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Mitigating arsenic accumulation in rice (*Oryza sativa* L.) from typical arsenic contaminated paddy soil of southern China using nanostructured α-MnO_2: Pot experiment and field application

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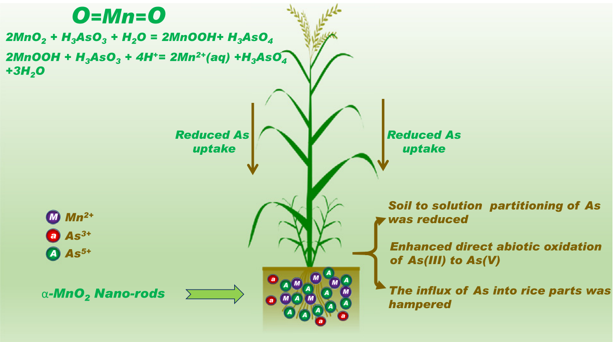
HIGHLIGHTS

- Nanostructured α-MnO_2 has been synthesized and successfully used for the remediation of As polluted paddy soil.
- α-MnO_2 nanorods can effectively control the soil-to-solution partitioning of arsenic
- Pot experiment and fields trials further proved that the α-MnO_2 nanorods can be used for paddy soil restoration.

GRAPHICAL ABSTRACT



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ABSTRACT

Manganese oxides are naturally occurring powerful oxidants and scavengers, which can control the mobility and bioavailability of arsenic (As). However, the effect of synthetic nanostructured manganese oxides on the mobilization and transportation of As at actual paddy soils are poorly understood, especially in soils with low or medium background Mn concentration. In the present study, a novel nano manganese oxide with superior reactivity and surface area has been synthesized. A 90-d soil incubation experiment combined with pot and field rice cultivation trials were designed to evaluate the effectiveness of exogenous α-MnO_2 nanorods on the mobilization and transportation of As in soil-rice systems. Our results proved that the addition of α-MnO_2 nanorods can effectively control the soil-to-solution partitioning of As under anaerobic conditions. After treatment with different amounts of α-MnO_2 nanorods, the content of effective As decreased, offset by an increase in residual As and insoluble binding As (Ca-As and Fe-As). Enhancing the oxidation of As(III) into As(V), the α-MnO_2 nanorods increased the adsorption of As onto indigenous iron (hydr)oxides which greatly reduced the soil porewater As content. In addition, pot experiments and field applications revealed that the influx of As into the aerial parts of rice plants (stems, husk and leaves) was strictly prohibited after treatments with different amount of α-MnO_2 nanorods; more interestingly, significantly negative correlations have been observed between As and Mn in rice, which indicated that as Mn is increased in soil, As in brown rice decreases. Our results

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demonstrated that the use of α-MnO_2 nanorods in As polluted paddy soil containing low levels of background Mn oxides can be a promising remediation strategy.

1. Introduction

Hunan province is world-renowned for its luxuriant deposit of non-ferrous metal ores (tungsten, bismuth, realgar) (Lei et al., 2015; Okkenhaug et al., 2012; Williams et al., 2009). In the past several decades, intensive mineral exploitation, ore extraction and refining activities have caused a large amount of toxic trace elements (Cd, Hg, Pb and As) to be discharged into farmland which has greatly affected the local soil and water environment (Li et al., 2017; Zhao et al., 2015). Among them, arsenic is a ubiquitous and highly toxic metalloid element that has caused severe contamination in Hunan province (Lei et al., 2013; Lei et al., 2015). It is reported that the arsenic-contaminated farmland in Hunan province has already seriously impaired the development of agriculture and posed a serious threat to the health of local residents, because rice is a dominant staple food (Li et al., 2016; Liao et al., 2005).

The forms (speciation) of arsenic may be more important than the total arsenic in the soil, which determine its effectiveness and toxicity to organisms. It is generally established that trivalent As species are more toxic than their pentavalent counterparts because they binds to sulfhydryl groups (—SH), impairing the function of many proteins (Fu et al., 2016; Liao et al., 2005; Liu, 2005). In paddy soils, arsenic is predominantly present as the inorganic species arsenate and arsenite (Takahashi et al., 2004). The extent of As mobility and bioavailability in paddy soil is, in part, regulated by the type of minerals that exist in the soil system and the oxidation state of As (Fendorf and Kocar, 2009; Ying et al., 2012). Generally, As(III) is far more mobile than As(V); and the relative content of arsenate and arsenite in paddy soil are primarily dependent on the redox status of soil (Yamaguchi et al., 2011). Arsenate often exists in anionic forms (e.g., $H_2AsO_4^-$, $HAsO_4^{2-}$) under aerobic conditions with the content account for ca. 65–98% of the total arsenic (Ohtsuka et al., 2013). Conversely, arsenite takes the form of an electrically uncharged molecule (H_3AsO_3) under anaerobic reducing conditions (Eh < 100 mV; pH < 9) (Han et al., 2011). The amount of Fe oxides in the soil plays an important role in controlling the concentration of As species in the soil solution; Typically, As(V) is strongly adsorbed with metal-(oxyhydr) oxides, whereas As(III) is poorly associated with soil minerals owing to its neutral charge (Chen et al., 2006; Ehlert et al., 2014); It's this property that renders As(III) comparatively more effective for plant uptake than the As(V) (Xu et al., 2017). However, it is well recognized that during aerobic-anaerobic transitions within paddy fields, the absorbed As will released into soil porewater (Ohtsuka et al., 2013; Xu et al., 2017). The mobilization of As in flooded paddy fields is because of two main processes. Firstly, the reductive dissolution of iron (oxyhydr)oxides have been triggered by soil flooding which caused the sorbed solid phase arsenic to release into the liquid phase (Lemonte et al., 2017; Weber et al., 2010; Yamaguchi et al., 2011). Secondly, the adsorbed As(V) is reduced to As(III) under the reductive conditions and the latter has a greater tendency to partitioning into the liquid phase than As(V) (Liu et al., 2015; Takahashi et al., 2004). Compared with other terrestrial plants, rice (*Oryza sativa* L.) is efficient in As uptake and translocation, because of the flooded conditions and highly expressed arsenic transporter (Si transporter, aquaporins and phosphate transporters) (Ma et al., 2008; Meharg, 2004; Meharg and Jardine, 2003). Thus, effective measures must be taken to reduce the bio-availability and mobility of As(III) in paddy soil during rice cultivation.

In the current literature, several measures have been proposed for reducing the bio-availability of As in soils, such as amendments stabilization (biochar, natural minerals, etc.) (Kumpiene et al., 2008; Li et al., 2018), electro-kinetics (Balasubramanian et al., 2009), acid flushing (Beiyuan et al., 2017; Tokunaga and Hakuta, 2002), phytoremediation (Gilloaiza et al., 2016; Jankong et al., 2007) and agronomic mitigation strategies (Limmer et al., 2018; Seyfferth et al., 2018). However, those methods are hard to meet the actual demand of paddy fields remediation. Due to either their high-cost (Liu et al., 2018), vast energy requirements (Villen-Guzman et al., 2017), or long treatment times (Wan et al., 2016); above all, high cost (or unsustainability) hinder the application of many technologies in polluted farmland (Bontempi, 2017). Chemical stabilization methods, in particular, have been widely accepted in the remediation of As-contaminated soils because they are relatively cost effective, sustainable and easy to operate and manage. Recently, engineered nanoparticle stabilizer such as zero valent iron (Gil-Díaz et al., 2017; Gil-Díaz et al., 2016) and iron phosphate (vivianite) nanoparticles (Liu and Zhao, 2007) has been shown to provide cost-effective solutions to some of the most intractable environmental restoration problems due to their large surface areas and high surface reactivity (Zhang, 2003). For the variable valence elements (As), in situ oxidation by chemical amendments which induce the transformation of As(III) to As(V) are considered to be a promising approach which can alleviate the associated environmental risks of As in paddy soil (Lin et al., 2017; Suda and Makino, 2016; Xu et al., 2017). However, to our knowledge, there are few related studies focused on the induction of As into lower-reactivity and lower-toxicity forms using oxidants in paddy soil.

Manganese oxides are naturally occurring powerful oxidants that can effectively catalyze the oxidation of As(III) to As(V) under natural conditions (Manning et al., 2002; Ehlert et al., 2014; Han et al., 2011; Lafferty et al., 2010). The As(III) oxidation by manganese oxides can occur across a wide pH ranged from 4.0–8.2, however, the oxidation rates are deeply associated with their structure, surface charge properties, mineral crystallinity and abundance (Oscarson et al., 1983; Scott and Morgan, 1995). The study conducted by (Manning et al., 2002) showed that As(III) can be quickly oxidized into As(V) in the presence of MnO_2 with only about 10% of the As(III) remaining after 10 h. while, Scott and Morgan (1995) found that birnessite (δ-MnO_2) can quickly oxidize As(III) to As(V), with about 80% of the reaction completing within 1 h; a process accompanied by the release of Mn^{2+}. Apart from the oxidation ability towards As(III) by manganese oxides, it was also reported that As(III), after being oxidized by Mn-oxides, can subsequently be adsorbed onto the surfaces of MnOOH (oxidation intermediates) and ferric-(oxyhydr) oxide (Ehlert et al., 2014; Nesbitt and Canning, 1998); thus the partitioning of As into solution was restrained. Although many studies (Manning et al., 2002; Ehlert et al., 2014) have been conducted on the oxidation of As(III) by manganese oxides, most of these however are concentrated on pure minerals in aqueous solution.

To the best of our knowledges, there are very few related studies on the oxidation of As(III) by synthetic nanostructured-MnO_2 in actual paddy soils; especially in soils with low or medium background Mn concentrations. In China, it has been reported that the content of Mn in soil varies between 10 and 5532 $mg \cdot kg^{-1}$ with an average of 710 $mg \cdot kg^{-1}$ (Liu et al., 1983). There soils with Mn concentrations below this average value of 710 $mg \cdot kg^{-1}$ can be classified as being low manganese sub-types. Recently, a soil incubation experiment conducted by Xu et al. (2017) showed that addition of synthetic Mn oxide (hausmannite) in low background Mn paddy soils can effectively control the partitioning of As from the solid phase to liquid phase due to the oxidation of As(III). However, they only considered the efficiency of micrometer scale Mn oxides under laboratory conditions and did not test the technology in field conditions. Therefore, we have proposed