Mitigating of arsenic accumulation in rice (*Oryza sativa* L.) from typical arsenic contaminated paddy soil of southern China using α -MnO₂ nano-flowers: pot experiment and field application

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ABSTRACT: Hunan province of China is famous in the world for its plenty of non-ferrous metal ore (tungsten, bismuth, realgar) deposit. In the past several decades, intensive mineral exploitation, ore extraction, and refining activities has caused a large amount of waste such as mining waste water, together with the dumping of mining and smelting waste (arsenic residue, arsenic ash) on the soil surface and subjected to erosion and weathering processes, greatly affected the surrounding area and causing long-term and severe impact on soil and water environment. Pollution of paddy fields by Arsenic caused a severe threat to human health in Hunan province, because rice is a staple food and could accumulates higher levels of As compared to other crops. In the present study, a novel Nano manganese oxide with higher reactivity and oxidation ability has been synthesized. Pot experiment combined with field application has been conducted to explorer the potential of α -MnO₂ Nano manganese oxides for the remediation of As polluted paddy soil. Results turns out that the application of α -MnO₂ Nano-flowers can effectively control the transportation and accumulation of arsenic from soil to rice.

1 INTRODUCTION

The biogeochemical cycle of As in paddy soils at varies conditions (pH, Eh, periodically flooded) was rather complexity. As mobilization in flooded paddy environment was subjected to two main processes. First, the reductive dissolution of iron (oxyhydr) oxides triggered by soil flooding which caused the sorbed solid phase As releasing into the liquid phase. Second, the sorbed arsenates were reduced to arsenite under the reductive circumstances and the latter has a greater tendency to partition into the liquid phase than arsenate. Thus, effective measures must be taken to reduce the bio-availability and mobility of As in paddy soils (Suda and Makino, 2016; Xu *et al.*, 2017; Yu *et al.*, 2017).

The major goal of this present study was to investigate the potential of synthetic α -MnO₂ nano-flowers for the mitigation of As accumulated in rice. A series of experiments, including soil incubation, green house pot experiments combined with filed applications, were designed and conducted using a typical As contaminated paddy soil from southern China in Hunan Province.

2 METHODS/EXPERIMENTAL

2.1 Pot experiment design

The pot experiment was carried out in a greenhouse of Hunan agricultural university. The soil was amended with α -MnO₂ Nano-flower at rates of 0.0%, 0.2%, 0.5%, 1.0% and 2.0% of soil weight. Each pot was then saturated with distilled water and drained down to an equilibrium state for 7 days under natural conditions. All the treatments were triplicated and randomly arrangement. Rice seedlings were transplanted to each

pot after 30 days. During the whole growth period, all pots were irrigated with distilled water daily to maintain water level of 3 cm above the soil surface. Rice was harvested at day 105. At each growth stage (tillering, heading and maturing stages) rice plants will collected, digested, and the concentrations of Mn and As in the organs (roots, stems, leaves and grains) of rice plants were analyzed. The pore water was extracted during the same time and the concentrations of Fe, Mn, As will analyzed.

2.2 Field application experiment design

The field experiment was carried out in 2013 at a paddy field in Dengjiatang, Chenzhou City, Hunan Province, (25°36'N, 113°00'E). Nano-MnO₂ were added into the soil at a rate of 0.0%, 0.2%, 0.5%, 1.0% and 2.0% of soil weight, respectively, and mixed thoroughly with top soil. All treatment was conducted in triplicate with a completely randomized factorial design, and three blank control is provided. Rice plants were harvested at each growth stage (tillering, heading and maturing stages). the concentrations of Mn and As in the organs (roots, stems, leaves and grains) of rice plants were analyzed. The pore water was extracted during the same time and the concentrations of Fe, Mn, As will analyzed.

3 RESULTS AND DISCUSSION

3.1 Characterization of synthesized α -MnO₂ nano-flowers

High-magnification SEM images show that the α -MnO₂ is a flower-like spherical with diameter of 1–1.5 μ m, which consists of several straight and

Figure 1. Concentrations of As (a) and Mn (b) in rice stalk under different dosage of α -MnO₂.

radially grown nano-rods with uniform diameter around 30–40 nm. The synthesized α -MnO₂ nanoparticles has an obvious characteristic diffraction peak in the XRD pattern, which indicates that the high crystallization degree of nanometer manganese dioxide, and the characteristic peak was in agreement with the standard data given in its JCPDS card (24-0072).

3.2 Pot experiment

In greenhouse pot experiments, whether or not to add α -MnO₂ Nano-flowers material, the content of arsenic in rice was in the order of root > stem > leaf > husk > brown rice. The As concentrations in soil solution decreased with the increasing dosage of 0.5%, 1.0%, and 2.0% in soils and thus greatly reduced the accumulation of As in rice. The relationship between manganese and arsenic in rice plants showed a significant negative correlation ($p < 0.05$), indicated that the concentration of arsenic in rice decreased with the increasing amounts of manganese in rice. The total As concentration in brown rice was reduced by 65.4% with the addition of 1.0% α -MnO₂ nano-flowers, and the corresponding inorganic As content was decreased to 0.19 mg kg⁻¹ which lower than the limited content of inorganic As in food.

3.3 Field application

In field experiment, the concentrations of As in roots were 2–7 times greater than the background value of the soil, and significantly higher than those in the stems and leaves, which demonstrated that the content of As in rice followed the order of root > stem > leaf > husk > brown rice (Table 1). There was a significant positive correlation between amount of iron plaque and As concentration in root at mature stage.

Interestingly, the amounts of iron plaque decreased with increasing of α -MnO₂ nano-flowers, indicated that there was more Mn plaque deposited on the rice roots. Meanwhile, a significant correlation between trans-location factors of As from iron plaque, root, stem and leaf to seed in mature stage has been

Table 1. Concentrations of As and Mn in rice husk and brown rice (field application).

		Total As/mg kg ⁻¹ (n = 3)		
	Treatments	Tillering stage	Heading stage	Maturation stage
Root	CK	476.20 ± 35.69	370.99 ± 42.36	552.57 ± 58.20
	0.2%	478.37 ± 42.36	380.30 ± 18.96	433.95 ± 32.15
	0.5%	297.53 ± 18.54	266.91 ± 32.58	368.46 ± 18.94
	1.0%	382.23 ± 21.95	126.28 ± 21.25	446.39 ± 45.96
	2.0%	153.45 ± 10.23	110.19 ± 10.21	321.93 ± 35.68
Stalk	CK	4.46 ± 2.32	7.12 ± 0.84	18.81 ± 2.65
	0.2%	0.89 ± 0.54	1.00 ± 0.08	8.64 ± 4.51
	0.5%	0.74 ± 0.36	1.21 ± 0.54	4.92 ± 1.20
	1.0%	2.43 ± 1.03	0.64 ± 0.24	6.10 ± 1.36
	2.0%	0.97 ± 0.38	1.24 ± 0.21	5.32 ± 0.98
Leaf	CK	4.73 ± 1.55	3.69 ± 1.27	12.11 ± 4.03
	0.2%	3.37 ± 0.23	1.92 ± 0.89	3.17 ± 0.25
	0.5%	1.56 ± 0.24	2.59 ± 1.23	1.77 ± 0.15
	1.0%	2.06 ± 1.03	0.66 ± 0.32	8.96 ± 1.08
	2.0%	1.17 ± 0.12	1.14 ± 0.11	6.24 ± 0.94

observed, which also indicated that there was a significant difference in As concentrations between same part of rice with different α -MnO₂ nano-flowers treatments ($p < 0.05$). The content of arsenic in rice were below the limit of arsenic in food with the dosage of 0.2%, 0.5% and 2.0%.

4 CONCLUSIONS

In this study, the potential of synthetic α -MnO₂ Nano-flowers for the remediation of arsenic polluted paddy soil has been investigated. Results turns out that the application of α -MnO₂ Nano-flowers can effectively reduce the bio-availability of As in paddy soil and control the transportation and accumulation of As in rice. These results highlight the potential of α -MnO₂ Nano-flowers to mitigate the phyto-accumulation of arsenic by rice and to thereby reduce As exposure risk associated with rice consumption.

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