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# Effects of red mud based passivator on the transformation of Cd fraction in acidic Cd-polluted paddy soil and Cd absorption in rice



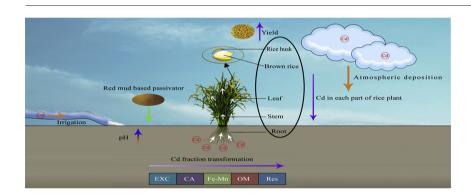
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#### HIGHLIGHTS

- Effective remediation of Cd-polluted paddy field by red mud based passivator
- A significant reduction of Cd concentration in each part of the rice
- Decreased EXC-Cd in the soil after remediation
- No negative impact on a physiological index of rice plus an increase in rice yield

#### GRAPHICAL ABSTRACT



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#### ABSTRACT

Highly effective, economical, and replicable ways of Cd-polluted paddy field remediation (in situ) are urgently needed. In this work, a yearlong field experiment (both early and late rice) was conducted to investigate the effects of red mud based passivator [red mud, diatomite, and lime (5:3:2)] on remediation of an acidic Cd-polluted paddy field in Hunan Province. Compared with the control, the addition of red mud based passivator in the early and late rice reduced Cd concentration in each part of the rice plant (with the most significant decrease rate of 59.18% and 72.11% for brown rice in the early rice and late rice seasons respectively). The effect of Cd reduction in the rice plant was persistent in the next growing season. The addition of red mud based passivator also reduced the exchangeable fraction of Cd in the soil and converted the exchangeable fraction into other unavailable fractions. This study demonstrated that the pH in acidic soil increased after the application of red mud based passivator. Furthermore, red mud based passivator had no effect on the concentrations of Olsen-K, Alkaline-N, Olsen-P in the soil, but increased rice grain yield. Overall, the results of this study indicated that the red mud based passivator at 0.6 kg m<sup>-2</sup> could be a recommendation for Cd-polluted acidic paddy soil stabilization, and it would be a suitable method for remediation of Cd-polluted acidic paddy soil.

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#### 1. Introduction

As industry and urbanization rapidly developed, there have been various heavy metals that could contaminate the soil through different channels and induce threats to the environment and public health

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**Table 1** Physical-chemical properties of tested soil.

Physical-chemical indexes	pН	${ m OM/g~kg^{-1}}$	Olsen-P/mg kg <sup>-1</sup>	Olsen-K/mg kg <sup>−1</sup>	Alkaline-N/mg kg <sup>-1</sup>	CEC/cmol kg <sup>-1</sup>
Soil Physical-chemical indexes Soil	$5.76$ Total Cd/mg kg $^{-1}$ $0.81$	$56.20$ EXC Cd/mg kg $^{-1}$ 0.06	13.34 CA Cd/mg kg <sup>-1</sup> 0.04	55.80 Fe-Mn Cd/mg kg <sup>-1</sup> 0.19	$\begin{array}{c} 153.20 \\ {\rm OM~Cd/mg~kg^{-1}} \\ 0.06 \end{array}$	11.05 Res Cd/mg kg <sup>-1</sup> 0.02

Note: OM: organic matter; CEC: cation exchange capacity; EXC: exchangeable; CA: bound to carbonates; Fe-Mn: bound to Fe-Mn oxides; OM: bound to organic matter; Res: residual.

either directly or indirectly (Guo et al., 2011; Zhou et al., 2016; R. Zhou et al., 2017; Y. Zhou et al., 2017; Zhu et al., 2012). To date, it is estimated that 20% of Chinese arable farming lands have been contaminated by heavy metals (Chen, 2007), including cadmium (Cd) (Yang et al., 2004). A large number of studies have been conducted regarding techniques to remediate Cd-polluted soil, including chemical washing, electro-remediation, phyto-remediation, and stabilization. Among these practices, in situ stabilization with several soil amendments was considered to be a relatively cost-effective and environmentally friendly choice for Cd-polluted farmland (Gu et al., 2011; Guo et al., 2011; Lee et al., 2009; Rao et al., 2013; Shaheen et al., 2014).

Previous pot experiments in laboratory had proved that several amendments, such as alkaline substances, clay minerals, phosphate fertilizers and organic materials, could effectively reduce the mobility and bioavailability of Cd in soils through adsorption, chelation and precipitation (Basta and McGowen, 2004; Gray et al., 2006; Lombi et al., 2002; Sun et al., 2015; Tang et al., 2016). For example, red mud is an inexpensive and effective material available for the in situ treatment of soil polluted with Cd by reducing the Cd mobility in the polluted soil and stimulating microbial abundance, diversity, and activity (Garau et al., 2007; Garau et al., 2011; Ok et al., 2011). In a short-term laboratory, the form of Cd in the soil was transformed from the exchangeable to the Fe-Mn oxides after adding the red mud of 2–5% (w/w). Thus the acid extractability of metals was decreased (Lombi et al., 2002). Lime can reduce the effectiveness and nulltransformation of Cd by increasing soil pH; it is also showed that the addition of amendments decreased the solubility of Cd significantly (P < 0.05) (Lim et al., 2014, Li et al., 2008). Diatomite has high porosity, large surface area and strong adsorption capacity, which allows the effective stabilization of the soil active state Cd. In addition, previous pot experiments determined that the exchangeable fraction of Pb, Zn, and Cd in contaminated farmland soil were reduced significantly after the application of red mud (Fan et al., 2012; Luo et al., 2012; R. Zhou et al., 2017; Y. Zhou et al., 2017). However, most of the studies about the effects of soil amendments such as red mud were merely in short-term laboratory and few studies were conducted in fields, which could barely reflect the actual consequence in application of agricultural production (Hanauer et al., 2011; Hong et al., 2007; Hu et al., 2013; Li et al., 2016; Shirvani et al., 2006; Simon, 2005; Trakal et al., 2017).

Hence, for more practical usage of red mud based passivator in acidic Cd-polluted paddy fields, this one yearlong field study (early and late rice) examined the remediation efficiency and the effects of red mud based passivation on physicochemical properties of the soil and growth of rice.

#### 2. Materials and methods

#### 2.1. Site, passivator and rice cultivar

#### 2.1.1. Site

This study started in March 2016, and it was conducted in an acidic paddy field in Changsha City, Hunan Province, China (113°15′4″E, 28°15′34″N) (Fig. S1). The original paddy field was mainly polluted by the irrigation stream, which was contaminated by livestock and poultry wastewater. The tested soil was Ultisol, and the concentration of Cd in the soil was higher than that of the soil environment quality standard

in China (0.3 mg  ${\rm kg}^{-1}$ ). The fundamental properties were shown in Table 1.

#### 2.1.2. Passivator

The red mud based passivator used in this research consisted of red mud, diatomite, and lime (5:3:2), based on the previous study of our research group. Red mud was supplied by Aluminum Inc. of the Great Wall in China, with Bayer sintering combined method. The diatomite was provided by East China diatomite products Co., Ltd. of Shengzhou City, Zhejiang Province, China. The lime was sourced from Chunhua village, Changsha County. The physical-chemical properties of the red mud based passivator are given in Table 2. The concentration of heavy metals (As, Cd, Pb, Hg and Cr) in red mud based passivator was lower than the standard limits for the water-soluble fertilizers (NY1110-2010, China): Hg  $\leq 5$  mg kg $^{-1}$ , As  $\leq 10$  mg kg $^{-1}$ , Cd  $\leq 10$  mg kg $^{-1}$ , Pb  $\leq 50$  mg kg $^{-1}$ , Cr  $\leq 50$  mg kg $^{-1}$ .

#### 2.1.3. Rice cultivar

The variety of early rice was Zhong zao 39, the variety of late rice was Yu zhenxiang.

#### 2.2. Experimental design

The field experiment consisted of three treatments in the early rice and five treatments in the late rice with different amounts of red mud based passivator added (Table 3). Each treatment was repeated three times. The red mud based passivator was applied to the soil surface of the paddy field and mixed with the plowing soil thoroughly before planting the rice. All the plots were separated by mud and plastic films with an artificial excavation to avoid mixing of water and fertilizer and arranged randomly. The management of growth period in this test field was consistent with the local fields. The early rice was flooded and plowed on April 7, 2016, planted on April 11, and harvested on July 6. The late rice was flooded and plowed on July 10, 2016, planted on July 15, and harvested on October 17.

#### 2.3. Sampling

The soil sample in each plot was the mixture of 5 random samples collected at the depth of 0–20 cm in different stages of both early and late rice seasons (Tillering: the 20th day after transplanting rice, Jointing: the 45th day after transplanting rice, Heeding: the 55th day after transplanting rice, Milky: the 65th day after transplanting rice, Ripening: the 80th day after transplanting rice). All the collected samples naturally dried at ambient temperature. Large particles and biological debris were removed by sieving the dried soil through a nylon mesh (2 mm), and the sieved soil was collected for analysis. The rice was

**Table 2** Physical-chemical properties of the red mud based passivator.

MgO	CaO	SiO <sub>2</sub>	$Al_2O_3$	Fe
33.58 (9%)	30.06 (%)	5.96 (%)	4.25 (%)	3.64 (%)
pH	Moisture	Particle size (≤5.00 mm)	Na	K
10.63	5.87 (%)	≥90 (%)	0.93 (%)	0.38 (%)
Pb	Cd	Cr	Hg	As
<0.001(%)	0.0004 (%)	0.0049 (%)	<0.0005 (%)	<0.001 (%)

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