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RESEARCH ARTICLE

Effects of rape straw and red mud on extractability and bioavailability of cadmium in a calcareous soil

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Abstract Screening of cost-effective soil amendments is important to develop "*in situ*" remediation techniques for cadmium (Cd) contaminated soils. In this study, different soil amendments, including red mud, a by-product of the alumina industry, and acid-treated, nano-treated by nano-particle milling, nano and acid-treated red muds, zeolite, corn straw, and rape straw, were evaluated to immobilize Cd in two added levels (2 and 5 mg $Cd \cdot kg^{-1}$ soil) in a calcareous soil by single and sequential extractions and by cucumber (*Cucumis sativus* L.) pot experiments. Results indicated that cruciferous rape straw significantly decreased the concentrations of water soluble, extractable Cd in soils, and Cd in cucumber plants, and it was more effective than gramineous corn straw. Also, red mud generally decreased the extractability and bioavailability of Cd added to calcareous soils more effectively than zeolite. Furthermore, the efficiency of red mud could be increased by the treatment of nano-particle milling due to the increase in specific surface area of red mud. It is potential to use rape straw and red mud as soil amendments to develop a cost-effective and efficient "*in situ*" remediation technology for Cd mildly contaminated calcareous soils.

Keywords red mud, rape straw, cadmium, immobilization, calcareous soil

1 Introduction

Cadmium (Cd) accumulation in crops is a growing concern globally because of increased fertilizer- and biosolids-borne Cd in agricultural soils [1–3]. Therefore, soil contamination with Cd poses long-term health risks to humans through food chains and accidental soil ingestion, so that remediation of Cd-contaminated soils is becoming a practical need for both food safety and human health protection.

Recently, in situ immobilization of Cd through the use of different soil amendments can be very effective at reducing Cd availability and phytotoxicity [4–6]. Among these amendments, red mud (RM), an alkaline and by-product of aluminum (Al) manufacturing, can be very effective in increasing Cd sorption and decreasing soluble Cd concentrations in Cd-contaminated and acidic soils under pot trials and field studies, and lead to a reduction in Cd uptake by plants [7–10]. Lombi et al. indicated that the increase in Cd-contaminated and acidic soil pH caused by the application of RM was one of the main mechanisms of immobilization of Cd. Also red mud is expected to show high surface reactivity to Cd contaminants apart from its alkaline pH [7,11]. Earlier observations had shown that the bioavailability of Cd in acidic soils is higher than that in calcareous soils [12,13], so that the effects of red mud on Cd bioavailability were studied mostly in acidic soils. However, so far little information is available on the effect of red mud on Cd bioavailability and extractability in calcareous soils. Additionally, grain size of red mud is also expected to affect the affinity and reaction mechanisms of the immobilizer for Cd contaminants [14]. Luo et al. [15] reported that both acidified and ball milling nanoparticle red muds could significantly enhance Cd sorption using batch sorption experiments. Therefore, the use of acidified and ball milling nanoparticle red muds to reduce further Cd availability in contaminated soils, especially in calcareous soils, should be deeply investigated.

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It has been documented that thiol (-SH) can reduce Cd bioavailabilty by mechanisms of chelation [16]. The cruciferous rape (*Brassica napus* L.) exhibited higher concentration of thiol (-SH) in straw than other crops [17]. However, the effect of the incorporation of rape straw into Cd-contaminated calcareous soil has never been investigated.

Therefore, the objectives of this study were 1) to investigate the effect of acidified and ball milling nanoparticle red muds on Cd bioavailability in mildly Cd-contaminated calcareous soils, 2) to investigate the influence of rape straw on the extractability of Cd in mildly Cd-contaminated calcareous soils, and 3) to investigate the effect of acidified, ball milling nanoparticle red muds and rape straw on the uptake of cucumber. To compare the effect of Cd immobilizing of red mud and rape straw, zeolite and corn straw as amendments were also used in the study.

2 Materials and methods

2.1 Effect of amendments and incubation time on Cd availability

2.1.1 Soil collection and treatment

Soil samples for the experiment were collected (0–20 cm depth) at a Long-term Monitoring Base for Fluvo-aquic Soil Fertility and Fertilizer Efficiency in Beijing (116°15′23″E, 40°13′12″N). The soil properties were as follows: soil pH (5:1 distilled water: soil) 8.11; organic matter (K_2CrO_7-H_2SO_4) 15.9 mg·kg^{-1}; total N (semiquantitative titration) 1.40 g·kg^{-1}; total P (ammonium molybdate spectrophotometry) 1.17 g·kg^{-1}; total K (HNO_3-$HClO_4$ digestion) 23.7 g·kg^{-1}. The concentration Cd (aqua-regia digestion) in the soil was initially 0.03 mg ·kg^{-1} soil as a control. The Cd-contaminated soils were prepared by spiking the soils with Cd (2 and 5 mg·kg^{-1} as $Cd(NO_3)_2 \cdot 4H_2O$), then mixing thoroughly and equilibrating for 2 months. During the equilibration the soil moisture was maintained at 80% of maximum water holding capacity by weighing. After 2 months, the soil samples were air-dried and passed through a 2-mm sieve.

2.1.2 Soil amendments and treatments

Soil amendments used in this study, natural or synthetic, organic or inorganic, were tested: 1) red mud (RM) (pH = 11.1, 5:1 distilled water: RM) from Zibo City, Shandong Province, China. The mineralogical composition of RM sample (XRD analysis) is a mixture of SiO_2 (20%), Fe_2O_3 (28%), Al_2O_3 (21%), CaO (6.2%), MgO (1.3%), TiO_2 (3.3%), K_2O (0.26%) and Na_2O (11%). X-ray diffraction (XRD) analysis was performed using a PANAnalytical X'Pert Pro X-ray (PANalytical BV, Almelo, the Netherlands) diffractometer equipped with a Cu source (Cu Kα). The specific surface area, determined by the BET/N_2-adsorption method (Sorptomatic CarloErba), was 12.2 m^2·g^{-1} for RM. Zinc and Cd concentrations in RM were 94 mg·kg^{-1} and < 0.01 mg Cd·kg^{-1}, respectively. The RM sample was dried overnight at 105°C, finely ground and sieved to < 1 mm, 2) acid-treated RM (RM_a). Aliquots of the red mud was acid-treated by washing twice with HCl (0.1 mol·L^{-1} for 4 h at the ratio 1:25 (w/v) of red mud/solution), then thoroughly washed with deionized water and dried overnight at 105°C, 3) nano-treated RM (RM_n). Another of aliquot was treated by ball milling (nano-particle milling) in order to examine the effect of grain size on Cd sorption by the red mud. The specific surface area was 17.2 m^2·g^{-1} for RM_n, 4) nano and acid-treated RM (RM_{na}). Also another aliquot of the RM_a was treated by ball milling (nano-particle milling) in order to examine the effect of grain size on Cd sorption by RM_{na}, 5) a natural clinoptilolite zeolite (Ø1-2.5 mm), derived from a layer found in Gongyi, China, 6) rape straw (RS). The rape straw sample was obtained from rape (*Allium cepa* L. cv. Zheshuang No. 6) grown at long-term experiment station of the Chinese Academy of Agricultural Sciences, Jiaxing city, Zhejiang Province, China (30°15′N, 120°20′E), which was oven-dried at 70°C to constant weight and then finely ground in a Retsch-grinder (Type: 1 mm, made in Germany) using a 1 mm mesh screen to ensure uniform plant tissue disruption and distribution in soil during the field experiment, 7) corn straw (CS). The corn straw sample was obtained from corn (*Zea mays* L. cv. Jingdan No. 28) grown at long-term experiment station of the Chinese Academy of Agricultural Sciences, Changping, Beijing, China (40°13′N 116°15′E). The sample was also oven-dried at 70°C to constant weight and then finely ground using a 1 mm mesh.

To determine the effects of different amendments on the bioavailability of Cd (2 and 5 mg·kg^{-1} Cd), RM, RM_n, RM_a, RM_{na} and ZT were added to 50 g soil at the rate of 20 g soil·kg^{-1}, and RS and CS were added to 50 g soil at the rates of 4 g soil·kg^{-1}. Each treated soil was incubated with 80% water holding capacity at 25°C±2°C for 1 month and 4 months, respectively. Samples were air-dried and passed through a 2.0 mm plastic sieve.

2.1.3 NH_4OAc extraction of Cd in amended soil

Two grams of amended soil were shaken at 25°C for 1 h with 10 mL of 1 mol·L^{-1} NH_4OAc in triplication. The suspensions were then centrifuged (20 min at 8000 r ·min^{-1}) and filtered through a 0.45 μm filter. Cadmium concentration in supernatant was determined by using inductively coupled plasma mass spectrometry (ICP-MS, Elan 5000, Perkin Elmer, USA). A reference soil material (GSS-6, China National Central for Standard Materials, Beijing, China) was used for quality. The Cd recovery rates were 90%±10%.

2.2 Pot experiment

2.2.1 Experimental treatments

The soil for plant incubation was same to the soil used as described in 2.1.1. The zeolite, RM, RM_n, RM_a, RM_{na}, RS and CS as amendments for pot trial were prepared in 2.1.2.

Two Cd exposures in soils (2 and 5 $mg \cdot kg^{-1}$) were used in the trial, and 700 g of air-dried soil was used in each pot for the experiment. Application rates of the amendments to Cd-contaminated soils (2 and 5 $mg \cdot kg^{-1}$ Cd) included: 0.5% RM (W/W), 0.5% zeolite (W/W), 0.5% RM_a (W/W), 0.5% RM_n (W/W), 0.5% RM_{na} (W/W), 0.1% CS (W/W), 0.1% RS (W/W). Amendments were added and thoroughly mixed by hand. All treatments were performed in four replicates. Four control pots per soil were also set up without amendment. Each treated soil was incubated with 80% water holding capacity and stored in a climate chamber, where they were left to settle a minimum of 6 weeks at room temperature before transplanting the cucumber plants.

2.2.2 Plant and soil analysis

Seed of cucumber (*Cucumis sativus* L. cv. Zhongnong No.8) was provided by the Institute of Vegetables and Flowers, Chinese Academy of Agricultural Sciences, Beijing, China. The pot trial was conducted in an experimental greenhouse at the Chinese Academy of Agricultural Sciences, Beijing, China. Before seeding, all cucumber seeds were disinfected in a 30% H_2O_2 (W/V) solution for 15 min, followed by thorough washing with deionized water, and then germinated in moist perlites. After one week, uniform seedlings were selected and transplanted to PVC pots (12 cm diameter and 10 cm height). Two seedlings were transplanted to each pot. During the plant growth period, the soil water was maintained 70% of maximum water holding capacity by weighing method. To ensure normal growth and development of cucumber seedlings, potassium sulfate (K_2SO_4) solution (in deionized water) was applied after transplantation of the seedlings to give 28.7 $mg \cdot kg^{-1}$, and nitrogen was supplied as a solution of urea [$CO(NH_2)_2$] (in deionized water) in four equal splits to give a total of 46.6 mg $N \cdot kg^{-1}$ soil during the plant growth period. The pot experiment was carried out in a greenhouse at 24°C during the days with natural light, and 16°C during the nights. All pots were arranged in a randomized completed block design during the plant-growing season. After 45 days, the aboveground portion of cucumber seedlings was harvested by cutting at 2 cm above the soil surface. The plant samples were washed thoroughly with tap water following with deionized water, and then oven-dried at 70°C to constant weight. There were 4 replications for each treatment in the experiments.

Oven-dried shoot samples were ground using a Retsch-grinder (Type: 2 mm, made in Germany), and digested with HNO_3 [18]. Plant samples were weighed (0.5 g) into 200 mL block digestion tubes, concentrated nitric acid (10 mL) added and allowed to stand overnight. They were then heated for 3 h for 60°C, followed by 6 h at 110°C. After cooling, the digests were passed through a pre-washed filter (Whatman No. 540), the digestion tubes were rinsed 4 times, passing through the filter and the filtrates made up to 50 mL volume using ultrapure water. Cadmium concentration was determined using inductively coupled plasma mass spectrometry (ICP-MS, Elan 5000, Perkin Elmer, USA). Blank and bush leaf material (BGW-07603) (China Standard Materials Research Center, Beijing, China) were used for quality control. The Cd recovery rates were all within 90%±10%. After harvest, the soil pH was measured using distilled water (1:5 soil/water suspension) with an ORION combined electrode.

2.2.3 Sequential extraction of Cd in amended soils

Sequential extraction was performed on air-dried soil samples from each pot (2 g in 40-mL polyethylene centrifuge tubes) according to the scheme of Ma and Uren [17], which is briefly listed in Table 1. The procedure separates Cd into eight operationally defined fractions: water soluble (WS), exchangeable (EXC), EDTA-extractable (EDTA), easily reducible Mn (ERMn), carbonate (CA), organic matter (OM), Fe and Al oxides (FeO_x), and residual forms (RES). After each extraction, the solution was separated from the solid by centrifugation at 8000 $r \cdot min^{-1}$ for 20 min. A reference soil sample (GSS-6, as mentioned above) was used to compare metal recovery based on sequential extraction with certified values. The Cd recovery rates were 90%±10%.

2.3 Statistical analysis

Statistical analysis including the analysis of variance was concluded using SPSS statistical package and significant differences were reported at $P < 0.05$ according to the Fisher's least significant test (LSD). Data are presented as arithmetic means with standard error (S.E.).

3 Results

3.1 Extractability of Cd after the application of various amendments

Compared with the unamended soils, the concentration of Cd extracted by 1 $mol \cdot L^{-1}$ NH_4OAc (NH_4Ac-Cd) in different amended soils were significantly ($P < 0.01$)

Table 1 Procedure for the sequential extraction of Cd from amended soils

form/association	Abbr.	Step	extraction method
water soluble	WS	1	distilled water, 1:5, shaking 30 min
exchangeable	EXC	2	1 $mol \cdot L^{-1}$ $MgCl_2$, pH 7.0, shaking 1 h
EDTA-extractable	EDTA	3	1% NaCaHEDTA in 1 $mol \cdot L^{-1}$ NH_4OAc, pH 8.3, 1:10, shaking 2 h
easily reducible Mn	ERMn	4	0.2% quinol in 1 $mol \cdot L^{-1}$ NH_4OAc, pH 7.0, 1:10, shaking 1 h
carbonate	CA	5	0.5 $mol \cdot L^{-1}$ NaOAc-0.5 $mol \cdot L^{-1}$ HOAc, pH 4.74, 1:10, soaking 15 hand shaking 3 h
organic matter	OM	6	5 mL 30% H_2O_2, pH 4.74, digested twice at 85°C and extracted by 0.5 $mol \cdot L^{-1}$ NaOAc-0.5 $mol \cdot L^{-1}$ HOAc for 1 h
Fe and Al oxides	FeO_x	7	0.175 $mol \cdot L^{-1}$ $(NH_4)_2C_2O_4$ – 0.100 $mol \cdot L^{-1}$ $H_2C_2O_4$, pH 3.25, 1:10, soaking 15 h and shaking 2 h in daylight
residual forms	RES	8	total minus sum of the extractable

decreased (Fig. 1), and the reduction (% of control) was significantly different ($P < 0.01$) among the amendment treatments, ranging from 12% (CS) to 56% (RS) under the exposure of 2 $mg \cdot kg^{-1}$ Cd, and from 14% (CS) to 56% (RS) under the exposure of 5 $mg \cdot kg^{-1}$ Cd (Fig. 1) when the Cd-contaminated soils with different amendments were incubated for 1 month. After incubation for 4 months, the Cd extractability (NH_4Ac-Cd) tended to decrease further (Fig. 1), which showed that the inorganic amendments, such as red much and zeolite, especially organic amendments, such as corn and rape straw, were effective for at least for 4 months. It is found that the effectiveness of the organic amendments did not decrease in period of at least 4 months.

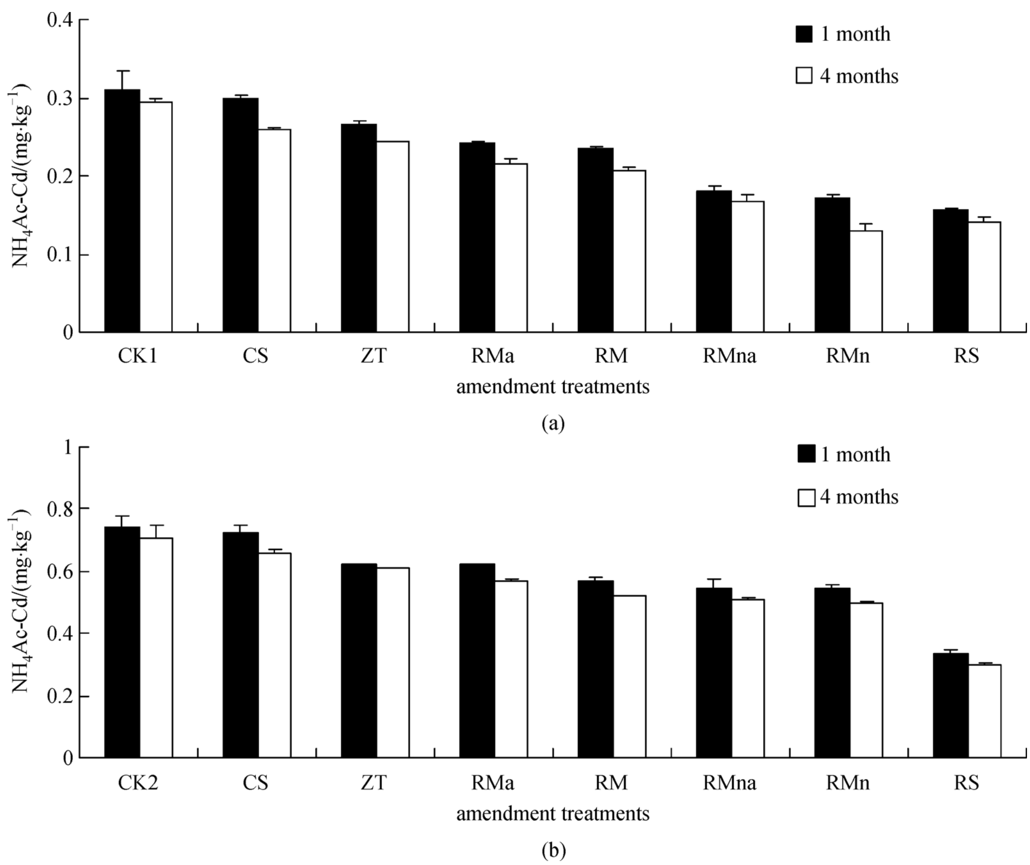

Fig. 1 Concentrations of NH_4Ac extractable Cd ($mg \cdot kg^{-1}$) under the 2 (a) and 5 (b) $mg \cdot kg^{-1}$ Cd exposures as affected by different amendments added to soils after 1 month and 4 months. CK1 and CK2 indicated 2 and 5 $mg \cdot kg^{-1}$ Cd exposures, respectively. CS, corn straw; ZT, zeolite; RM, red mud; RM_a, acid-treated RM; RM_{na}, nano and acid-treated RM; RM_n, nano-treated RM; RS, rape straw

3.2 Phytoavailability of cadmium

The concentrations and uptake of Cd in the shoot of cucumber under 2 and 5 $mg \cdot kg^{-1}$ Cd exposures with amendment treatments are presented in Table 2. Compared with the cucumber grown in unamended soil, the concentrations of Cd in the shoot of the cucumber were decreased under amendment treatments, and the reduction (% of control) was significantly different ($P < 0.05$) among the different amendment treatments. The reduction of Cd concentration in cucumber ranged from 11% to 34% under 2 $mg \cdot kg^{-1}$ Cd exposure, and from 20% to 45% under 5 $mg \cdot kg^{-1}$ Cd exposure, with lowest for ZT treatments and highest for RS treatments.

3.3 Fractionation of Cd after the application of various amendments

As shown in Fig. 2, the proportion of Cd in the control (total Cd 2 and 5 $mg \cdot kg^{-1}$) soils were averagely 0.37% in WS-Cd, 21.4% in Exch-Cd, 29.5% in EDTA-Cd, 6.03% in ERMn-Cd, 5.70% in CA-Cd, 6.50% in OM-Cd, 15.4% in FeO_x-Cd, and 19.8% in Res-Cd (Fig. 2). The distribution of different fractions of Cd is similar to the cited Cd-contaminated soils reported by others [19,20].

After addition of different amendments, the concentrations of WS-Cd and Exch-Cd were significantly lower ($P < 0.05$) in the amended soil than that in the unamended soil (Table 3). Under the two Cd exposures, addition of amendments to soil with cucumbers remarkably decreased from 22% to 57% of WS-Cd, and from 21% to 39% of EXC-Cd, with RS and RM_n being the more effective treatments. The addition of the RM, RM_n, RM_a and RM_{na} remarkably increased the FeO_x-Cd about 10% and Res-Cd about 14% in the amended soils. As for ZT treatment, EDTA-Cd was increased about 17%. And for RS and CS treatments, the EDTA-Cd and OM-Cd were increased about 28% and 12%, respectively.

4 Discussion

Various amendments, organic or inorganic, such as RM, zeolite, HA, PR, rice straw and other materials have been widely used to immobilize Cd in soils to decrease its phytotoxicity to and accumulation by plants [7,9,14,20–23]. The results in the study indicated that the amendments used, including organic or inorganic, decreased NH_4Ac-Cd concentration under the two Cd exposures, although not always significantly. The mechanisms involved in the reduction of NH_4Ac-Cd might be various and depend on the amendments characteristics, which play an essential role in Cd availability. For inorganic amendments used, one of the main key process of Cd immobilization is the specific sorption of Cd by amendments that made of some compounds, such as Fe and Al oxides in RM and hydrous aluminosilicate minerals in ZT, which resulting in low solubility of Cd in soil [7,14,21]. In addition, our results

Table 2 Shoot yield and concentrations and uptake of Cd in cucumber plants in response to different amendments under the 2 and 5 $mg \cdot kg^{-1}$ Cd exposures

Cd addition /($mg \cdot kg^{-1}$ soil)	amendments	shoot Cd concentration/($mg \cdot kg^{-1}$)	shoot Cd uptake/($mg \cdot plant^{-1}$)	shoot yield/($g \cdot plant^{-1}$)
2	CK	0.193±0.003 a	0.220±0.013 a	1.14±0.12 a
	RM	0.143±0.009 cd	0.168±0.021 c	1.18±0.07 a
	RM_n	0.128±0.008 e	0.150±0.017 d	1.17±0.16 a
	RM_a	0.138±0.007 d	0.157±0.023 d	1.14±0.08 a
	RM_{na}	0.133±0.006 de	0.150±0.011 d	1.13±0.13 a
	ZT	0.171±0.010 b	0.195±0.015 b	1.14±0.13 a
	CS	0.154±0.005 c	0.183±0.026 bc	1.19±0.13 a
	RS	0.127±0.004 e	0.154±0.018 d	1.21±0.11 a
5	CK	0.388±0.009 a	0.419±0.034 a	1.08±0.09 a
	RM	0.266±0.004 c	0.295±0.025 d	1.11±0.17a
	RM_n	0.212±0.014 e	0.244±0.029 f	1.15±0.09 a
	RM_a	0.242±0.005 d	0.286±0.014 de	1.18±0.13 a
	RM_{na}	0.237±0.009 d	0.268±0.019 e	1.13±0.09 a
	ZT	0.309±0.010 b	0.362±0.031 b	1.17±0.20 a
	CS	0.278±0.008 bc	0.317±0.029 c	1.14±0.08 a
	RS	0.214±0.006 e	0.248±0.024 f	1.16±0.07 a

Note: Mean values±standard error ($n = 4$) followed by the same letter within amendment treatments under the 2 and 5 $mg \cdot kg^{-1}$ Cd exposures do not differ significantly at 5% level ($P < 0.05$) according to the Fisher's least significant test (LSD) revealed that RM_n was the most effective inorganic amendment used, with RM_n-soil being the lowest NH_4-Ac Cd concentration after one month and four months incubation, which suggested that RM_n with a larger specific surface area ($17.20\,m^2 \cdot g^{-1}$) could immobilize more Cd in the soil. For organic amendments, added organic matter, such as plant materials, can immobilize Cd by forming solid organo-metal complexes [23,24]. The present results indicated that the crop straw used could remarkably decreased NH_4Ac-Cd concentration under the two Cd exposures, with RS being the most effective organic amendment. However, an increase in dissolved organic matter (DOM) might contribute to the enhancement of metal concentration in soil solution [25]. Cui et al. [23] have revealed that the soluble organics from added rice straw are able to raise Cu carrying capacity of soil solution while lower Cd carrying capacity of soil solution. Our results also showed that the CS and RS added to Cd-contaminated soil could immobilize Cd, maybe by forming solid organo-metal complexes, even though high DOM content in the crop straw.

Previous studies showed that addition of amendments to Cd-contaminated soils could effectively decrease Cd uptake and accumulation in plants [7–9,14]. The present study also clearly showed that there was a remarkable decrease in concentrations and content of Cd in cucumber seedlings treated with amendments compared with the control under 2 and 5 $mg \cdot kg^{-1}$ Cd exposures (Table 2). The decrease in Cd concentrations in cucumber by amendment treatments was not mainly caused by a “dilution effect” because the shoot yield of the cucumber under both Cd exposures was not significantly increased by amendment treatments (Table 2). Thus, the total Cd amount in cucumber under the two Cd exposures was remarkably decreased by amendment treatments (Table 2). The results from the present study also showed that the decreased concentration of Cd by the cucumber grown in Cd-contaminated soils amended was related to the decrease of the bioavailable fractions of Cd. The decrease of bioavailable fraction of Cd was amendment- dependent. As shown in the study (Fig. 2), the WS-Cd and Exch-Cd in the amended soils averagely decreased 39% and 30%, respectively, while for RM_n, RM_a and RM_{na} treatments, the FeO_x-Cd increased about 10% and the Res-Cd increased about 14% and for RS and CS treatments, the EDTA-Cd and OM-Cd averagely increased at 28% and 12%, respectively, suggesting that the addition of RM could lead to Cd transformation from WS-Cd and Exch-Cd to Res-Cd, while the addition of CS and RS could lead to Cd transformation from WS-Cd and Exch-Cd to EDTA-Cd and OM-Cd. Among the fractions, WS-Cd and Exch-Cd were more pronouncedly affected by the treatment of amendments than the other fractions, which suggested that WS-Cd and Exch-Cd were transformed to the non-extractable forms in the amended soil.

In the present study, among the amendments the RS and RM_n was the more effective, with the greatest reductions in WS-Cd and Exch-Cd under both Cd exposures. The reason might be ascribed mainly to different mechanisms of bindings of Cd between these amendments. Lombi et al. [14] indicated that specific sorption of Cd by Fe and Al oxides in red mud was more stable than simple pH moderated sorption. Recently, there was increasing evidence that RM_a and RM_n, especially RM_n, significantly enhanced Cd sorption and facilitated transformation of Cd into less extractable fractions [15]. And the addition of RS and CS, especially RS, also induced an obvious decrease of WS-Cd and EXC-Cd (Table 3), which suggested that RS had higher efficiency to lower Cd availability in soil compared to CS. The reason might be ascribed to their different major component. Major component of corn straw is (semi) cellulose while rape straw is volatile sulfur compounds (thiol) [17]. Wang [26] indicated that garlic straw and rape straw, which both had higher volatile sulfur compounds (thiol), showed higher Cd binding capacity compared to corn straw on the basis of their characteristics of Cd adsorption isotherms. Thus, in the present study, CS and RS with different characteristics, especially RS with higher thiol, associated with the soils could effectively limit Cd bioavailability.

Many studies showed that typical amounts of RM addition to Cd contaminated soil were 1%–5% (w/w), which was dependent on soil pH, soil types and soil total Cd [7–10,27–29]. In the present study, the application of RMs (0.5%, W/W) to the mildly Cd-contaminated and calcareous soil had little effect on the final soil pH (Table 3), which suggested that specific sorption of Cd by Fe and Al oxides in RM was the main mechanism [14]. Similar to RM, the application of RS (0.1%, w/w) and CS (0.1%, w/w) to the calcareous soil also had little effect on soil pH (Table 3), which suggested that the tendency of Cd to form stable complexes with organic ligands was the main mechanism [23,24].

To our knowledge this is the first study showing, through a sequential extraction procedure, that nanoparticle red mud and rape straw addition are able to reduce the bioavailability Cd in a mildly Cd-contaminated and calcareous soil and increase residual fraction and organic fraction, respectively. Therefore, nanoparticle red mud and rape straw might act as an efficient, economic, and practical method for decreasing Cd uptake and accumulation in edible parts of crops grown in Cd-contaminated and calcareous soils.

5 Conclusions

This study clearly demonstrated that the treatment of amendments, especially RS and RM_n, significantly ($P < 0.05$) decreased Cd solubility in the mildly Cd-

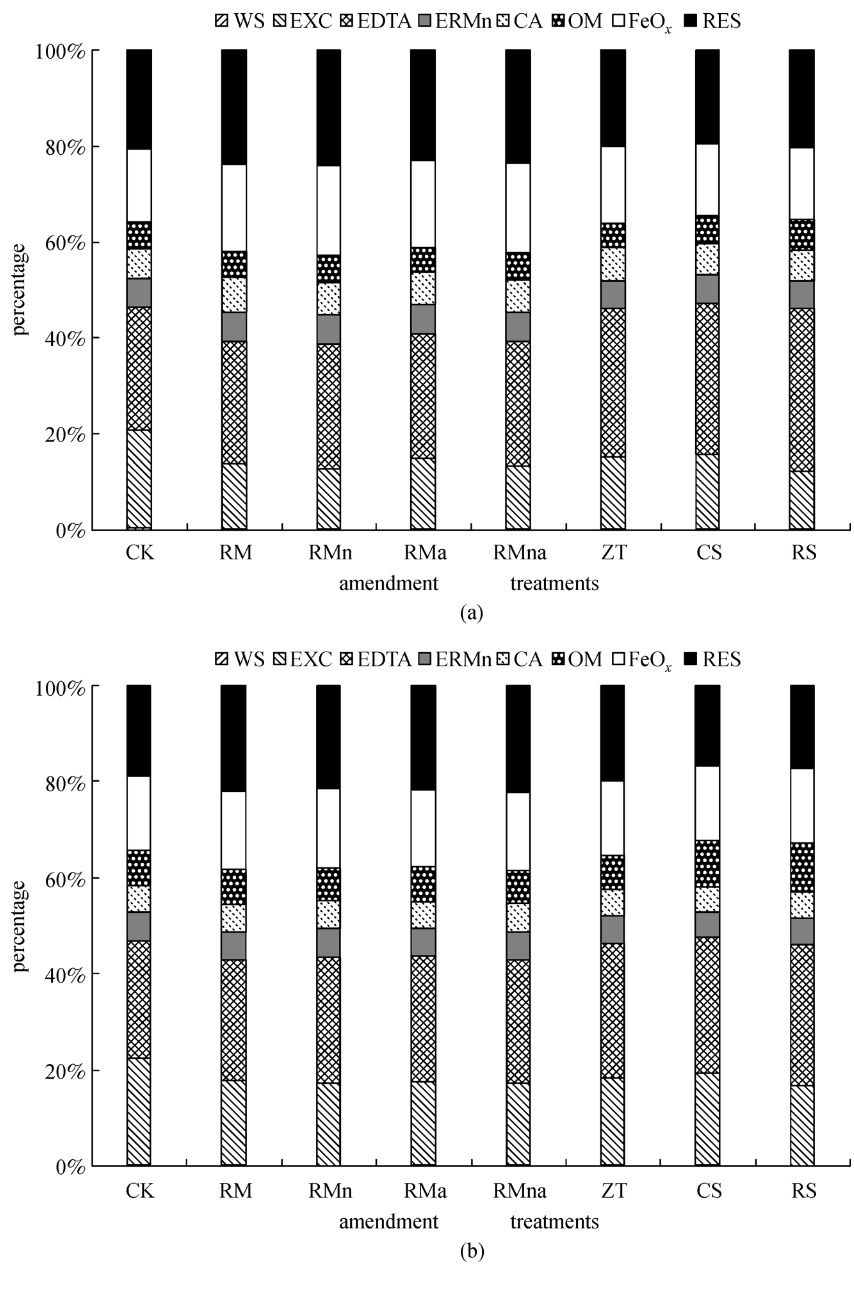

Fig. 2 Speciation of Cd in 2 (a) and 5 (b) $mg \cdot kg^{-1}$ Cd soils after treatment with various amendments. WS, water soluble; EXC, exchangeable; EDTA, EDTA-extractable; ERMn, easily reducible Mn; CA, carbonate; OM, organic matter; FeO$_x$, Fe and Al oxides; RES, residual forms

Table 3 Concentrations of Cd ($mg \cdot kg^{-1}$) in various fractions as affected by different amendments under the 2 and 5 $mg \cdot kg^{-1}$ Cd exposures

Cd addition/($mg \cdot kg^{-1}$ soil)	amendments	pH	WS	EXC	EDTA	ERMn	CA	OM	FeO_x	RES
2	CK	8.11	0.009±0.002a	0.41±0.011a	0.51±0.020b	0.121±0.004a	0.120±0.006b	0.112±0.002b	0.306±0.005b	0.412±0.026b
	RM	8.14	0.006±0.001bc	0.27±0.016bc	0.51±0.016b	0.125±0.010a	0.140±0.004a	0.111±0.003b	0.362±0.016a	0.476±0.008a
	RM_n	8.16	0.005±0.001c	0.25±0.006c	0.52±0.014b	0.122±0.003a	0.137±0.005a	0.110±0.007b	0.374±0.012a	0.482±0.022a
	RM_a	8.09	0.007±0.002b	0.29±0.009b	0.52±0.015b	0.122±0.007a	0.139±0.006a	0.102±0.004b	0.363±0.015a	0.457±0.018a
	RM_{na}	8.1	0.006±0.001bc	0.26±0.011bc	0.52±0.015b	0.122±0.017a	0.137±0.012a	0.110±0.005b	0.374±0.006a	0.471±0.021a
	ZT	8.02	0.007±0.002b	0.30±0.015b	0.62±0.028a	0.113±0.009a	0.136±0.004a	0.106±0.003b	0.315±0.006b	0.403±0.023b
	CS	8.08	0.007±0.002b	0.31±0.023b	0.63±0.022a	0.119±0.015a	0.124±0.012b	0.122±0.011a	0.300±0.026b	0.388±0.021b
	RS	8.07	0.005±0.001c	0.24±0.026c	0.68±0.037a	0.114±0.016a	0.126±0.017b	0.129±0.009a	0.301±0.024b	0.405±0.032b
5	CK	8.1	0.014±0.003a	1.11±0.033a	1.22±0.042b	0.30±0.013a	0.27±0.011ab	0.37±0.016b	0.77±0.026a	0.95±0.025ab
	RM	8.12	0.007±0.002c	0.88±0.026cd	1.26±0.028b	0.29±0.013a	0.29±0.015a	0.36±0.018b	0.81±0.011a	1.10±0.035a
	RM_n	8.14	0.006±0.001c	0.85±0.017cd	1.30±0.037b	0.30±0.017a	0.30±0.026a	0.34±0.020b	0.82±0.014a	1.08±0.034a
	RM_a	8.08	0.009±0.002b	0.87±0.019cd	1.30±0.036b	0.29±0.018a	0.28±0.013ab	0.36±0.011b	0.80±0.029a	1.09±0.059a
	RM_{na}	8.06	0.008±0.002bc	0.86±0.032cd	1.29±0.027b	0.29±0.016a	0.30±0.013a	0.34±0.012b	0.81±0.016a	1.10±0.033a
	ZT	7.99	0.009±0.002b	0.91±0.021c	1.40±0.035a	0.29±0.021a	0.27±0.012ab	0.35±0.016b	0.78±0.023a	0.99±0.036ab
	CS	8.03	0.009±0.002b	0.96±0.012bc	1.41±0.042a	0.26±0.018b	0.26±0.011b	0.49±0.027a	0.77±0.021a	0.84±0.025b
	RS	8.05	0.006±0.001c	0.84±0.022d	1.46±0.036a	0.28±0.023ab	0.27±0.016ab	0.51±0.025a	0.78±0.034a	0.86±0.028b

Note: Mean values±standard error (n = 4) followed by the same letter within amendment treatments under the 2 and 5 $mg \cdot kg^{-1}$ Cd exposures do not differ significantly at 5% level ($P < 0.05$) according to the Fisher's least significant test (LSD) contaminated soil. This was attributed to the amendments were efficient in transforming Cd fractions from to easily extractable fraction to the non-extractable fraction in the amended soils. The reduction in Cd solubility of soil resulted in remarkable decrements in the Cd concentration in the shoot parts of cucumber by 11%–45%. The present results suggested that the application of RS and RM_n could significantly decrease the bioavailability and increase the geochemical stability of soil Cd in mildly Cd-contaminated calcareous soils.

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