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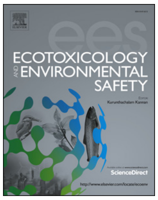

Effects of clay combined with moisture management on Cd immobilization and fertility index of polluted rice field

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ABSTRACT

A field-scale trial was conducted to investigate the remediation effects of sepiolite on Cd-polluted paddy soils under different moisture managements, using a series of variables (pH and extractable Cd of soil, plant Cd concentration, plant nutrition and enzyme activity in soil). Results revealed that soil pH increased significantly after sepiolite addition, which promoted the reduction in extractable Cd in soil. After applying 0.5–2.5% sepiolite into soil, due to higher pH and lower TCLP Cd concentration, brown rice Cd reduced by 17–67% under continuous flooding, 14–62% under conventional irrigation, and 13–61% under wetting irrigation ($p < 0.05$). The activities of phosphatase and invertase increased compared with unamended soil ($p < 0.05$). The available phosphorus in clay treated soil showed a remarkable raise, with a maximum increase by 14.5%, 16.9% and 18.1% under three moisture managements ($p < 0.05$). The increasing values of enzyme activity and then plant nutrition in soil revealed that clay application improved the ecological condition of Cd-contaminated paddy soil. The sepiolite application in combination with continuous flooding provided an efficient and safe remediation technology for Cd-polluted rice field.

1. Introduction

As the rapid development of agricultural technique, and mass-usage of chemical fertilizers, pesticides and irrigation sewages which are rich in heavy metal, metal pollutant accumulation in soil ecosystem become more and more serious, along with few yield and poor quality of agricultural products (Li et al., 2006; Zhou et al., 2005). China Soil Pollution Investigation Bulletin revealed Cd-contaminated soils was nearly 5.33×10^6 ha in 2014, which accounted for 7% of agricultural acreage. Due to higher mobility in soils, cadmiferous rice was over 10% for a nationwide survey. What is more, 60% of investigated rice was polluted by cadmium in certain regions of South China, such as Hunan, Guangdong and Jiangxi province (Wei et al., 2013). The Cd accumulation in human body, mainly via food chain, could result in various diseases, such as kidney damage, decline in bone density and mental disorder (Sun et al., 2009).

The two kinds of techniques were being used for metal polluted soils remediation. Firstly, reduction in total amount of heavy metal in polluted soils primarily through phytoextraction and engineering measures. Secondly, change in form, mobility and bioavailability of heavy metal by chemical immobilization and microbial remediation. In addition, remediation cost and efficiency, and secondary pollution were factors restricting large-scale popularization of contaminated soil remediation. The implementation of engineering measure was limited for high cost and destruction on soil structure, and low target biomass production, long remediation cycle and subsequent plant disposal were some defects faced with phytoextraction (Li et al., 2014a, 2014b; Singh and Prasad, 2015). However, chemical immobilization was a process of transforming highly active metals into inert state by interactions among metals, soil particles, and active binders. This technique was less destructive, cost-efficient, and high-efficiency and then a proper selection for a wide range of contaminated soils remediation (Cao et al., 2008; Han et al., 2014; Komárek et al., 2013; Li et al., 2014a, 2014b; Liang et al., 2011; Ma et al., 1995; Sizmur et al., 2011; Wang et al., 2011; Xu et al., 2003).

The soil Cd extractability and bioavailability have been proved to be different under different water management regimes. Compared to traditional irrigation, continuous flooding resulted in lower Cd availability, which was caused by higher available phosphorus, available iron and pH in paddy soils (Hu et al., 2010; Li and Xu, 2017). In recent years, beside chemical extraction and plant-based test of heavy metals, microbiological and biochemical indexes were increasingly used for

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pollution toxicity assessment (Garau et al., 2007; Sun et al., 2013).

At present, we investigated the remediation effects of clay (sepiolite) on Cd-polluted paddy soils under different moisture managements. Under different soil treatment, pH and Cd TCLP concentration in soils, plant biomass, plant Cd concentration, as well as selected enzyme activity and plant nutrition of soils were tested to estimate remediation efficiency.

2. Materials and methods

2.1. Characteristics of soil and sepiolite

Soil samples were collected from rice field at a depth of 0–20 cm. Soil materials passed through a 20 mesh sieve were used for chemical analysis. The pH, total P, organic matters, CEC and Total Cd were 5.61, 0.51 g/kg, 19.8 g/kg, 17.3 cmol/kg and 0.71 mg/kg. Sepiolite, a natural clay mineral with 65% $CaCO_3$, 8% $Mg_3Si_2(OH)_4O_5$, 9% $Si_3O_6{\cdot}H_2O$, 18% $CaMgSi_2O_6$, was used as amendment for Cd-polluted soil remediation. It had a high cation exchange capacity (CEC = 0.51 meq/g) and pH at a point of zero charge (pH = 10.3). Clay mineral, main part of soil colloids, which was used to remediate metal contaminated paddy soils, based on a natural course.

2.2. Experimental project

The field-scale trial was conducted in Hunan province, China. The local farmland was polluted by Cd due to mining and smelting actions. Thirty days before transplant of rice seeding, clay mineral (sepiolite) was mixed into the topsoil (a depth of 0–20 cm) using uncovering plough. We set applied concentrations of 0.00 kg/m^2 (no immobilization treatment), 0.50 kg/m^2, 1.00 kg/m^2, 1.50 kg/m^2, 2.00 kg/m^2 and 2.50 kg/m^2. Moisture management included continuous flooding (5–7 cm surface water during the whole growth period of rice plant), conventional irrigation (moist soil surface during the late tillering state and grain filling stage, and 5–7 cm surface water during the other growth stages of plant), and wetting irrigation (moist soil surface during the whole growth period of plant, about 70% of field water-holding capacity). There were totally 18 treatments (6 × 3) and 54 plots (each measuring 5 m × 6 m).

The seedling (TY-272) transplanting was completed 30 days after sepiolite application. A 250 g mixed top soil sample was collected in each plot using five-point sampling. The rice plant was harvested after 90 days of growth. The plant was divided into rice straw and brown rice, and dried to a constant weight at 65 °C, plant sample was smashed and passed through a 60 mesh sieve prior to chemical analysis.

2.3. Analytic methods

2.3.1. pH and Cd TCLP concentration

The in situ pH test in plot was carried out by auto pH analyzer (FJA-6) before and after plant harvest. The toxicity characteristic leaching procedure (TCLP) was conducted to evaluate the bioavailability of Cd in soils (Sun et al., 2009).

2.3.2. Total Cd in plant and soil

The plant and soil samples were digested with mixtures of HNO_3-$HClO_4$ and HNO_3-HF-$HClO_4$, respectively. The Cd in solution was determined by inductively coupled plasma mass spectrometer (ICP-MS). As for determination of Cd in soil samples, a certified reference GBW08303 (polluted farmland soils) and a blank were employed for quality control, recovery of reference material was 85.7%. Concerning Cd test for plant samples, bush leaf (GBW07603, China) material, as certified reference material, was used in the digestion process, the accuracy obtained using reference material was 3.3% (RSD), and cadmium recovery in bush leaf was 94.3%.

2.3.3. Available N, P and K in soil

The soil hydrolysable N was determined by Alkaline Hydrolysis Diffusion Method. The available P in soil was tested using Sodium Hydrogen Carbonate Solution-Mo-Sb Anti Spectrophotometric Analysis. The soil available K test was done by means of Flame Photometry Scheme (Lu, 2000).

2.3.4. Enzyme activity

Soil urease activity was determined by the method of Tabatabai (1994). Urease activity was determined with urea as substrate, incubating at pH 7.1 (0.2 M phosphate buffer) and 37 °C for 24 h. The residual urea was determined by a colorimetric method. The enzyme activity was expressed as mg/g/h NH_4–N. Invertase activity was determined using a sucrose solution as a substrate and incubation at 37 °C for 24 h, before measuring the produced glucose with a colorimetric method. The enzymatic activity was expressed as mg/g/h (Kandeler et al., 1999). Phosphatase activity was measured by Sodium Bis (p-nitrophenyl) phosphate as substrate, incubating at pH 14.0 and 30 °C for 10 min, and residual substrate was determined by colorimetric method (Bhattacharyya et al., 2008).

2.4. Statistical analysis

All experimental treatments were replicated three times. Means and standard deviations were calculated using Microsoft Office Excel 2010. Variance analysis and data correlation analysis were done by statistical software SAS 9.1. Multiple comparisons were made using LSD test when significant differences were observed among treatments ($p < 0.05$).

3. Results

3.1. Growth response of plant

The changes in grain production of rice plant were lined in Table 1. In control group, compared with conventional irrigation, grain biomass reduced by 11.5% and 23.7% under continuous flooding and wetting irrigation ($p < 0.05$). Relative to respective controls, grain yields in sepiolited treated soils increased by 1.3–10.0% in continuous flooding, 3.0–12.2% under conventional irrigation, and 2.4–14.1% in wetting irrigation ($p < 0.05$). However, statistically significant difference with the controls were only found in 1.0% and 1.5% clay treatment ($p < 0.05$), and the maximum increment for brown rice biomass was observed for 1.5% sepiolite addition under three moisture

Table 1
The biomass of brown rice under different treatments.

Water management	0	0.5%	1.0%	1.5%	2.0%	2.5%
Biomass yield (kg/plot)						
Continuous flooding	10.3 ± 1.1c (b)	10.1 ± 0.8c (ab)	10.4 ± 1.3b (b)	11.3 ± 1.3a (ab)	10.2 ± 0.8c (b)	10.4 ± 0.7b (b)
Conventional irrigation	11.6 ± 1.5bc (a)	12.0 ± 1.1b (a)	12.3 ± 1.1ab (a)	13.0 ± 1.5a (a)	12.1 ± 0.9b (a)	11.3 ± 1.3c (a)
Wetting irrigation	8.9 ± 0.7c (c)	9.1 ± 0.5b (b)	9.4 ± 0.9b (c)	10.1 ± 1.1a (b)	9.2 ± 0.5b (c)	8.7 ± 0.8c (c)

Means followed by different letters differ at $p < 0.05$. Letters beside means refer to differences for the same water management, and letters enclosed in parentheses refer to differences at the same clay additional concentration.