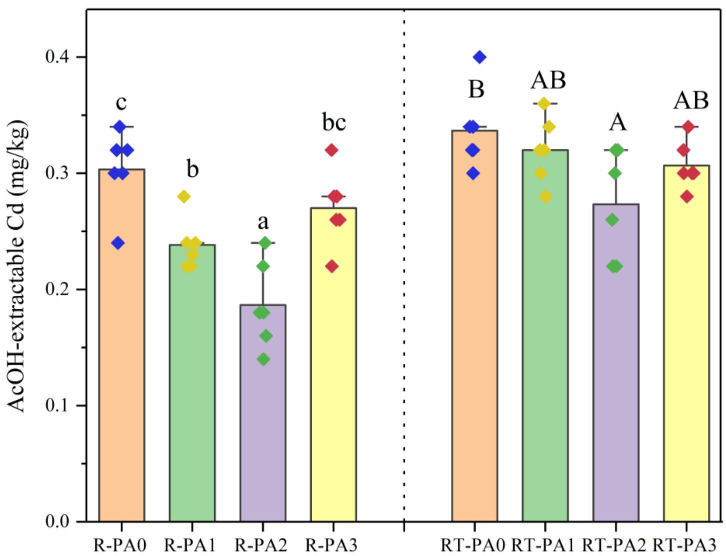

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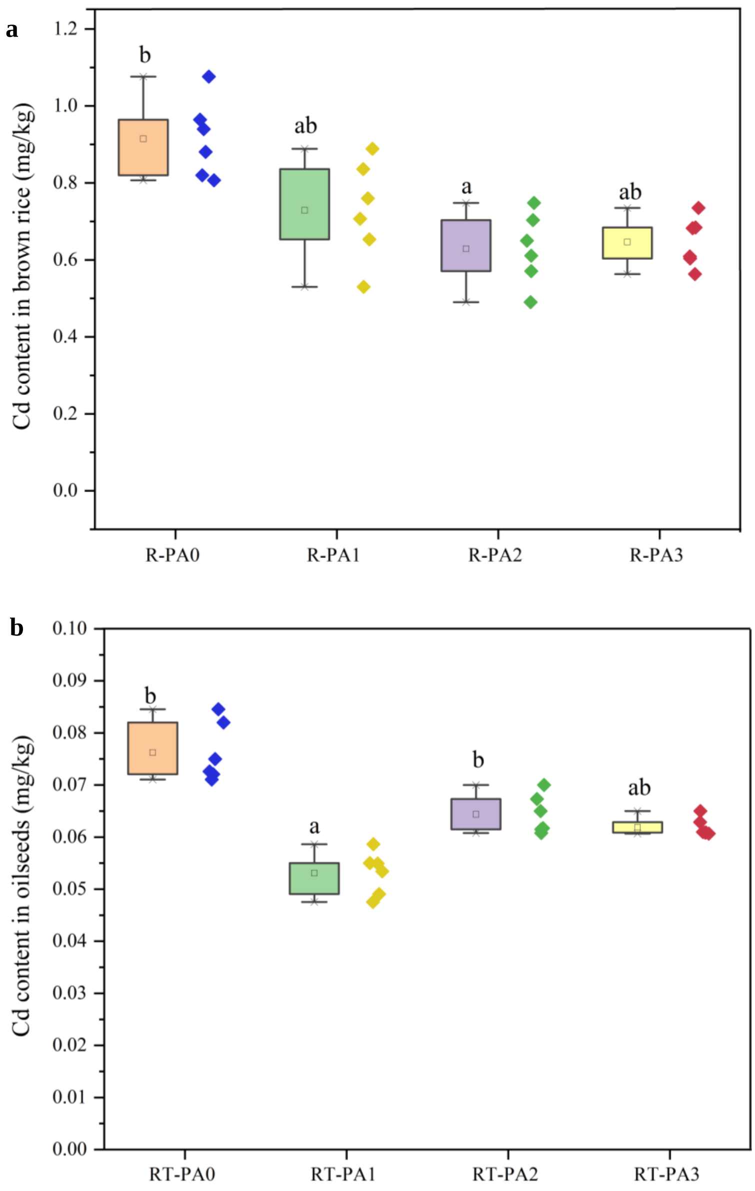

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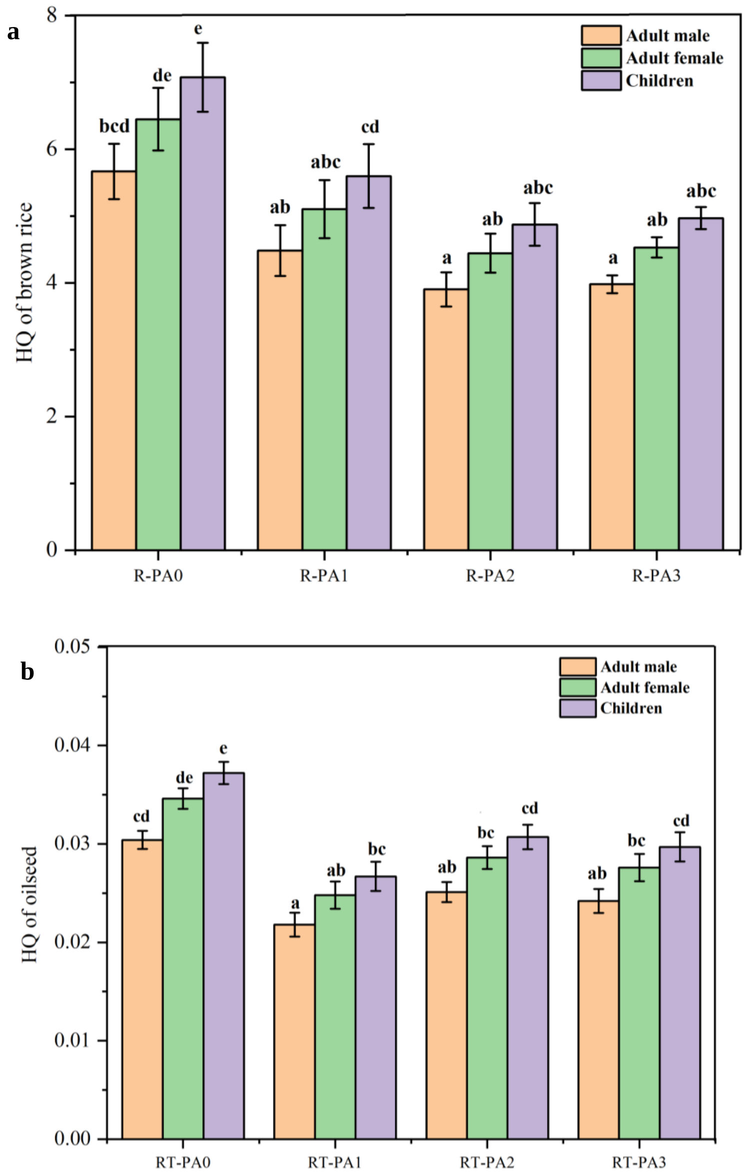

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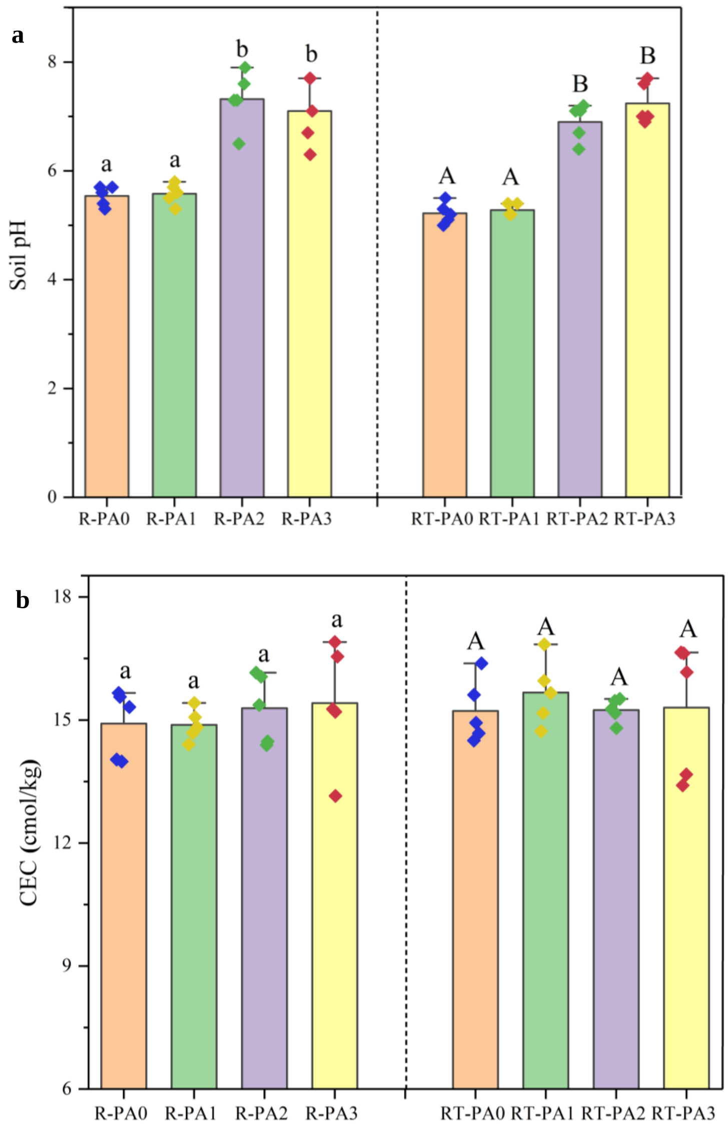

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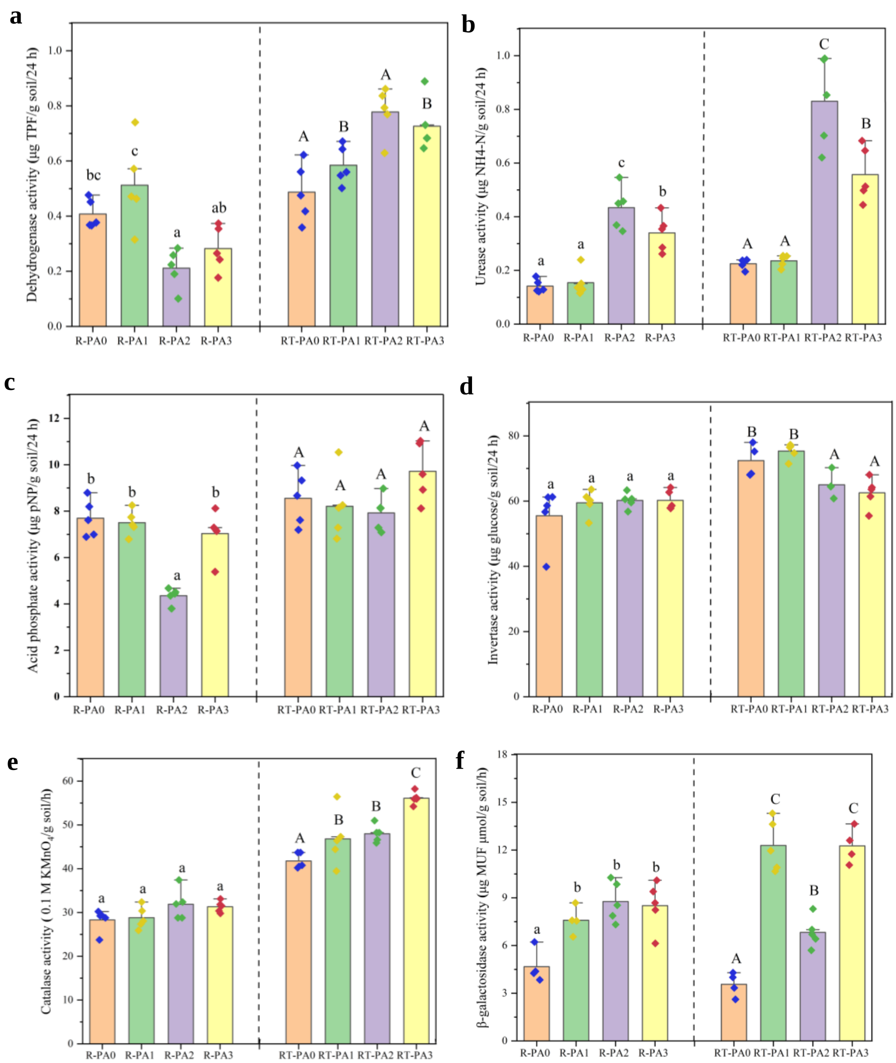

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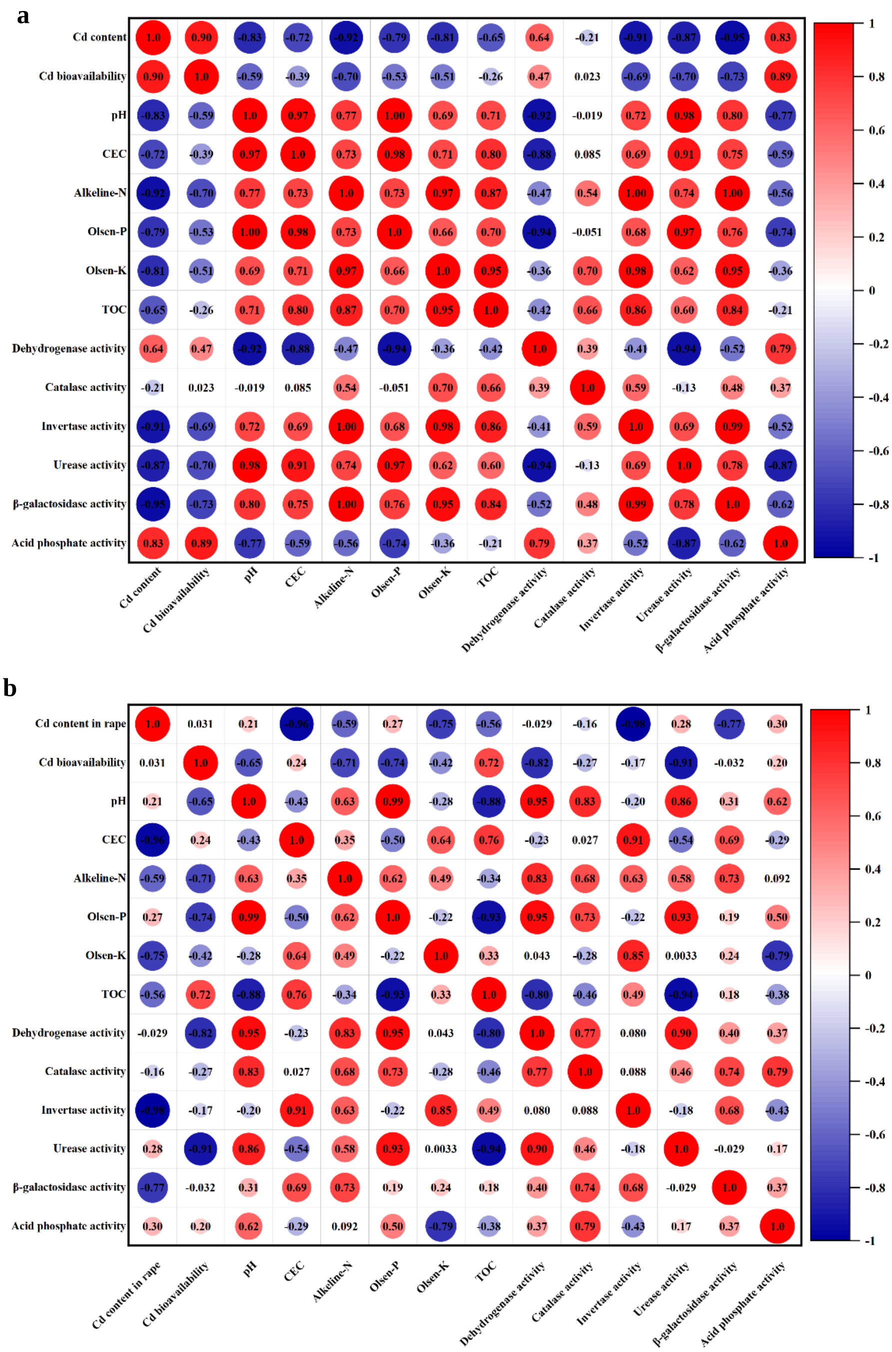

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https://doi.org/10.5194/soil-2021-145
Preprint. Discussion started: 24 January 2022

Code/Data availability

The data refering to this paper was all presented in the Supplemental file.

Author contribution

Bin Wu: Investigation, Writing Original Draft, Supervision

Jia Li: Writing - Review & Editing

Mingping Sheng: Investigation

He Peng: Investigation, Visualization

Dinghua Peng: Investigation, Data Curation

Heng Xu: Conceptualization, Resources, Funding acquisition

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.