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Microbial siderophores and root exudates enhanced goethite dissolution and Fe/As uptake by As-hyperaccumulator *Pteris vittata*[☆]

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ABSTRACT

Arsenic (As) in soils is often adsorbed on Fe-(hydro)oxides surface, rendering them more resistant to dissolution, which is undesirable for phytoremediation of As-contaminated soils. Arsenic hyperaccumulator *Pteris vittata* prefers to grow in calcareous soils where available Fe and As are low. To elucidate its mechanisms of acquiring Fe and As from insoluble sources in soils, we investigated dissolution of goethite with pre-adsorbed arsenate (AsV; As-goethite) in presence of four organic ligands, including two root exudates (oxalate and phytate, dominant in *P. vittata*) and two microbial siderophores (PG12-siderophore and desferrioxamine B). Their presence increased As solubilization from As-goethite from 0.03 to 0.27–5.33 mg L⁻¹ compared to the control. The siderophore/phytate bi-ligand treatment released 7.42 mg L⁻¹ soluble Fe, which was 1.2-fold that of the sum of siderophore and phytate, showing a synergy in promoting As-goethite dissolution. In the ligand-mineral-plant system, siderophore/phytate was most effective in releasing As and Fe from As-goethite. Moreover, the continuous plant uptake induced more As-goethite dissolution. The continued release of As and Fe significantly enhanced their plant uptake (from 0.01 to 0.43 mg plant⁻¹ As and 2.7–14.8 mg plant⁻¹ Fe) and plant growth (from 1.2 to 3.1 g plant⁻¹ fw) in *P. vittata*. Since microbial siderophores and root exudates often coexist in soil rhizosphere, their synergy in enhancing dissolution of insoluble As-Fe minerals may play an important role in efficient phytoremediation of As-contaminated soils.

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1. Introduction

Iron (Fe) is an essential nutrient for plants, which often presents as insoluble Fe-(hydro)oxides in soils and limits plant uptake. Though total Fe content in soils is high, the available Fe concentrations in most soils are below the optimal for plant growth, which are at 10⁻⁹–10⁻⁴ M Fe in soil solution (Masalha et al., 2000). This is especially true for calcareous soils where available Fe cannot always meet plant demand. In soils, arsenic (As) is often present in the oxidized form arsenate (AsV), which is readily adsorbed onto Fe-(hydro)oxide surface (Gräfe et al., 2004; Sharma and Sohn, 2009), thus reducing the availability of both Fe and As.

It is known that plants and microorganisms produce organic

ligands to solubilize Fe from poorly available sources. Microbial siderophores are low molecular weight (LMW) organic ligands with high affinity for Fe³⁺, with stability constants of 10³⁰–10⁵² (Ahmed and Holmstrom, 2014). They are produced by microorganisms under Fe-deficient conditions, serving as their main strategy to acquire Fe from insoluble forms (Masalha et al., 2000). In addition, plant roots release exudates into the rhizosphere to enhance their uptake of nutrients (e.g., Fe and P) from insoluble sources (Jones and Darrah, 1994). Among root exudates, LMW organic acids (LMWOAs) are of particular importance due to their ubiquitous presence in soils and their ability to mobilize insoluble nutrients (Dong et al., 2004; Zhu et al., 2011).

Pteris vittata (Chinese Brake fern), the first known As-hyperaccumulator (Ma et al., 2001), prefers to grow in calcareous soils, which is characterized by low available Fe and As contents (Lessl and Ma, 2013). This suggests that *P. vittata* and the associated rhizobacteria may have evolved efficient strategies to acquire Fe

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and mobilize As from insoluble Fe-minerals in soils. For example, siderophores produced by As-resistant rhizobacterium PG12 isolated from *P. vittata* rhizosphere are 40–60% more effective in dissolving FeAsO₄ mineral than the common fungal siderophore desferrioxamine B (DFO-B) (Liu et al., 2015). Root exudates of *P. vittata* are 4–6 times more efficient in dissolving FeAsO₄ mineral than non-hyperaccumulator *Nephrolepis exaltata* (Tu et al., 2004). The effect of root exudates on goethite dissolution has been studied extensively, especially citrate and oxalate (Persson and Axe, 2005; Zhong et al., 2013). However, limited information is available regarding how phytate affects goethite dissolution. As the predominant form of P storage in plants (Graf and Eaton, 1990; Park et al., 2006), phytate is detected in the root exudates of some ferns like *P. vittata*, which may contribute to its efficient Fe acquisition and As uptake (Liu et al., 2016; Tu et al., 2004). Besides, in the rhizosphere, microbial siderophores and root exudates often coexist, both influencing plant Fe acquisition (Ahmed and Holmstrom, 2014; Kraemer, 2004). However, their effects on Fe-mineral dissolution and the subsequent plant uptake, especially in hyperaccumulation plants, are not well understood.

The synergic effect between LMWOAs and siderophores on Fe/Mn oxide dissolution has been observed (Reichard et al., 2005, 2007; Saal and Duckworth, 2010). It is mainly attributed to the high affinity of siderophores for Fe³⁺, wresting Fe³⁺ from Fe-organic acid complexes (Ito et al., 2011). The organic acids released from the Fe-organic acid complexes can react with goethite again, resulting in more Fe release (Zhong et al., 2013). A similar synergic effect has also been shown for δ-MnO₂ dissolution (Saal and Duckworth, 2010). However, studies have focused on the effects of organic ligands on surface-controlled dissolution and weathering reactions of Fe minerals, limited attention has been paid to Fe minerals pre-adsorbed by AsV, which are common in soils and may have different solubility. Many ligands affect the surface-controlled dissolution of Fe minerals. Bondietti et al. (1993) suggested that oxalate and citrate form mononuclear surface complexes, promoting dissolution of Fe minerals. On the other hand, AsV and P form binuclear surface complexes with Fe on the surface, inhibiting their dissolution. Therefore, attention must be paid to the effect of ligands on dissolution of Fe minerals pre-adsorbed with AsV, which is yet to be elucidated.

In this study, goethite with pre-adsorbed AsV (As-goethite) was used as an insoluble source of Fe and As. The overall objective was to determine the effects of organic ligands on As release and Fe dissolution from As-goethite and their subsequent uptake by *P. vittata*. Goethite was chosen for its ubiquity in soils and its importance as a sorbent for AsV (Gräfe et al., 2004; Schwertmann and Cornell, 2008). The organic ligands included two plant root exudates (phytate and oxalate) and two microbial siderophores (PG12-siderophore and DFO-B). PG12-siderophore (PG12-S) is produced by As-resistant rhizobacterium PG12 from *P. vittata* rhizosphere and DFO-B represents common siderophore in soils (Liu et al., 2015; Zhong et al., 2013). While both phytate and oxalate are present in the root exudates of *P. vittata*, phytate is specific to *P. vittata* and oxalate is common to all plants (Liu et al., 2016; Tu et al., 2004). The specific objectives of this study were to: 1) quantify the effects of microbial siderophores (PG12-S and DFO-B) and/or root exudates (phytate and oxalate) on dissolution of As-goethite, and 2) investigate their effects on Fe and As plant uptake and plant growth in As-hyperaccumulator *P. vittata*.

2. Materials and methods

2.1. Goethite synthesis and characterization

Goethite (α -FeOOH) was synthesized following Schwertmann

and Cornell (1991). Briefly, 180 mL of 5 M KOH solution was added rapidly to 100 mL of 1 M Fe(NO₃)₃ solution in a 2 L polyethylene flask under stirring. The suspension was then brought to 2 L volume with Milli-Q water (Millipore, USA) and heated at 70 °C for 60 h. The product was repeatedly washed and centrifuged with Milli-Q water until supernatant pH was near neutral. After final washing, the product was centrifuged and freeze-dried (FreeZone 12, LabConco, Kansas City, USA) (Reichard et al., 2007). The goethite was verified with X-ray diffraction (data not shown) and the specific surface area was 52 m² g⁻¹ determined by a multipoint BET N₂ adsorption method. The goethite was stored as a powder in a desiccator.

To prepare AsV-adsorbed goethite, equal volumes of 50 mg L⁻¹ AsV (Na₂HAsO₄·7H₂O; Sigma-Aldrich, St. Louis, USA) and 1 g L⁻¹ goethite stock suspensions were mixed and agitated at 25 °C on a rotary shaker at 180 rpm for 2 h (Wolff-Boenisch and Traina, 2007), which was then centrifuged, filtered and freeze-dried for further use. The selection of 2 h was based on a preliminary adsorption experiment, which showed that the equilibration time of the sorption reaction was ~100 min (Cheah et al., 2003). The obtained goethite contained 0.25 mM g⁻¹ As and is referred as As-goethite.

The point of zero charge (PZC) of goethite and As-goethite was determined using two methods. For the salt addition method, a solution of 0.01 M NaCl was used as the background electrolyte. Aliquots of 10 mL of solution were apportioned into 11 flasks and the pH was maintained at 2 to 11 using 0.1 M NaOH or 0.1 M HCl solution. Then 0.05 g of the mineral sample was added into the flasks and agitated on a horizontal shaker for 24 h at 25 °C. Then the final pH values were recorded. The difference between initial and final pH values (Δ pH) was plotted against initial pH values. PZC value was identified at the pH when Δ pH was zero, i.e., the initial pH was equal to the final pH (Mushtaq et al., 2014; Mustafa et al., 2002).

For the potentiometric mass titration method, a 0.06 M NaCl solution was prepared in deionized water. Four 10 mL aliquots were transferred into four titration flasks, and 0, 0.02, 0.04, and 0.06 g of goethite or As-goethite was transferred to the respective flasks. All four solutions were equilibrated at room temperature under nitrogen atmosphere for 24 h. Then 0.5 mL of 0.1 M NaOH was transferred to the solution under stirring. After recording the initial pH value, the solution was titrated against 0.1 M HCl solution using 0.02 mL addition. The pH was recorded every 30 s and the titration curves were plotted. The intersection point between blank and sample solutions was considered as the PZC value (Farooq et al., 2011; Mushtaq et al., 2014).

2.2. Adsorption of arsenic and organic acids on goethite

To examine the adsorption of As and organic acids on goethite, the suspensions of goethite (2.5 g L⁻¹) were hydrated in 0.01 M NaNO₃ electrolyte with pH adjusted to ~6 with 0.5 M MES buffer, which was maintained at ~6 after adding 500 μ M As or organic acids (phytate or oxalate) using 0.01 M NaOH or HCl and solution redox potential was maintained at 67.2 mV (Wolff-Boenisch and Traina, 2007). Suspensions containing the same volumes of 0.5 M MES buffer without As and organic acids were used as blanks. Purified phytate and oxalate (M_w = 660 and 90) were purchased from Aladdin Industrial Inc (Shanghai, China). After 24 h of equilibration on an orbital shaker at 200 rpm and 25 °C, the suspension was centrifuged and the supernatant was filtered through a 0.45 μ M nylon filter for subsequent As and ligands concentrations analysis.

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