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Effects of the Combined Application of Chinese Milk Vetch (*Astragalus sinicus* L.) and Red Mud to Remediate the Cadmium-Polluted Acidic Paddy Soil

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Abstract: In this study, we conducted field experiments to assess the effects of the combined application of Chinese milk vetch (*Astragalus sinicus* L., CMV) and red mud (RM) to remediate the cadmium-polluted acidic paddy soil. The results showed that the combined application increased the yield component index and improved the grain yields, compared with the control, RM1, RM2, and CMV treatments. However, the increased range of soil pH values in the CMV-RM1 and CMV-RM2 treatments was smaller than that of the RM1 and RM2 treatments at the different rice growth stages. The soil organic matter (SOM) contents of the RM-only treatments did not differ throughout the whole period, but were significantly different ($p < 0.05$) between CMV-RM2 and the control. Compared with the control, the combined application decreased the concentration of exchangeable Cd in the early rice soil. The combined application of CMV and RM substantially decreased the rice uptake of Cd. However, we found no significant difference ($p < 0.05$) between the CMV-RM1 and CMV-RM2 treatments. Therefore, compared with remediation with RM or CMV alone, we recommend the combined application of CMV and RM as an economical, highly effective, and replicable amendment for remediating acidic, Cd-polluted paddy soil. Considering the restorative effect and proper use of RM, we recommend CMV-RM1 treatment.

Keywords: cadmium; contamination; red mud; Chinese milk vetch; rice; paddy soil

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1. Introduction

Cd is highly toxic to humans, and a readily bioconcentrated heavy metal with a biological half-life of 15–30 years [1]. The harm to human life posed by cadmium (Cd) contamination is regarded as a major environmental issue on a global scale. At the moment, Cd contamination is a major issue [2] and has received a lot of attention in several agricultural regions of China [3]. Cd can lead to a variety of diseases by damaging the respiratory, urinary, and skeletal systems. Consequently, the remediation of Cd-contaminated soils has become a research focus for scientists worldwide [4]. Many studies have been conducted in China and globally on remediation techniques for heavy-metal-contaminated soils [5]. As a result of its ease of use, high efficacy, and cheap cost, in situ stabilization using several soil amendments is an economical and effective method for treating Cd-contaminated cultivated land [6].

Red mud (RM), a potentially harmful byproduct of the manufacturing of alumina, has the ability to cement porous aerial structures and has very fine dispersion, high specific surface area, and good adsorption capabilities [7]. RM is an excellent material for remediating the acidic Cd-polluted farmed soil, since it is inexpensive and simple to obtain. Numerous studies on the use of red mud in agricultural output have been successful [8]. Red mud application has been shown in numerous research, including both laboratory and field tests, to speed up the chemical conversion of soil Cd into Fe/Mn oxide fractions and organic matter-bound fractions. RM contains low levels of essential nutrients such as K, Mg, Cu, Zn, and Mn. Thus, RM application can significantly promote crop growth and reduce Cd accumulation, which is attributed to the high pH [9]. The addition of red mud (RM) considerably increases the conversion of heavy metals to a stable state in farmlands [10–13], showing that the application of RM effectively reduces heavy metal concentrations in lettuce. However, RM is an industrial solid waste discharged from Al extraction in the Al industry [14–17] that also contains metals. The main metals in RM are Cd, Pb, As, Cr, amongst others. Thus, the excessive application of RM poses certain environmental risks [18].

Compared with physical and chemical methods, phytoremediation is an environmentally friendly, low-cost, and sustainable soil restoration technique, and has gradually attracted the attention of researchers [18–20]. Organic regulation is one of the most effective methods of phytoremediation for heavy metal pollution in soil. Chinese milk vetch (*Astragalus sinicus* L., CMV) is commonly used as an organic regulatory plant for the remediation of heavy-metal-contaminated soils [21]. According to recent studies, the CMV can also remove heavy metals from contaminated soils [21–23]. CMV is a biennial Astragalus Linn., Leguminosae herb that has been widely planted in southern China for centuries as a type of green manure [22]. As an amendment, it alters the solubility of Cu and Cd in the soil and reduces their uptake by rice [24]. The introduction of CMV decreased Cd bioavailability through changing the soil's physical characteristics and reshaping the microbial population, ultimately lowering Cd levels in rice grains [23]. However, the use of CMV still faces some constraints, as with other phytoremediation techniques, such as with long-term treatment and the relatively low remediation efficiency.

In this study, we investigated the feasibility of using a combination of CMV and RM to remediate Cd-polluted soils by performing field experiments. We evaluated the main effects of the interaction between CMV and RM, focusing on whether the combined treatment with CMV and RM can be used as an amendment for the remediation of heavy-metal-polluted farmland.

2. Materials and Methods

2.1. Site Description, Soil, RM and CMV

The experimental field was located in Xiangtan city, Hunan province, China (27°54′50″ N, 112°58′30″ E). The test area is 1500 m away from the Xiangjiang River, which has rich aquatic resources. The use of the Xiangjiang River water for irrigation has been the leading cause of the recent Cd pollution in the area. The soil is a reddish clayey soil, formed from the laterite parent material of the quaternary period: an acidic fluvo-aquic paddy soil that developed from river alluvium.

The region has a double-cropping system, with early rice cultivated from April to July and late rice cultivated from July to October. The average annual temperature of the site is 16.7–17.4 °C, and the total annual precipitation is 1200–1500 mm. The main soil properties of the 0–200 mm layer in the study field are described in Table 1.

RM, which was produced by a combined Bayer and sintering process, was supplied by the China Great Wall Aluminum Corporation. The pH of the RM was 11.3. The concentrations of available nitrogen, available phosphorus and available potassium were 7.21, 1.18, and 4.1 mg kg^{-1}, respectively. The total concentration of Cd in the RM was 0.48 mg kg^{-1}.

Table 1. Values of main soil properties in this study.

pH	Organic Matter (OM) g kg^{-1}	Available N (AN) mg kg^{-1}	Available P (AP) mg kg^{-1}	Available K (AK) mg kg^{-1}	Cation Exchange Capacity (CEC) mmol kg^{-1}
5.4 ± 0.3	31.6 ± 1.1	375.2 ± 10.2	7.2 ± 0.8	103.5 ± 2.3	154.8 ± 5.6

For CMV, Xiangzi 4 (registration number: XPD015-2015) was the experimental variety, which was selected and bred at the Hunan Academy of Agricultural Sciences, Changsha, China.

2.2. Experimental Setup and Sampling

We applied six treatments, as follows: (1) control: without RM and without CMV; (2) RM1: application of 3000 kg hm^{-2} RM; (3) RM2: application of 4500 kg hm^{-2} RM; (4) CMV: application of CMV; (5) CMV-RM1: application of CMV and 3000 kg hm^{-2} RM; and (6) CMV-RM2: application of CMV and 4500 kg hm^{-2} RM. For the trial, we applied a randomized complete block group design, with three replicates in each treatment group. We planted all treatments with early rice only. We conducted the field study between April and July 2019. For our experiment, we divided one experimental field into 18 subplots (4 × 5 m for each pot), which we separated by a ridge that was 400 mm wide.

The ground was turned and raked, the fresh CMV in the CMV treatment was cut 10 days before early rice transplanting, and 22,500 kg hm^{-2} was incorporated into the soil in April 2019, 15 days in advance of rice transplanting. We used the same application rates of conventional fertilization (N, P, and K of 150.00, 32.75, and K 74.68 kg hm^{-2}, respectively), in the subplots as a base fertilizer at 18 days before rice transplanting. We transplanted seedlings (Xiangzaoxian 45, Hunan Rice Research Institute, a conventional rice variety) on 23 April 2019 and harvested them on 29 July 2019 after 96 days of growth. In brief, from the flowering to the tillering stage, we intermittently applied irrigation to the subplots under continuously tilling until day 54. The subplots were then drained for 7 days (days 55 to 61), and were then kept under dry-wet alternations until day 81. Finally, the subplots were exposed for 82–96 days. Other field management practices during the growing season in this trial were consistent with those applied in local fields.

We collected soil samples before planting and after harvesting the rice. The fresh soil sample in each plot for a mixed sample was collected at a depth of 0–20 cm. Soil samples were air-dried in the shade and pulverized with an agate mortar. Subsequently, the sample was passed through 2 mm and 0.149 mm sieves, to determine the basic physical and chemical properties and the mass ratio of different forms of Cd in the soil. The basic physical and chemical properties of red mud were determined by conventional methods. Soil and red mud were digested with HNO_3-$HClO_4$-HF. Wet digestion with HNO_3-$HClO_4$ was used for rice digestion. Poplar leaves (GBW0764) as an internal standard were used for quality control. After the first soil sample collection, we sowed the rice. During the various rice growth stages, including at early tillering, active tillering, booting, milk production, and maturity, we analyzed the soil pH and Cd fraction of the soil samples. After the samples had been completely digested, we drove the acid to nearly dry, added a small amount of dilute nitric acid solution to dissolve it, and transferred a fixed volume to be tested. The method of Tessier [25] was used to determine the content of Cd in the soil. After harvesting the rice, we measured the index of the yield components, and collected rice grains to analyze the yield and Cd content. We collected and removed all the rice straw from the plots, to determine the yield.

2.3. Analytical Methods

We determined the Cd content in rice as follows: we separated brown rice and rice hulls using a dehusker (JLGJ4.5, Taizhou Food, Taizhou, China). We digested the brown rice, 0.5 g (dry weight) using HNO_3 and $HClO_4$ (4:1, v/v). After cooling, solutions were diluted to 25 mL using 2% HNO_3. and then filtered. We measured the Cd concentrations in the digested solutions using a flame atomic absorption spectrometer (AA6300, Shimadzu, Tokyo, Japan), and calculated the Cd concentrations in the brown rice. We quantified the SOM content using the $K_2Cr_2O_7$ oxidation method. We analyzed the total Cd in the soil, based on previously reported methods [12,14]. We used a TZS-RHW-4HG device (Zhejiang Topu Yunnong Technology Co., Ltd., Hangzhou, China) to measure soil pH in the field. All chemicals and reagents were of analytical grade and provided by Changsha Yufusheng Chemical Glass Instrument Co., Ltd. (Changsha, China). We determined the fraction of Cd in the soil following a previously reported method [25]. We used Statistical Product and Service Solutions (SPSS, version 21.0, International Business Machines Corporation, Armonk, NY, USA) to perform a three-way analysis of univariate statistics and correlation analysis.

One-way analysis of variance (ANOVA) was used for multiple comparisons of LSD ($p < 0.05$, $p < 0.01$). The graphs were generated using the Origin 2021. Pearson's correlation coefficients (R values) with the respective probabilities (P) were used to determine the significance between different parameters ($p < 0.05$, $p < 0.01$).

3. Results and Discussion

3.1. Yield Component Characters of Rice

Among the treatments, CMV-RM2 plants were the tallest, had the most effective spikes, greatest number of grains on the spike, and fruit set, and the highest 1000-grain weight (Table 2). Plant height was not significantly different between the–CMV-RM2 treatment and the other treatments ($p > 0.05$), except for the control group. The effective panicles and grain number per panicle were significantly different between CMV-RM2 and the other treatments ($p < 0.05$), except for the CMV-RM1 treatment. Seed setting significantly differed between the CMV-RM2 treatment and the other treatments ($p > 0.05$), except for the CMV and CMV-RM1 treatment. The 1000-grain weight did not significantly differ between the CMV-RM2 treatment and the other treatments ($p > 0.05$), except for the control and RM1 treatments. Plant height, effective panicles, grain number per panicle, 1000-grain weight, and seed setting rate, were not significantly different between the CMV-RM1 and CMV-RM2 treatments ($p > 0.05$). The combined CMV and RM application increased plant height, effective panicles, grain number per panicle, 1000-grain weight, and seed setting rate. These indices demonstrate the positive effect of the combined application of CMV and RM on increasing rice yield.

Table 2. Plant height, effective panicles, grain number per panicle, seed setting rate, and 1000-grain weight increases (%) of CMV-RM2 compared with the other treatments.

		Compared with				
		Control	**RM1**	**RM2**	**CMV**	**CMV-RM1**
CMV-RM2 increased %	plant height	5.85	3.41	2.78	1.31	0.95
	effective panicles	24.30	19.82	12.71	10.83	3.91
	grain number per panicle	15.36	11.99	6.98	5.80	3.51
	seed setting rate	6.94	4.15	3.29	2.33	1.27
	1000-grain weight	4.55	3.69	3.27	2.85	2.43

Note: Control, without RM and without CMV; RM1, application of 3000 kg hm^{-2} RM; RM2,: application of 4500 kg hm^{-2} RM; CMV, application of CMV; CMV-RM1, application of CMV and 3000 kg hm^{-2} RM; CMV-RM2, application of CMV and 4500 kg hm^{-2} RM.

3.2. Rice and Straw Yield

Rice and straw yields fluctuated for the different treatments (Figure 1). The rice yield positively correlated with the combined application of CMV and RM. The grain and straw yields did not significantly differ between the CMV-RM1 and CMV-RM2 treatments. The grain yields of the CMV-RM1 and CMV-RM2 treatments were significantly ($p < 0.05$) higher than those of the control and the RM1, RM2, and CMV treatments by 14.65%, 10.07%, 8.73%, and 4.84%, and by 13.52%, 8.98%, 7.65%, and 3.80%, respectively; however, we found no significant difference when comparing the CMV-RM1 and CMV-RM2 treatments with the CMV treatment. The straw yield in the CMV-RM1 and CMV-RM2 treatments was significantly higher ($p < 0.05$) than in the control and the RM1, RM2, and CMV treatments, by 6.95%, 4.47%, 2.63%, and 0.40%, and 6.59%, 4.12%, 2.29%, and 0.06%, respectively. However, we found no significant difference between the CMV-RM1 and CMV-RM2 treatments and the CMV treatment.

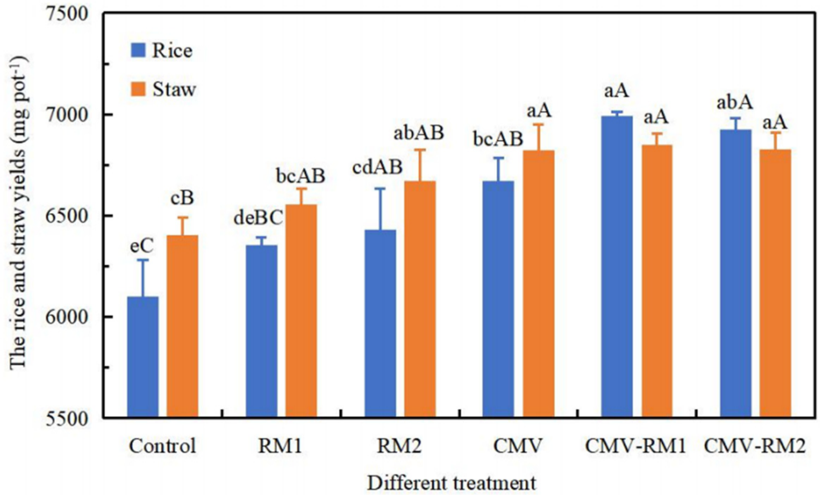

Figure 1. Rice and straw yields under different treatments (LSD Test, different letters above the bars represent statistically significant different, $p < 0.05$, $p < 0.01$). Note: Control, without RM and without CMV; RM1, application of 3000 kg hm^{-2} RM; RM2,: application of 4500 kg hm^{-2} RM; CMV, application of CMV; CMV-RM1, application of CMV and 3000 kg hm^{-2} RM; CMV-RM2, application of CMV and 4500 kg hm^{-2} RM.

Therefore, we found that the combined application of CMV and RM had a remarkable effect on early rice and straw yields. Accordingly, we recommend the CMV-RM1 treatment in terms of rice and straw yields.

3.3. Change in Soil pH

The soil pH values of the different treatments and stages in the early rice seasons fluctuated (Figure 2). Compared with the control and CMV treatments, the pH value of the soil increased as the RM application rate increased at the different rice growth stages. The pH in the RM treatment decreased as the growth period progressed. However, the soil pH of the CMV-RM1 and CMV-RM2 treatments was lower than that of the RM1 and RM2 treatments at the different rice growth stages. The soil pH of the CMV treatment was generally the lowest among all the treatments at the different rice growth stages. At the different growth stages, the pH value of the soil treated with RM was higher than in the control group, mainly because the RM was alkaline, and an acid-base neutralization reaction occurred when the RM was applied to acidic soil, which increased the soil pH. Over time, the soil pH value gradually decreased during the tillering and booting stages, and tended to stabilize during the milk and mature stages. We provide the following explanations as a possible reason for this decrease: we incorporated the CMV into the paddy soil before we transplanted the rice and prepared the field, and CMV had a phased effect on soil pH. The pH of the CMV decreased in the early to middle stages. Decreasing soil pH after plant material addition has also been reported previously. In the later stages, the pH of the CMV increased in the treatments, compared with the control group [26,27].

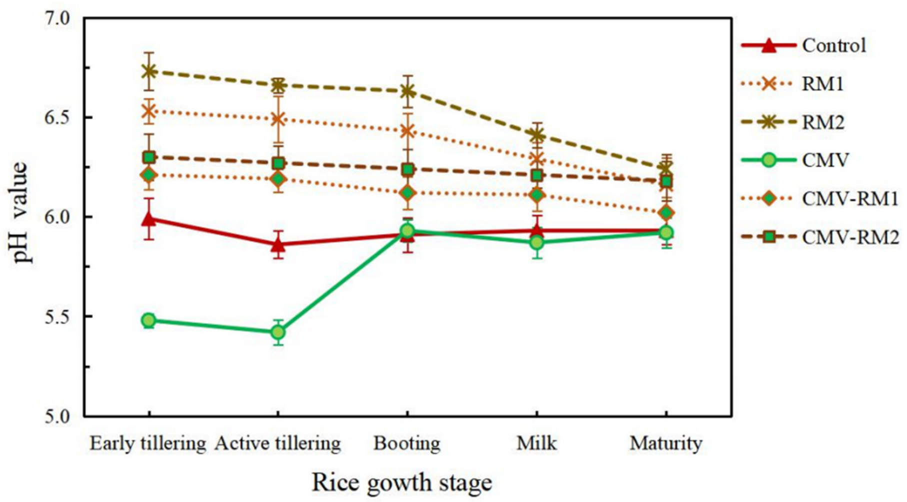

Figure 2. Soil pH value of different treatments and different stages (data are represented as average ± SD, *n* = 3). Note: control, without RM and without CMV; RM1, application of 3000 kg hm^{-2} RM; RM2; application of 4500 kg hm^{-2} RM; CMV, application of CMV; CMV-RM1, application of CMV and 3000 kg hm^{-2} RM; CMV-RM2, application of CMV and 4500 kg hm^{-2} RM.

The soil has a self-buffering capacity. The pH of the soil tended to return to its initial level. In contrast, rice roots produce secretions during growth, containing large amounts of H^+ and organic acids (such as lactic, oxalic, malic, and formic acids). These secretions increase the concentration of H^+ in the soil, acidify the rhizosphere soil, and decrease soil pH. In the tillering and booting stages, rice grows vigorously, the production of root exudates is relatively high, and the soil pH is also relatively strongly regulated. Except for the control and CMV treatments, the pH values of all soils in the RM treatments were higher than those of the background soil at different rice growth stages, which indicated that the application of RM increased the soil pH value in a short time and that this increase was sustainable. Considering the effects on soil pH, when applied to remediate heavy-metal-contaminated soils, RM may provide beneficial long-term results.

3.4. Soil Organic Matter in Paddy Soil

The SOM content is a critical factor affecting crop productivity because of its essential role in maintaining the physical, chemical, and biological [28–30] properties of the soil [31–34]. In this study, the SOM content decreased throughout the growth period (Figure 3). The SOM content of the different treatments changed minimally over the entire growth period, with a maximum change of only 3.4 g kg^{-1}. The SOM content did not differ significantly between the RM-only and control groups ($p > 0.05$). The SOM content differed significantly between the CMV treatment and the control treatment, but not significantly amongst the CMV, CMV-RM1, and CMV-RM2 treatments in the early tillering stage. Except for the CMV-RM2 treatment, the SOM content did not differ significantly amongst the other treatments during the active tillering stage ($p > 0.05$). Except for the CMV-RM1 and CMV-RM2 treatments, the SOM content did not differ significantly amongst the different treatments in the booting, milk, or maturity stages ($p > 0.05$). Therefore, treatment with RM alone produced no differences in the SOM over the entire period. We observed a significant difference between the CMV-RM2 treatment and control groups ($p < 0.05$), potentially related to the composition of the RM. Moreover, as a type of green manure, the use of CMV in soil is a beneficial practice for agricultural production. Sustainable cultivation systems can be enhanced by improving soil nutrients [31,33,34], stimulating microbial activity [35,36], and reducing weed density and abundance [37].

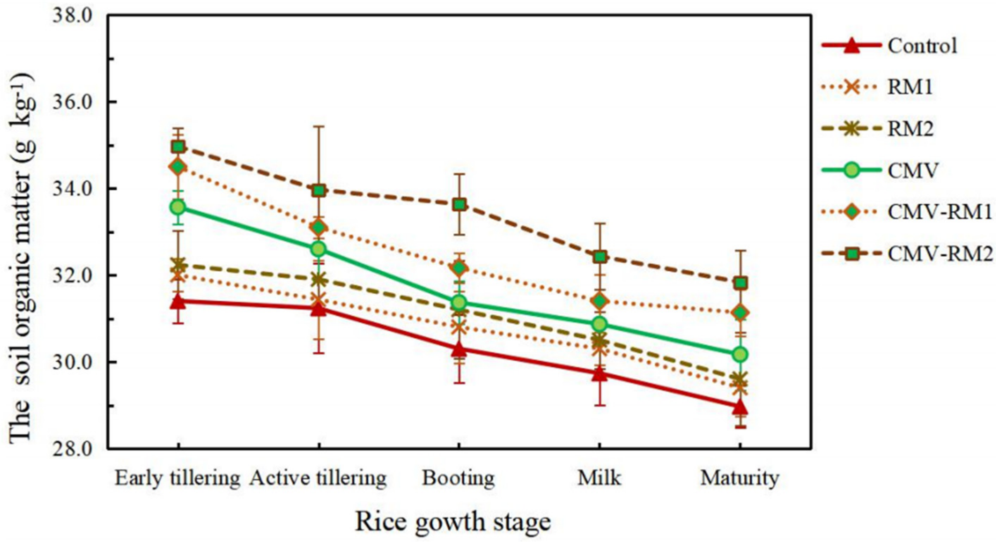

Figure 3. The SOM of different treatments and different stages (standard error). Note: control, without RM and without CMV; RM1, application of 3000 kg hm^{-2} RM; RM2; application of 4500 kg hm^{-2} RM; CMV, application of CMV; CMV-RM1, application of CMV and 3000 kg hm^{-2} RM; CMV-RM2, application of CMV and 4500 kg hm^{-2} RM.

3.5. Cd Fractions

We used the continuous extraction method to analyze the effectiveness of the combined CVM-RM application in remediating the soil. The five forms of Cd in soil are exchangeable (EXC), carbonate (CA), manganese oxide (Fe-Mn), organic matter bound (OM), and residual (RES) [38]. Normally, metals in the aqueous phase are directly uptaken by field crops. In addition, field crops prefer to uptake EXC when both EXC and CA are present. The other three forms are unavailable components and difficult for field crops to take up. The structure and distribution of the Cd forms in the soil are shown in Figure 4.

The exchangeable forms accounted for less than 30% of the Cd in the soil during the early rice cultivation stage. Compared with that in the control, the concentration of EXC-Cd decreased in the early tillering stage by 11.46% (RM1), 17.01% (RM2), 4.31% (CMV-RM1), and 9.12% (CMV-RM2). Except for CMV, EXC-Cd decreased in the active tillering stage by 14.84% (RM1), 20.04% (RM2), 4.93% (CMV-RM1), and 8.69% (CMV-RM2). Except for CMV, EXC-Cd decreased in the booting stage by 4.81% (RM1), 20.01% (RM2), 9.03% (CMV-RM1), and 13.44% (CMV-RM2). Except for CMV, EXC-Cd decreased in the milk stage by 6.84% (RM1), 11.21% (RM2), 4.28% (CMV), 16.21% (CMV-RM1), and 22.44% (CMV-RM2), and in the maturity stage by 13.67% (RM1), 21.53% (RM2), 18.39% (CMV), 24.82% (CMV-RM1), and 30.85% (CMV-RM2). Exchangeable Cd is the most toxic form. With the combined application of CMV and RM, EXC-Cd transformed into CA-Cd, Fe-Mn-Cd, and Res-Cd.

When applied to rice soils as green manure, CMV not only enhances fertility but also improves the structure of soil macroaggregates and stimulates microbes. Many organic acids and polysaccharides are produced and released by enhanced microbial activity in fertilized soil [31,38–40]. In addition, the micropores in soil macroaggregates are transformed into macropores by organic acids and polysaccharides [41]. The accumulation of Zn and Cd in wheat straw or cereals does not increase following the application of organic manure or compost, part of which can be attributed to the dilution of these two elements in the larger biomass [42,43]. The results of this experiment are consistent with those reported by Jarrell and Beverly [44]. Treatment with CMV decreased the amount of available Cd.

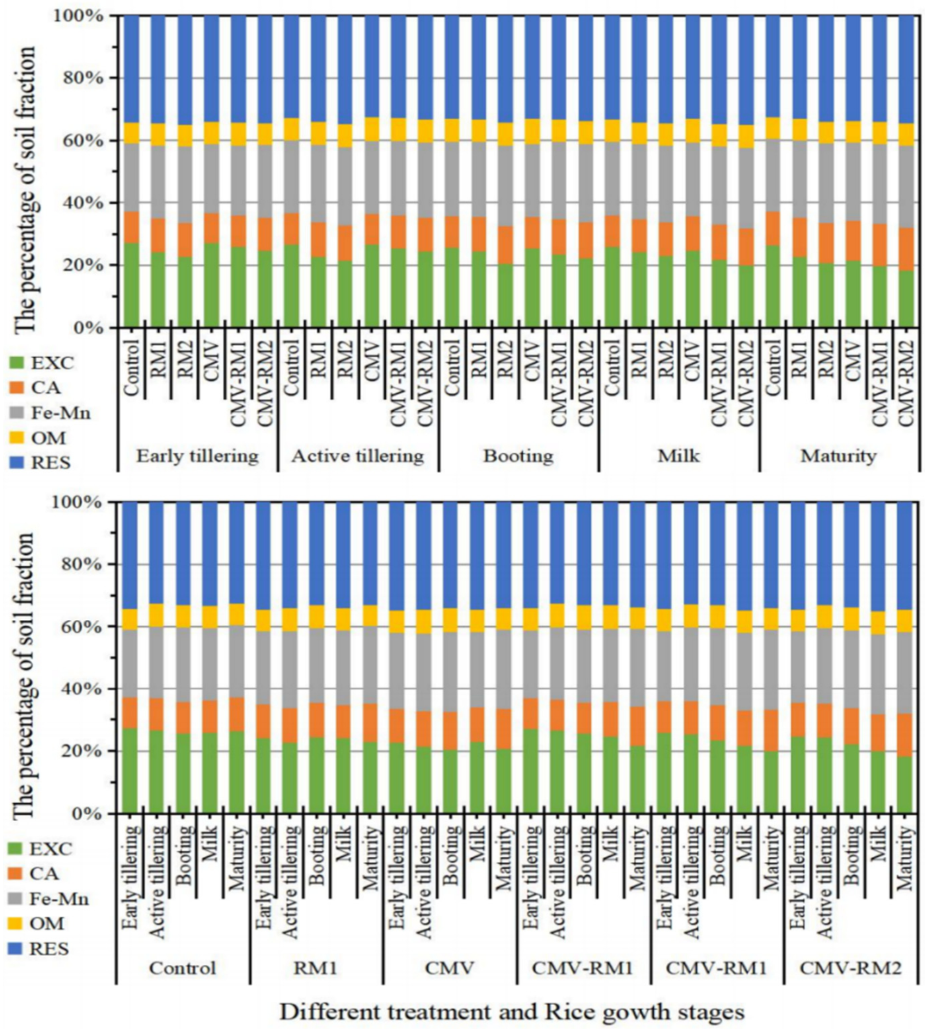

Figure 4. Geochemical fractions of soil Cd at early tillering, active tillering, booting, milk, maturity and different stages of rice growth: EXC, CA, Fe-Mn, OM and Res are exchangeable, carbonate bound, iron-manganese oxide bound, organic and residual fraction. Note: control, without RM and without CMV; RM1, application of 3000 kg hm^{-2} RM; RM2; application of 4500 kg hm^{-2} RM; CMV, application of CMV; CMV-RM1, application of CMV and 3000 kg hm^{-2} RM; CMV-RM2, application of CMV and 4500 kg hm^{-2} RM.

The Fe and Al oxides in RM contain surface-active sites that are associated with heavy metals. The general combination fixes heavy metals, thus forming iron aluminum oxide combined with heavy metals, which are difficult for field crops to take up and use [45]. Fe and Al oxides introduce new adsorption surfaces to the soil, which can stabilize heavy metals through physisorption, chemisorption, or physicochemical adsorption. An increase in pH is the most direct reason for decreases in Cd activity in the soil. Of the five Cd species, four (all except OM-Cd) were affected by the change in soil pH in this study. As RM was alkaline, once we applied the RM to the soil the increase in soil pH caused a large amount of soluble Cd to enter the insoluble state.

Therefore, compared with the CMV-only and RM-only methods, the combined application/repair of CMV and RM prevented both the pH decrease produced by CMV and decomposition, increased the pH with the addition of RM, and improved the structure of the soil aggregates.

3.6. Cd Concentration of Brown Rice

We also observed a reduction in the total Cd concentration in rice in this study (Figure 5). Compared with the control, the Cd concentrations in the RM1, RM2, CVM, CVM-RM1, and CVM-RM2 treatments decreased by 13.79%, 41.38%, 20.69%, 44.83%, and 55.18%, respectively. Thus, the Cd reduction with the combined application in the CMV-RM1 and CMV-RM2 treatments was greater than in the other treatments. However, we observed no significant difference. This result suggests that the combined application of CVM and RM as a soil remediation method substantially reduced the uptake of Cd by rice.

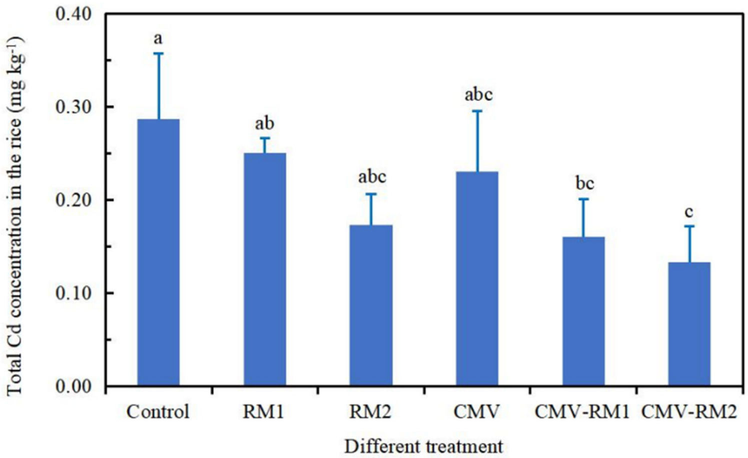

Figure 5. Total Cd concentration of different treatments in rice (LSD Test), defferent letters above the bars represent statistically significant different, $p < 0.05$. Note: control, without RM and without CMV; RM1, application of 3000 kg hm^{-2} RM; RM2: application of 4500 kg hm^{-2} RM; CMV, application of CMV; CMV-RM1, application of CMV and 3000 kg hm^{-2} RM; CMV-RM2, application of CMV and 4500 kg hm^{-2} RM.

4. Conclusions

The combined application of Chinese milk vetch (*Astragalus sinicus* L.) and red mud decreased Cd bioavailability and the Cd content of rice. The application of a certain amount of red mud in acid tide mud fields with moderate and mild Cd pollution can significantly improve rice yield, while significantly increasing soil pH value and SOM; reducing the available Cd mass ratio in soil reduced the Cd mass ratio in brown rice. The use of joint repair technology overcomes the shortcomings of using red mud or Chinese milk vetch to a certain extent, improves the repair efficiency, and reduces the repair cost and risk from only red mud or Chinese milk vetch. The results of the field trials showed that the combined application of CMV and RM is an economical, efficient, and replicable amendment for the remediation of Cd-contaminated fields. We found no significant differences between the CMV-RM1 and CMV-RM2 treatments. Given the restorative effect, and with an appropriate use of RM, we recommend the CMV-RM1 treatment. In future studies, researchers should widen the selection of CMV species from a set of joint remediation models, and apply them to the remediation and protection of contaminated farmland soil after testing.

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