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Immobilization of Cd in a paddy soil using moisture management and amendment

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HIGHLIGHTS

- Moisture management and amendment had impacts on Fe in root of plant.
- Gradual increase of Fe^{2+} in soil was reason for low Cd bioavailability.
- Competition for adsorption sites in root between Fe^{2+} and Cd^{2+} caused low plant Cd.

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ABSTRACT

To offer basis for remediation of Cd-polluted paddy soil under reasonable water condition, pot experiment was conducted to study the effects of moisture management and amendment on the immobilization of Cd in paddy soil. Application of sepiolite in combination with phosphate fertilizer reduced exchangeable Cd by 18.2%, 13.7% and 12.5%, brown rice Cd by 52.3%, 46.0% and 46.8%, under continuous flooding, conventional irrigation and wetting irrigation, respectively, compared to the control groups. Under no amendments, the content of Fe(II) in root coating in the continuous flooding treatment was 2.3 and 3.6 times of that in the conventional and wetting irrigation treatments, but Cd content in root coating in the continuous flooding treatment was only 82.6% and 73.8% of that in the conventional and wetting irrigation treatments. Amendments application increased Fe(II) in root coating by 40.1%, 70.2% and 78.0%, but reduced the Cd content in root coating by 35.3%, 42.4% and 38.6% under continuous flooding, conventional irrigation and wetting irrigation, respectively. The lower availability of Cd in soil and the competition for adsorption sites in root coating of rice plant between Cd^{2+} and Fe^{2+} etc. reduced form bivalent ions in paddy soil resulted in lower Cd concentrations in brown rice in amended soil treatments.

1. Introduction

The widespread contamination of soils with heavy metals was a environmental and toxicological concern due to an increase in population and urbanization. Cadmium (Cd) had been recognized as one of the most toxic environmental contaminants with a distinct role in various human diseases for its persistence in soils and accumulative effects in human beings (Gupta and Gupta, 1998). Rice plant was an important food crop in China, paddy rice yield nearly accounted for 40% of gross grain yield (Tang, 2007). An investigation conducted by Ministry of Agriculture of China in 2003 indicated that brown rice Cd amounted to 0.4–1.0 mg kg^{-1} in some regions, Cd-polluted brown rice was above 10%.

Several measurements were under development for remediation of heavy metals polluted soils. Common remediation technologies, like excavation, thermal treatment and electro-reclamation, were not suitable for practical application because of high cost, low efficiency and environmentally destructive (Khan et al., 2004). Although phytoremediation has received considerable attention in recent years, one of major problems was low metal removal rates (McGrath et al., 2002; Rattan et al., 2002). Consequently, chemical stabilization process for contaminated soils has been gaining prominence because of its cost-effectiveness and rapid implementation as well as its appearance as a alternative technique for a wide range of polluted sites (Garau et al., 2007; Cao et al., 2008). Common amendments for chemical immobilization of heavy metals in soils included natural and synthetic additives, such as clay minerals (Kumpiene et al., 2008; Xu et al., 2010), phosphorus-containing materials (Boisson et al., 1999; Cao et al., 2002; Mirelzky and Fernandez-Cirelli, 2008), organic matter residues (Baldwin and Shelton, 1999; Bolan and Duraisamy, 2003; Crecchio et al., 2004), hydrous oxides of Fe/Mn (Mench et al., 1994; Chen et al., 2000), they have been tested for their capability to immobilize heavy metals in soils.

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The moisture management had important influences on soil Cd availability and Cd assimilation by rice plant, the Cd concentration in brown rice was much lower in continuous flooding than in conventional and wetting irrigation treatments (Zhang et al., 2006; Hu et al., 2010). Rice plant root had strong oxygen carrying capacity, high concentration of Fe^{2+} in the paddy soil were oxidized and deposited to form Fe oxides membrane in root coating (Chen et al., 1980). The Fe in root coating governed soil Cd assimilation by rice plant and had important impacts on Cd concentration in rice plant (Yi et al., 1994; Ye et al., 2003; Liu et al., 2008).

Although much had been done on chemical immobilization of heavy metals in polluted paddy soils, studies of immobilization of heavy metals in paddy soils under different water conditions were rarely reported. This study demonstrated effectiveness of sepiolite combined with phosphate fertilizer to reduce Cd concentrations in brown rice under continuous flooding, conventional irrigation and wetting irrigation, and provide basis for change of Cd concentrations in brown rice in the different soil treatments by means of data of soil Cd chemical fraction and Fe content in root coating of rice plant.

2. Materials and methods

2.1. Soil and amendments characterization

2.1.1. Soil characteristics

The soil samples used were collected from rice fields in the soil layer of 0–20 cm in Hunan Province, China. The selected physical and chemical properties were listed in Table 1, the determination of soil characteristics followed the standard measures recommended by Analysis Methods of Soil Agricultural Chemistry (An official reference book for soil basic properties analysis) issued in 2000 (Lu, 2000).

2.1.2. Amendments properties

Natural sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$, pH 9.1, Cd 0.18 mg kg^{-1}) sample was purchased from a Sepiolite Developing Company Limited, and phosphate fertilizer (pH 8.5, Cd 0.15 mg kg^{-1}) was obtained from a horticultural merchant.

2.2. Pot experiment

Moisture management involved continuous flooding (Topsoil kept 3–4 cm water layer during the whole growth period of rice plant), conventional irrigation (Topsoil kept wet condition during the late tillering state and grain filling stage, and 3–4 cm water layer during the other growth stages) and wetting irrigation (Topsoil kept wet condition during the whole growth period of rice plant). Amendments included sepiolite combined with phosphate fertilizer (SP + P) and CK (untreated soil as control). This resulted in six soil treatments: untreated soil with continuous flooding (CKys), untreated soil with conventional irrigation (CKgs), untreated soil with wetting irrigation (CKsr), amended soil with continuous flooding (SP + Pys), amended soil with conventional irrigation (SP + Pgs), and amended soil with wetting irrigation (SP + Psr).

7.5 kg of surface soil samples which were ground to pass through a 4-mm sieve was placed in plastic pots, then sepiolite and phosphate fertilizer were blended into contaminated soils at concentrations of 5.0 g kg^{-1} and 4.0 g kg^{-1}, which had been determined by research group members in consideration of remediation effect and economic benefit (Liang et al., 2011). The plastic pots used for experiment were arranged in randomized block, each treatment was replicated in triplicate, the soils were incubated for 30 d at level of 75% of field water-holding capacity, and loss of water was made up with tap water (no Cd detected), then four rice seedlings (low-accumulation cultivar) were planted into each pot. After 120 d growth, the plants were harvested and washed with tap water, and then rinsed 3–4 times with deionized water. The plant sample was separated into root, rice straw, rice hull and brown rice, then oven dried to a constant weight at 75 °C, plant samples were ground with a stainless mill and passed through a 0.25-mm sieve prior to analysis.

The transfer capability of cadmium from root to brown rice was described using translocation factor (TF) calculated according to formula: TF = Cd concentration in brown rice (mg kg^{-1} DW)/Cd concentration in root (mg kg^{-1} DW).

Table 1
Selected physical and chemical properties of tested soil.

Characteristics	Value
Particle size distribution (%)	
Clay	40.1
Silt	10.3
Sand	49.6
pH	5.61
Organic matter (% w/w)	1.98
Cation exchange capacity (cmol kg^{-1})	17.3
Total N (g kg^{-1})	1.03
Total P (g kg^{-1})	0.51
Total Fe (g kg^{-1})	21.3
Total Cd (mg kg^{-1})	0.71
Total Cu (mg kg^{-1})	23.5
Total Pb (mg kg^{-1})	41.2

2.3. Analytic methods

2.3.1. Soil Oxidation–Reduction Potential (ORP)

The rice seedlings were planted into plastic pots followed by the first in situ measurement of ORP of middle soil in pots using automatic ORP analyzer (FJA-6), then the next survey at interval of 20 d.

2.3.2. Chemical fraction of Cd

Sequential Extraction Procedure (Tessier et al., 1979) was conducted to evaluate Cd availability. The method partitioned metal into five operationally defined chemical fractions: exchangeable (1 M $MgCl_2$, agitation for 1 h), bound to carbonates (1 M CH_3COONa, plus CH_3COOH of pH 5, agitation for 5 h), bound to Fe/Mn oxides (0.04 M $NH_2OH \cdot HCl$ in 25% CH_3COOH, agitation for 6 h at the temperature of 96 ± 3 °C), bound to organic matters (0.02 M HNO_3 and 30% H_2O_2, agitation for 5 h at the temperature of 85 ± 2 °C) and residual Cd.

2.3.3. Total Cd

Plant and soil samples were digested with solution of HNO_3–$HClO_4$ and HNO_3–HF–$HClO_4$, respectively. The Cd concentrations were determined by atomic absorption spectroscopy (Solaar M6, Thermo Fisher Scientific, USA).

2.3.4. Fe and Cd contents in root coating

The roots were firstly extracted with 0.1 M $Al_2(SO_4)_3$ solution for reducing substances in root coating (Lu, 2000), Fe(II) in extract was determined by atomic absorption spectroscopy, the roots were sequentially extracted using DCB (0.03 M $Na_3C_6H_5O_7 \cdot 2H_2O$, 0.125 M $NaHCO_3$ and 0.6 g $Na_2S_2O_4$) solution (Taylor and Crowder, 1983), Fe(II) in extract, from the reduction of Fe(III) in root coating, was determined by atomic absorption spectroscopy, then the roots were dried and weighed, the sum of Cd in the first two extracts were counted as Cd in root coating, Cd in root coating plus Cd in root having extracted in the first two extraction steps were calculated as total Cd in root.