



Remediating flooding paddy soils with schwertmannite greatly reduced arsenic accumulation in rice (*Oryza sativa* L.) but did not decrease the utilization efficiency of P fertilizer[☆]

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ABSTRACT

Planting rice (*Oryza sativa* L.) in As-contaminated paddy soils can lead to accumulation of arsenic (As) in rice grains, while the application of phosphorus (P) fertilizers during rice growth may aggravate the accumulation effect. However, remediating flooding As-contaminated paddy soils with conventional Fe(III) oxides/hydroxides can hardly achieve the goals of effectively reducing grain As and maintaining the utilization efficiency of phosphate (Pi) fertilizers simultaneously. In the present study, schwertmannite was proposed to remediate flooding As-contaminated paddy soil because of its strong sorption capacity for soil As, and its effect on the utilization efficiency of Pi fertilizer was investigated. Results of a pot experiment showed that Pi fertilization along with schwertmannite amendment was effective to reduce the mobility of As in the contaminated paddy soil and meanwhile increase soil P availability. The schwertmannite amendment along with Pi fertilization reduced the content of P in Fe plaque on rice roots, compared with the corresponding amount of Pi fertilizer alone, which can be attributed to the change in mineral composition of Fe plaque mainly induced by schwertmannite amendment. Such reduction in P retention on Fe plaque was beneficial for improving the utilization efficiency of Pi fertilizer. In particular, amending flooding As-contaminated paddy soil with schwertmannite and Pi fertilizer together has reduced the content of As in rice grains from 1.06 to 1.47 mg/kg to only 0.38–0.63 mg/kg and significantly increased the shoot biomass of rice plants. Therefore, using schwertmannite to remediate flooding As-contaminated paddy soils can achieve the dual goals of effectively reducing grain As and maintaining the utilization efficiency of P fertilizers.

1. Introduction

Arsenic (As) is widely recognized as a highly toxic carcinogen and also one of common contaminants in paddy soil (Wang et al., 2015; Yin et al., 2020). Compared with other cereal crops, rice accumulates much more As in its grains due to the flooding conditions during rice cropping and its inherent capacity of transferring As (Dai et al., 2020; Su et al., 2010; Wang et al., 2019). Given the fact that about three billion people around the world eat rice as their main food (Zhao et al., 2010), the consumption of As-contaminated rice and rice-based food products

poses a great threat to human health (Li et al., 2011; Yin et al., 2019). It is thus necessary to mitigate As accumulation in rice grains during rice cropping, consequently reducing the health risk of As intake via diet.

As in aerobic soils, being of low mobility and bioavailability, mainly exists in the form of arsenate [As(V)] and is firmly adsorbed by poorly crystalline iron (oxyhydr) oxides in soil (Ying et al., 2011), but it is greatly mobilized to enhance the bioavailability when paddy soils are flooded during rice cropping. In flooding paddy soils, the reductive dissolution of poorly crystallized Fe(III) (oxyhydr) oxides releases a considerable amount of As(V) (Dai et al., 2020; Das et al., 2016; Yi et al.,

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2019), which can be readily reduced by microbes to arsenite [As(III)] that is much more toxic and mobile than As(V) (Dai et al., 2020; Takahashi et al., 2004; Zobrist et al., 2000). In order to effectively reduce the transfer of As from paddy soils to rice, amending paddy soils with Fe(III) oxides/hydroxides has been recommended as one of effective ways to immobilize As in paddy soils and consequently reduce the accumulation of As in rice grains (Kumarathilaka et al., 2020; Maguffin et al., 2020; Matsumoto et al., 2016). Since phosphorus (P) is an essential nutrient to promote rice growth and development, P fertilization is employed as a common agricultural strategy to improve rice yield (Song et al., 2021). Although phosphate (Pi) and As(V) share the same transport pathway in rice, implying the possible inhibited uptake of As by Pi application (Muehe et al., 2014; Shin et al., 2004), several studies revealed that the application of Pi fertilizers in As-contaminated paddy soils did not inhibit but even increased the uptake of As by rice to aggravate the health risk of As in paddy soils (Lee et al., 2016; Yang et al., 2020). It is due to the fact that Pi and As have similar physicochemical structure characteristics and can be adsorbed by Fe(III) oxides/hydroxides existing in soil via ligand exchange mechanisms. In such a way, the application of Pi fertilizers in As-contaminated paddy soils would compete with As for binding sites in soil solid to increase As concentration in soil porewater (Jiang et al., 2014; Yang et al., 2020). As a result, amending As-contaminated paddy soils with conventional Fe(III) oxides/hydroxides, with the aim of immobilizing As in paddy soils, would inevitably lower the biological availability of soil P (Hu et al., 2020), while the application of Pi fertilizers in As-contaminated paddy soils potentially decrease the efficiency of Fe(III) oxides/hydroxides in immobilizing As (Kanematsu et al., 2013; Ngantcha-Kwimi and Reed, 2020). Therefore, it is a great challenge to achieve the dual goals of effectively reducing grain As and maintaining the utilization efficiency of Pi fertilizers when using iron-based materials to remediate As-contaminated paddy soils.

Schwertmannite, a kind of iron oxide hydroxyl sulfate mineral that can be expressed as $\text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_{x(1-x < 1.75)}$, has attracted intensive attentions in recent years, since it is capable of removing a large amount of As from the environment as a result of its huge surface area and special tunnel structure (Chai et al., 2016; Liao et al., 2011; Meng et al., 2021; Paikaray et al., 2012; Yang et al., 2017). Although schwertmannite usually occurs in acidic mine water (AMD) and acidic sulfate soil (ASS) environment (Zhang et al., 2018), it can also be synthesized by chemical or biological methods to facilitate its environmental application in remediating As-contaminated waters or soils (Zhang et al., 2018). On the one hand, schwertmannite shows greatly higher adsorption capacity for either As(III) or As(V) than ordinary iron-based materials, such as goethite, ferrihydrite and iron-impregnated biochar (Gil-Díaz et al., 2017; Hu et al., 2015b; Meng et al., 2021; Ramirez-Muñiz et al., 2018). On the other hand, several studies reported that in water environment, the adsorption capacity of schwertmannite for Pi is much lower than As, and Pi hardly affects the adsorption removal of As by schwertmannite (Eskandarpour et al., 2006; Liao et al., 2011; Meng et al., 2021; Paikaray et al., 2011; Schoepfer et al., 2017). It is thus reasonable to presume that amending flooding As-contaminated paddy soils with schwertmannite may effectively reduce the transfer of As from paddy soils to rice and meanwhile maintain the effectiveness of Pi fertilization to support the growth of rice, which warrants in-depth investigation.

Fe plaque on the root surface of rice is considered as an important barrier to prevent rice from absorbing As (Pan et al., 2014; Wu et al., 2016; Yang et al., 2020), the mineral composition of which is goethite, amorphous $\text{Fe}(\text{OH})_3$, ferrihydrite and minor siderite (Fu et al., 2016; Hansel et al., 2001; Wang and Peeverly, 2000). These ferric (hydr)oxides in Fe plaque can adsorb not only As but also a large amount of Pi (Hu et al., 2020; Kalaitzidou et al., 2022; Song et al., 2021). In addition, Pi fertilization would decrease the formation of Fe plaque on the root surface of rice (Fu et al., 2014; Yang et al., 2020), but the introduction of iron-based materials may promote the formation of Fe plaque on rice

roots via increasing the content of Fe ions (Fe^{2+} and Fe^{3+}) in soil (Hu et al., 2020). Hence, the effect of schwertmannite introduction on the interaction among As, Pi and Fe plaque in soil-rice system may greatly influence the bioavailability of As and Pi to rice. Therefore, the objectives of this study are to (1) compare the effect of Pi fertilization alone or along with schwertmannite amendment on the mobility and bioavailability of As and Pi in flooding As-contaminated paddy soil; (2) explore the feasibility of effectively reducing the transfer of As from paddy soils to rice, but without decreasing the utilization efficiency of Pi fertilizer, by using schwertmannite amendment; (3) study the influence of Pi fertilization and/or schwertmannite amendment on the retention of As and P by Fe plaque. The findings of the present study would be meaningful for understanding the co-impact of schwertmannite amendment and Pi fertilization on the behaviors of As and Pi in soil-rice system and providing valuable guidance to remediate flooding As-contaminated paddy soils by using schwertmannite.

2. Materials and methods

2.1. Sampling of As-contaminated paddy soil and the preparation of schwertmannite

The As-contaminated soil was collected from the surface (0–20 cm) of paddy fields (113°1'N, 25°35'E) located in Chenzhou City, Hunan Province in China. The soil was air-dried in a greenhouse and then passed through a 2 mm sieve. The physicochemical properties and element contents of the paddy soil are shown in Table S1, and the content of As in the soil was as high as 88.64 mg/kg. Schwertmannite was biosynthesized through oxidizing ferrous sulfate by *Acidithiobacillus ferrooxidans* LX5, and the detailed synthesis process is described in Text S1. XRD patterns of the prepared iron precipitates (Fig. S1) confirmed that it is pure schwertmannite, and its chemical formula can be expressed as $\text{Fe}_8\text{O}_8(\text{OH})_{4.16}(\text{SO}_4)_{1.74}$. The respective adsorption capacity of As-contaminated soil and schwertmannite for As and Pi was studied via batch isotherm experiments, the details of which is shown in Text S2.

2.2. The pot experiment

The As-contaminated paddy soil was divided into two groups. One group was amended with Pi fertilizer ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) alone, while the other group was amended with Pi fertilizer and schwertmannite together. According to the results of our preliminary experiments, amending the As-contaminated paddy soil with 0.5% (w/w) schwertmannite was sufficient to immobilize As in the tested paddy soil. The application rate of Pi fertilizer was set to 0, 75, 150, 300, 600 mg Pi/kg soil. There were totally ten treatments, which included: (1) without either Pi fertilizer or schwertmannite (Control); (2) 75 mg/kg Pi alone (75 Pi); (3) 150 mg/kg Pi alone (150 Pi); (4) 300 mg/kg Pi alone (300 Pi); (5) 600 mg/kg Pi alone (600 Pi); (6) 0.5% (w/w) schwertmannite alone (0.5% Sch); (7) 75 mg/kg Pi and 0.5% (w/w) schwertmannite (75 Pi + 0.5% Sch); (8) 150 mg/kg Pi and 0.5% (w/w) schwertmannite (150 Pi + 0.5% Sch); (9) 300 mg/kg Pi and 0.5% (w/w) schwertmannite (300 Pi + 0.5% Sch); (10) 600 mg/kg Pi and 0.5% (w/w) schwertmannite (600 Pi + 0.5% Sch). Each treatment was performed in triplicates. The application rate of base fertilizer was 0.2 g N/kg soil by $\text{CO}(\text{NH}_2)_2$ and 0.08 g $\text{K}_2\text{O}/\text{kg}$ soil by KCl. For each pot, 3 kg of As-contaminated soil was manually and thoroughly mixed with Pi fertilizer and/or schwertmannite, and the mixture was then transferred to a 5 L PVC pot. Each pot was submerged with tap water for one week before rice planting. Uniformed rice seedlings were selected and then transplanted to experimental pots with three plants in each pot. Tap water was added daily into each pot to maintain the flooding of the soils until harvest. In the controlled greenhouse (day 32 ± 3 °C/night 24 ± 3 °C), all pots were placed randomly. During the rice growth (from August 10 to December 11), the redox potential (Eh) of soil was regularly determined at 8 cm below the soil surface using Pt/Ag–AgCl electrodes.

2.3. Collection and analysis of soil porewater samples

Soil porewater was collected using rhizo-samplers (Rhizon SMS, Rhizosphere Research Products). During rice cultivation, 10 mL of soil porewater was collected at each sampling time, which was split into two aliquots. One aliquot was immediately used for the determination of pH, and the other one was filtered through 0.45 μm membrane filter to remove any particles. In order to prevent the precipitation of As and Fe ions, the filtrate was immediately acidified with 5% hydrochloric acid (HCl) and then stored at 4 °C before analysis. The total Pi and As concentrations in soil porewater samples were determined by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer NexION 300X, USA). The dissolved Fe concentration in soil porewater samples was determined by 1,10-phenanthroline method, and the concentration of SO_4^{2-} in soil porewater samples was determined by turbidimetric analysis (Burton et al., 2008).

2.4. Analysis of soil and plant samples

Around of 5 g of soil sample was collected from each pot at Day 60, 90 and 120 of rice growth. Upon collection, the soil was freeze-dried and then determined for the content of available As and P. The extraction of available As followed the method described by Sun et al. (2019). Briefly, 1 g of freeze-dried soil was weighted and then placed in a 50 mL polyethylene centrifuge tube, which was added with 25 mL of 0.5 mol/L sodium bicarbonate solution (NaHCO_3 , pH 8.5), shaken at 180 rpm and 25 °C for 4 h, and finally centrifuged at 3000 rpm for 10 min. The supernatant was filtered through 0.45 μm cellulose membrane and then used for the determination of available As. The soil available P was also extracted using 0.5 mol/L NaHCO_3 solution according to Hu et al. (2020).

At mature stage, rice plants were harvested, washed with tap water, and then rinsed with deionized water for more than three times. The shoot biomass of mature rice plants was measured. The rice plants were divided into four parts, i.e., root, straw, husk and rice grain. Each part of rice plants was oven-dried at 70 °C to a constant weight. The dry tissues were ground in stainless steel mill to fine homogenized powders, digested using $\text{HNO}_3/\text{H}_2\text{O}_2$ (4:1, v/v), and finally determined for As and P using ICP-MS.

2.5. Analysis of As, P and Fe in Fe plaque

At mature stage, a part of cleaned rice roots was used for Fe plaque analysis. Fe, As and P in Fe plaque on the surface of fresh rice root were extracted with dithionite-citrate-bicarbonate (DCB) solution (Dai et al., 2020; Hu et al., 2020). The harvested rice roots were firstly washed with deionized water. Around 5 g of the cleaned rice roots was placed in 40 mL of extraction solution with 0.03 mol/L sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) and 0.125 mol/L NaHCO_3 for 10 min. After that, the extraction solution was added with 0.6 g of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), shaken at room temperature for 1 h, and finally filtered through 0.45 μm cellulose membrane. The concentration of Fe, As and P in DCB extraction solution was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer Optima, 2000DV, Waltham, MA, USA). After DCB extraction, the roots were thoroughly rinsed with deionized water, dried at 70 °C for 48 h, and then weighted to obtain its dry weight.

In addition, the species of S, Fe and As in Fe plaque on the surface of freeze-dried rice root were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi), and the C1s peak of the aliphatic carbons at 284.8 eV was used to calibrate the spectra binding energy (Yang et al., 2020).

2.6. Data analysis

Data analysis was performed using SPSS 20 software package (IBM,

USA). Data presented herein represent means ($n = 3$) \pm standard deviation (SD). Duncan's test was applied to check the least significant differences between the mean values of treatments at the level of $P < 0.05$. The XPS spectra were deconvoluted using the Avantage software.

3. Results

3.1. Effect of Pi fertilization along with schwertmannite amendment on the concentration of dissolved As, Pi and Fe in the porewater of As-contaminated paddy soil

As shown in Fig. 1a, in soils amended with Pi fertilizer alone the As concentration in soil porewater showed an obvious increase depending on the amount of Pi applied, and in each treatment the As concentration in soil porewater increased steadily with rice growth and remained stable after around 60 days. The As concentration in porewater of the soil amended with 75 mg/kg Pi alone was in a range of 199.1–288.9 $\mu\text{g/L}$ during rice growth, which was insignificantly different or only slightly higher than that in porewater of soil without either Pi or schwertmannite amendment. However, amending the soil with 150–600 mg/kg Pi alone increased the As concentration in soil porewater to 234.7–854.7 $\mu\text{g/L}$ during rice growth, while the peak values were as high as 517.0 $\mu\text{g/L}$, 464.3 $\mu\text{g/L}$ and 854.7 $\mu\text{g/L}$ in soils amended with 150, 300, and 600 mg/kg Pi alone, respectively. When the As-contaminated paddy soil was amended with Pi fertilizer and schwertmannite together, the As concentration in soil porewater was obviously reduced, in comparison to that with the corresponding amount of Pi fertilizer alone. The As concentration in porewater of soil amended with 0.5% (w/w) schwertmannite and 0, 75, 150, 300 or 600 mg/kg Pi was only 42.4–171.6, 54.5–170.8, 49.3–343.4, 53.6–231.7 and 98.6–395.4 $\mu\text{g/L}$, respectively. It is noteworthy that, during the early growth stage of rice (Day 10–30), the As concentration in porewater of soil amended with Pi fertilizer and schwertmannite together was in a range of 42.4–105.5 $\mu\text{g/L}$, only being 17.3%–33.2% of As concentrations in porewater of soil amended with Pi fertilizer alone or even without Pi fertilization. Even though they increased slightly during the late growth stage of rice (Day 60–120), they were still much lower than that of soil amended with Pi fertilizer alone. These results obviously show that Pi fertilization alone would increase the As concentration in porewater of As-contaminated paddy soil, but schwertmannite amendment that was along with Pi fertilization was very effective to reduce the As concentration in soil porewater during rice growth.

As shown in Fig. 1b, amending the paddy soil with 600 mg/kg Pi, either alone or along with schwertmannite, significantly increased ($P < 0.05$) the dissolved Pi in soil porewater, while the amendment with 75, 150 and 300 mg/kg Pi, regardless of alone or in combination with schwertmannite, exhibited marginal effect on the Pi concentration in soil porewater. In addition, in comparison to the Pi fertilization alone, amending the paddy soil with Pi fertilizer and schwertmannite together slightly reduced the dissolved Pi concentration in soil porewater at Day 0–30, but the difference between the groups with or without schwertmannite gradually disappeared at the late growth stage of rice (Day 60–120). It is also noteworthy that during the whole growth period of rice the concentration of Pi in soil porewater was always at a low level, only 0.16–0.93 mg/L, which may be attributed to the strong adsorption and immobilization ability of paddy soil for Pi. During the growth of rice, the concentration of dissolved Fe in soil porewater of all treatments gradually increased and then remained stable (Fig. 1c). On the one hand, amending the paddy soil with Pi fertilizer alone did not lead to any significant increase in the dissolved Fe concentration in soil porewater, in comparison to that of control. On the other hand, amending the paddy soil with Pi fertilizer and schwertmannite together significantly increased the concentration of dissolved Fe in soil porewater at Day 0–60 ($P < 0.05$), but the difference gradually decreased with the growth of rice (Day 90–120). These results clearly show that schwertmannite was the main contributor to the dissolved Fe in soil porewater when the

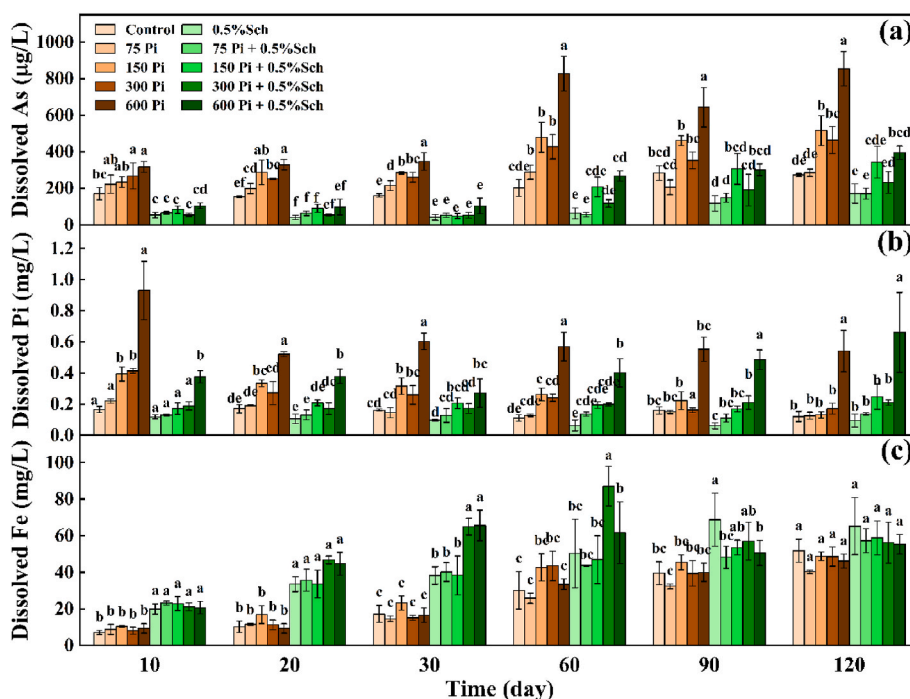


Fig. 1. Changes in the concentration of dissolved As (a), Pi (b), and Fe (c) in soil porewater during the growth of rice planted in paddy soil that was amended with 0–600 mg/kg Pi alone or along with 0.5% (w/w) schwertmannite. Columns marked with the same letter in one group do not differ significantly from each other at $P < 0.05$.

flooding As-contaminated paddy soil was amended with Pi fertilizer and schwertmannite together.

3.2. Effect of Pi fertilization along with schwertmannite amendment on the contents of available P and As in paddy soil

As shown in Fig. 2a, the content of available P in the As-contaminated paddy soil was around 9.98, 9.94 and 8.01 mg/kg on Day 60, 90 and 120, respectively. Although amending the paddy soil with 75 mg/kg Pi alone did not significantly increase the available P content in soil, the soil available P content has been significantly increased by the fertilization of 150, 300 and 600 mg/kg Pi alone. In

particular, amending the paddy soil with 600 mg/kg Pi alone drastically increased the soil available P content to as high as 24.43–29.98 mg/kg during rice growth. Schwertmannite amendment that was along with Pi fertilization did not significantly change the effect of Pi fertilization on the soil available P content during rice growth. These results suggested that when As-contaminated paddy soil was amended with Pi fertilizer and schwertmannite together, schwertmannite did not reduce the availability of soil P.

Amending the As-contaminated paddy soil with 75–300 mg/kg Pi alone did not significantly increase the content of available As in soil, in comparison to that of control, but the fertilization of 600 mg/kg Pi alone resulted in an increase of soil available As to 4.18–5.26 mg/kg during

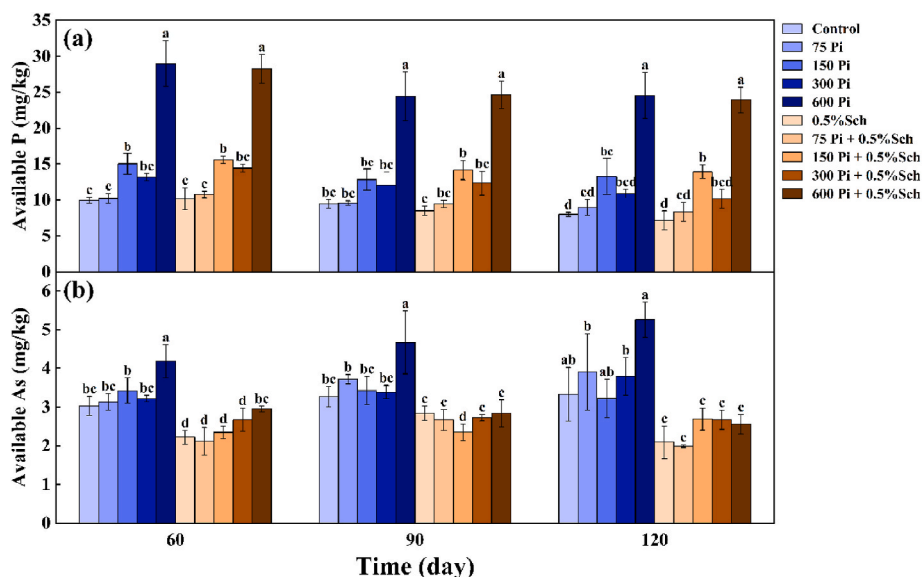


Fig. 2. Changes in the contents of available P (a) and available As (b) in the As-contaminated paddy soil that was amended with 0–600 mg/kg Pi alone or along with 0.5% (w/w) schwertmannite. Columns marked with the same letter in one group do not differ significantly from each other at $P < 0.05$.

rice growth (Fig. 2b). This means that the fertilization of high dosage Pi alone can enhance the mobility of As in soil and may consequently increase the health risk associated with As in paddy soil. However, compared with Pi fertilization alone, amending the As-contaminated paddy soil with Pi fertilizer and schwertmannite together markedly ($P < 0.05$) reduced the content of available As in soil by 19.62%–51.37% during rice growth. These results show that even though the Pi fertilization has the potential of increasing soil available As content, schwertmannite amendment was still useful to reduce the mobility of As in soil, regardless of Pi fertilization.

3.3. Effect of Pi fertilization along with schwertmannite amendment on the contents of Fe, As and P in Fe plaque on rice root surface

As shown in Fig. 3a, the Fe content in Fe plaque on rice root surface did not change significantly when the paddy soil was amended with 75–600 mg/kg Pi alone or along with 0.5% (w/w) schwertmannite. Although amending the paddy soil with 75–600 mg/kg Pi fertilizer alone did not significantly change the content of As in Fe plaque, the amendment of Pi fertilizer and schwertmannite together has reduced the As content in Fe plaque by 53.86%–70.77% (Fig. 3b). The content of P in Fe plaque was significantly increased by the amendment of 150, 300 or 600 mg/kg Pi alone. However, the P content in Fe plaque was obviously reduced by the amendment of 150, 300 or 600 mg/kg Pi along with schwertmannite, in comparison to that with corresponding dosage of Pi alone (Fig. 3c). These results show that amending the As-contaminated paddy soil with Pi fertilizer and schwertmannite together can reduce the retention of P by Fe plaque, thus probably increasing the usefulness of Pi fertilization in improving rice growth.

The oxidation states of S, Fe and As in Fe plaque were determined by XPS. The S 2p spectrum of Fe plaque showed the splitting peaks of sulfate (SO_4^{2-}), elemental sulfur (S_0), polysulfide (S_n^{2-}) and sulfide ion (S^{2-}), corresponding to binding energies of 168.19–168.69 eV, 164.17–164.91 eV, 163.02–163.49 eV and 161.24–162.02 eV, respectively (Fig. 4 and Fig. S2). Obviously, S^{2-} band did not appear in S 2p spectrum of Fe plaque formed in the treatments with Pi fertilization alone (Fig. 4 a-b and Fig. S2 a-c), whereas S^{2-} accounted for 4.27%–10.41% of the peak areas in the treatments with schwertmannite alone or along with Pi fertilizer (Fig. 4 c-d and Fig. S2 d-f). These results

indicated that schwertmannite amendment has changed sulfur species in Fe plaque, regardless of Pi fertilization.

The results of Fe $2p_{3/2}$ spectrum (Fig. 5 and Fig. S3) showed that the Fe species of Fe plaque included Fe(II) and Fe(III), and their proportions were 48.95%–66.54% and 33.46%–51.05%, respectively. Specifically, Fe plaque contained Fe (II)-S, Fe (II)-O, Fe (III)-S and Fe (III)-O components, which corresponded to the peak locations at 707.93–708.10 eV, 709.33–710.65 eV, 711.53–712.18 eV and 713.44–714.64 eV, respectively. The proportion of Fe–O compounds was greater than those of Fe–S compounds in Fe plaques formed in all treatments. In addition, when the As-contaminated paddy soil was amended with Pi fertilizer and schwertmannite together, the proportion of Fe–S compound in Fe plaque was obviously increased, in comparison to that with the corresponding amount of Pi fertilizer alone (Fig. 5 and Fig. S3).

Fig. S4 showed the XPS As 3d of Fe plaque on root surface. Previous studies indicated that the peak at 43.8 eV was related to As(III) species, while the peak at 45.5 eV was assigned to As(V) species (Hu et al., 2015b; Prucek et al., 2013). When the As-contaminated soil was amended with Pi fertilizer alone or along with schwertmannite, As(III) was the main species existing in Fe plaques, which accounted for 62.73%–78.55% of the total As. In comparison, a small fraction of As(V) (21.45%–35.29%) was observed in Fe plaque. Obviously, the species of As in Fe plaque has not greatly changed by either Pi fertilization or schwertmannite amendment.

3.4. Effect of Pi fertilization along with schwertmannite amendment on the shoot biomass and As content in different tissues of rice plants

Fig. 6a shows the shoot biomass of rice that was planted in As-contaminated soil amended with Pi fertilizer alone or along with schwertmannite. In the control, the rice shoot biomass was 0.093 kg/plant. Pi fertilization, regardless of alone or along with schwertmannite, significantly increased the shoot biomass to 0.115–0.128 kg/plant, even though the increase in shoot biomass did not depend on the amount of Pi fertilizer applied. Additionally, the shoot biomass of rice that was planted in As-contaminated soil amended with Pi fertilizer and schwertmannite together did not differ significantly from that with Pi fertilizer alone. All these results show that schwertmannite amendment did not decrease the effectiveness of Pi fertilization in improving rice

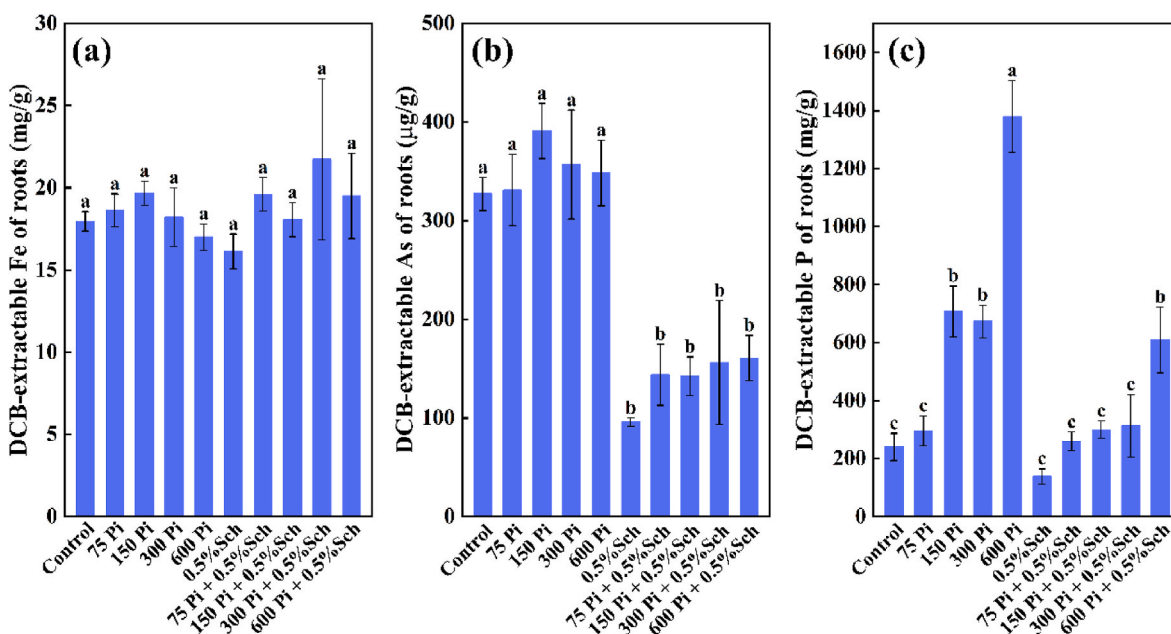


Fig. 3. DCB-extractable Fe (a), As (b) and P (c) contents on the root surface of rice plants. Columns marked with the same letter in one group do not differ significantly from each other at $P < 0.05$.

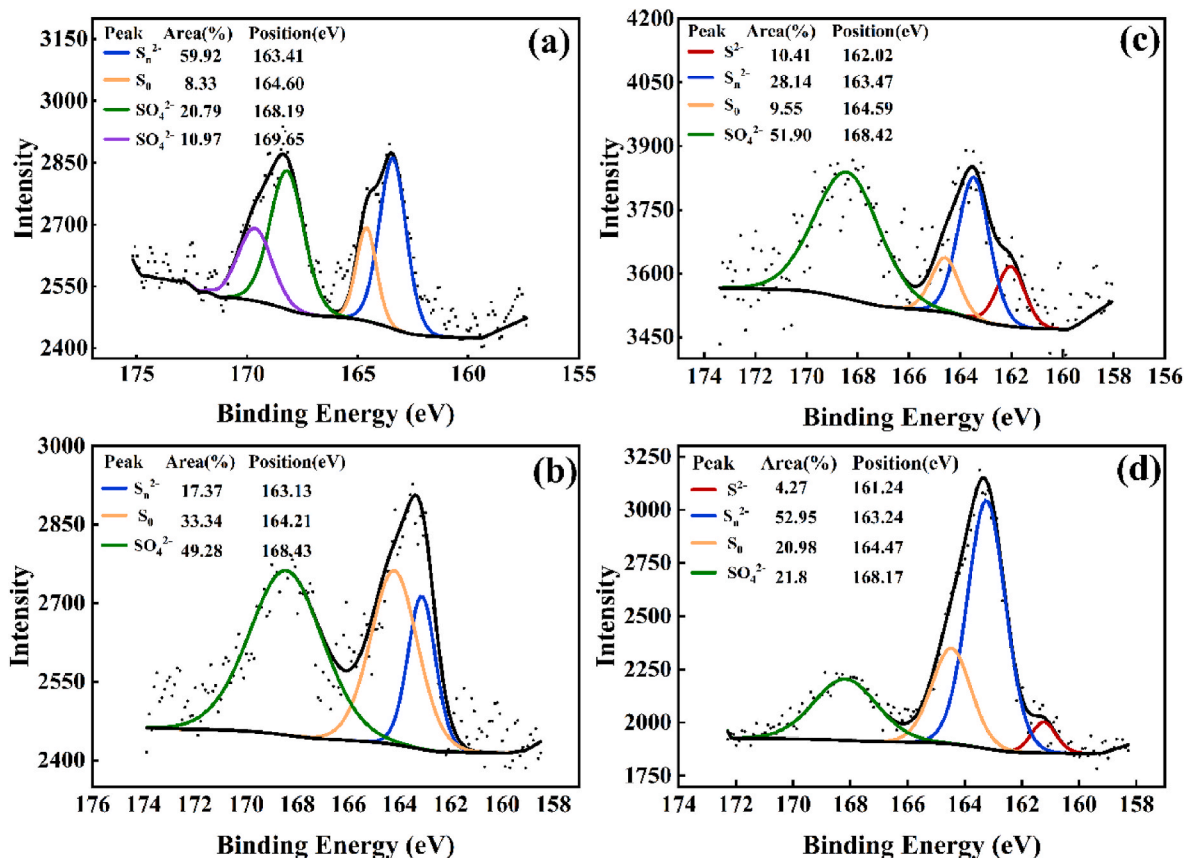


Fig. 4. XPS spectra of S 2p in Fe plaques on rice roots. (a), (b), (c), (d) represent the treatments of control, 600 mg/kg Pi, 0.5% (w/w) schwertmannite, 600 mg/kg Pi and 0.5% schwertmannite, respectively.

growth.

The content of As in rice tissues at maturity is shown in Fig. 6 b-d. The As content in different tissues of rice plant followed the order of root > straw > husk > rice grains. Compared with the control, Pi fertilization alone did not significantly change the As content in root, straw and husk, and even grains, except that the fertilization of 600 mg/kg Pi alone slightly decreased the As content in rice grains. Although schwertmannite amendment alone or with Pi fertilization together had no significant effect on As content in rice straw and husk, they indeed reduced the As content in root and, in particular, drastically decreased the As content in grains. The As content in rice grains of the control and the treatments with Pi fertilization alone was in a range of 1.06–1.47 mg/kg, while the As content in rice grains of the treatments amended with schwertmannite alone or along with Pi fertilizer was only 0.38–0.63 mg/kg (Fig. 6d).

4. Discussion

4.1. Pi fertilization along with schwertmannite amendment was effective to reduce the mobility of As in flooding paddy soil and meanwhile increase soil P availability

When paddy soil is flooded, the dissimilative reduction and dissolution of Fe minerals containing As leads to a considerable release of As into soil solution (Dai et al., 2020). Additionally, Pi fertilization in As-contaminated paddy soil may aggravate the degree of As release because of the competition of Pi for As-binding sites on the surface of soil particles (Anawar et al., 2018; Wu et al., 2022). In the present study, Pi fertilization alone obviously increased the As concentration in porewater of paddy soil (Fig. 1a), which can be explained as that the occupancy of As-binding site on the surface of soil particles by Pi resulted in

the stripping of As from soil surface and its consequent release into soil porewater. In fact, this is consistent with the results of Lee et al. (2016) and Yang et al. (2020). It is noteworthy that when schwertmannite was applied together with Pi fertilizer, the As concentration in soil porewater was greatly decreased to the level even much lower than that of control ($P < 0.05$) (Fig. 1a). These results indicated that schwertmannite was effective to reduce the mobility of As in flooding As-contaminated paddy soil, since schwertmannite has a strong adsorption capacity for As (142.7 mg/g, Fig. 7 and Table S2) and can quickly adsorb the released As resulting from both dissimilative reduction and dissolution of iron minerals and Pi fertilization, without being affected by Pi (Dou et al., 2013; Meng et al., 2021; Paikaray et al., 2012, 2011). The decrease in soil available As content achieved by schwertmannite amendment (Fig. 2b) further proved that schwertmannite has greatly reduced the mobility of As in contaminated paddy soil, no matter whether the paddy soil was amended with Pi fertilizer. Burton and Johnston (2012) and Burton et al. (2008) confirmed that in drained sediment and re-flooded soil, schwertmannite would undergo mineral phase transformation through Fe (II)-pathway, which was initiated by Fe (II) produced by bacterially mediated Fe(III) reduction. In the present study, the lower soil Eh (Fig. S5a) was suitable for the reduction of schwertmannite, and the release of SO₄²⁻ also proved that the mineral phase transformation of schwertmannite occurred (Fig. S6). In spite of the recrystallization of schwertmannite, the concentration of As in soil porewater still remained at a low level during the rice growth (Fig. 1a). This phenomenon can be attributed to the fact that in the process of Fe(II)-catalyzed recrystallization of schwertmannite to form new minerals, the As adsorbed on the surface or tunnels of schwertmannite most probably can be embedded in the interior of the newly minerals such as goethite, which has a strong stability and can greatly retard the re-release of As (Handler et al., 2014). Additionally, it is hard to rule out the possibility that

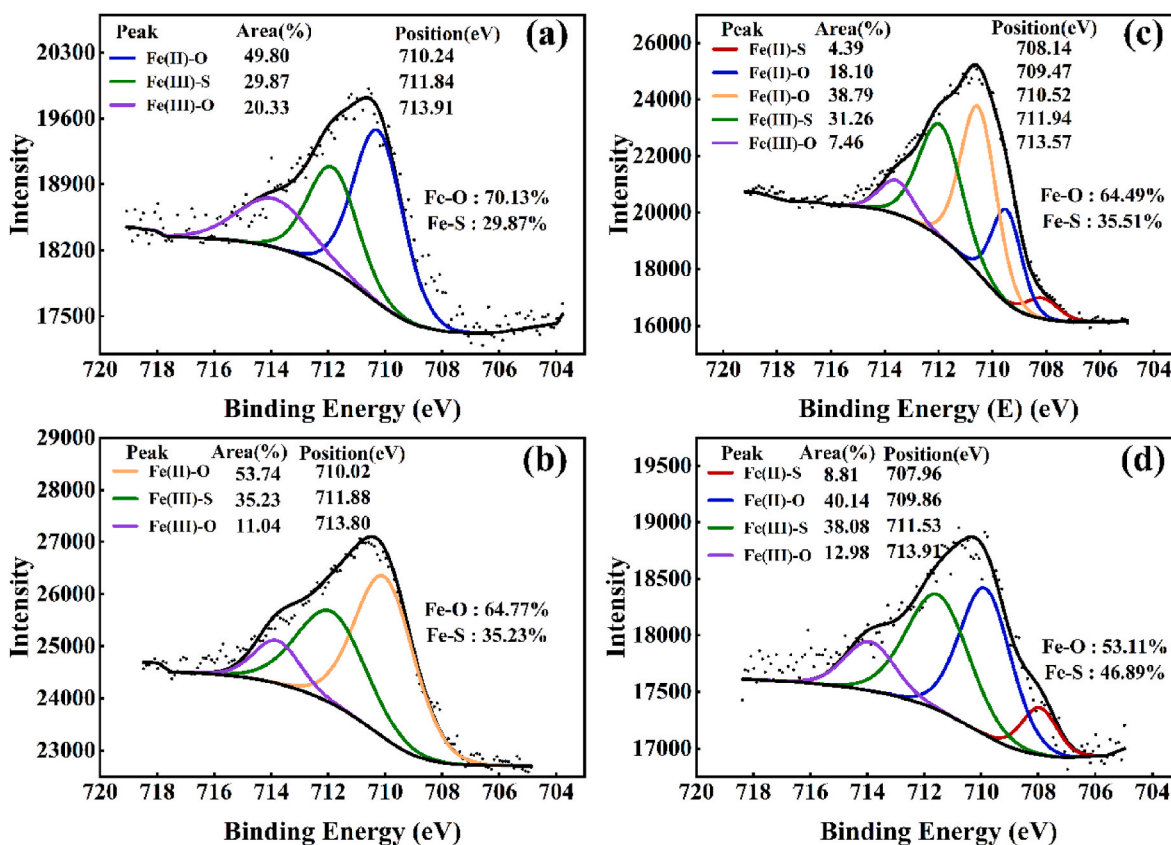


Fig. 5. XPS spectra of Fe 2p_{3/2} in Fe plaques on rice roots. (a), (b), (c) and (d) represent the treatments of control, 600 mg/kg Pi, 0.5% (w/w) schwertmannite, 600 mg/kg Pi and 0.5% schwertmannite, respectively.

schwertmannite may serve as an electron acceptor to compete with As (V) for accepting electrons, consequently lowering the reduction of As (V) and decreasing its availability.

Previous studies showed that when the amount of Fe (III) oxides/hydroxides was more than 0.2% (w/w), the content of available P in soil can be significantly reduced (Hu et al., 2020). On the other hand, the application of Pi fertilizers in As-contaminated paddy soils may lower the immobilizing ability of Fe(III) oxides/hydroxides for soil As (Im et al., 2015; Ngantcha-Kwimi and Reed, 2020). In the present study, schwertmannite amendment significantly reduced soil available As ($P < 0.05$) but did not change soil available P (Fig. 2a), indicating that schwertmannite did not change the distribution of P between the solid and liquid phases in paddy soil. In other words, amending As-contaminated paddy soil with schwertmannite would not lower the utilization efficiency of Pi fertilizers.

Paddy soils have strong retention capacity for P (Fox and Kamprath, 1970; Lee et al., 2016), and the maximum retention capacity of the tested paddy soil for Pi reached 1.66 mg/g (Fig. 7, Table S2). Such high Pi retention led to the low Pi concentration in soil solution (< 0.54 mg/L, Fig. 1b) at the end of the pot experiment when the tested paddy soil was amended with Pi fertilizer alone, since a large amount of Pi was adsorbed by soil particles. When the tested paddy soil was amended with Pi fertilizer and schwertmannite together, the Pi concentration in soil solution was still as low as that of Pi fertilization alone, implying that soil particles still played important roles in retaining large amounts of P even when schwertmannite was present in the paddy soil. Although the maximum adsorption amount of schwertmannite for Pi can be 20.6 mg/g, much higher than that of soil particles for Pi (Fig. 7, Table S2), the amount of schwertmannite being introduced into the paddy soil was only 0.5% (w/w) of the paddy soil amount. It can thus be calculated that the total maximum amount of Pi retained by soil particles and schwertmannite can be 4980 mg and 309 mg in each pot, respectively,

revealing that the mobility of P in the paddy soil mainly depended on the soil particles rather than schwertmannite. Since the exchange coefficient of As(III)/SO₄²⁻ ($K = 0.299$) is greater than that of Pi/SO₄²⁻ ($K = 0.070$) (Fig. S7), schwertmannite is more likely to adsorb As(III) rather than Pi. In addition, the low Pi concentration in soil solution (< 0.66 mg/L, Fig. 1b) at the end of pot experiment, when the tested paddy soil was amended with schwertmannite alone or along with Pi fertilizer, was not enough to compete with As(III) for the adsorption sites on schwertmannite. For instance, Liao et al. (2011) showed that only when Pi concentration in solution reached at least 310 mg/L, the As(III) adsorbed on the surface of schwertmannite began to desorb. Therefore, amending the As-contaminated paddy soil with schwertmannite can effectively reduce the mobility of soil As in the paddy soil but without decreasing the bioavailability of P.

4.2. Schwertmannite amendment has reduced the adsorption of As and P on Fe plaque

Previous studies showed that extreme P deficiency in paddy soils promoted the formation of Fe plaque on rice roots, but Fe plaque was not affected when soil P was sufficient (Fu et al., 2014; Yang et al., 2020). In the present study, the total P content in the tested paddy soil was as high as 619.7 mg/kg (Table S1), which may explain why amending it with Pi fertilizer alone or along with schwertmannite has not influenced the formation of Fe plaque on rice roots. It is noteworthy that compared with Pi fertilization alone, amending the tested paddy soil with schwertmannite, either alone or with Pi fertilizer together, has greatly reduced the As content in Fe plaque on rice roots (Fig. 3b). Given the fact that schwertmannite with extremely high sorption capacity for As had effectively immobilized the released As to lower As amount in soil solution, so much lower As in soil solution was available for Fe plaque to retain.

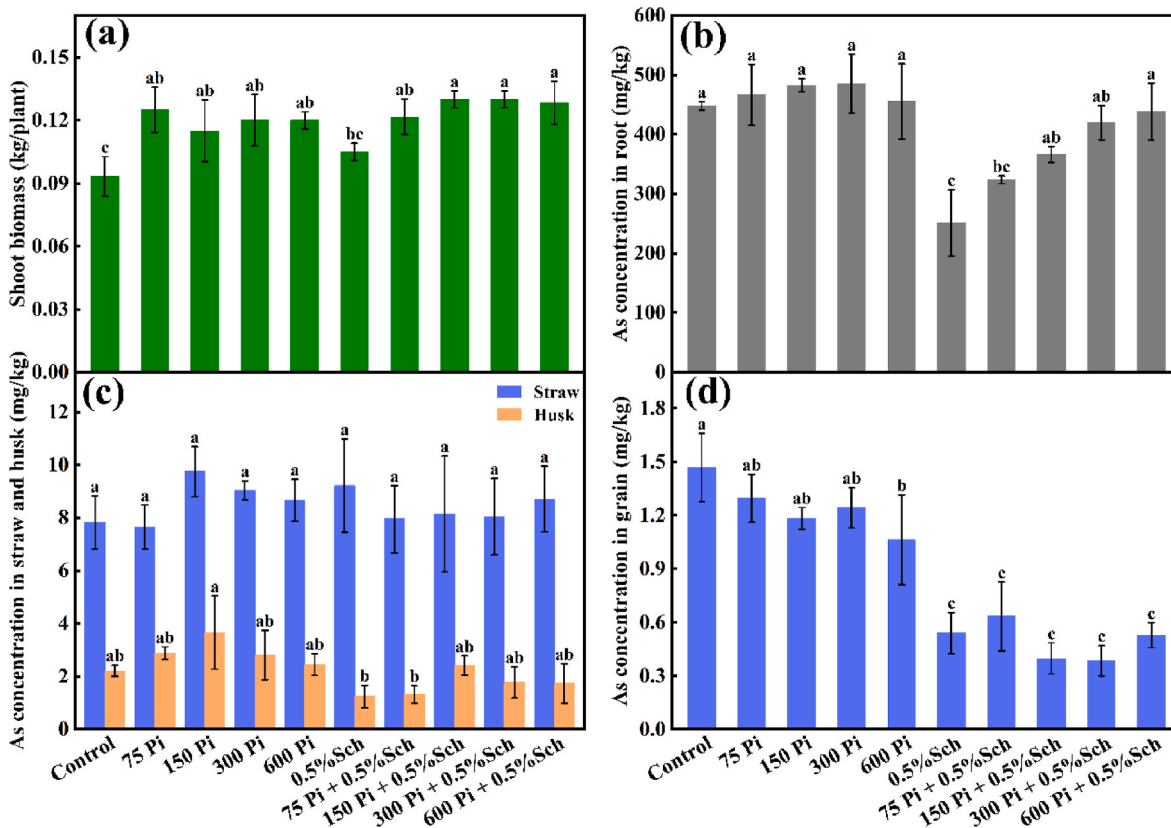


Fig. 6. The shoot biomass of rice plants (a), the content of As in roots (b), straw, husk (c) and grains (d) at harvest. Columns marked with the same letter in one group do not differ significantly from each other at $P < 0.05$.

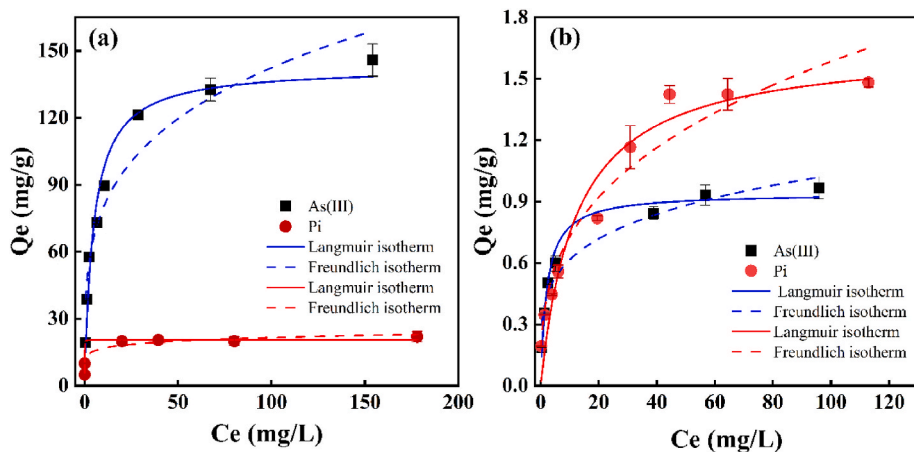


Fig. 7. Adsorption isotherm of As(III) and Pi on schwertmannite (a) or As-contaminated soil (b). Experimental conditions: schwertmannite adsorbent = 0.5 g/L, initial As(III) concentration = 0–300 mg/L and initial Pi concentration = 0–200 mg/L, initial pH = 6.5, background solution containing 0.1 M NaCl, 0.05 M MOPS and 0.05 M EMS, equilibrium time = 6 h (As(III)) or 48 h (Pi); Soil adsorbent = 20 g/L, initial As(III) and initial Pi concentration = 0–150 mg/L, background solution: 0.01 M CaCl₂, pH 7.0, equilibrium time = 7 d.

In the present study, schwertmannite amendment that was along with Pi fertilization did not affect the dissolved Pi in soil porewater and soil available P (Figs. 1b and 2a), but these treatments significantly ($P < 0.05$) reduced P content in Fe plaque on rice roots (Fig. 3c). In addition, although there was no difference in the amount of Fe plaque among all treatments (Fig. 3a), the color of Fe plaque was changed from rusty red to black and brown by schwertmannite amendment (Fig. S8). It can thus be speculated that the change of the mineral composition of Fe plaque may lead to the reduction of P retention in Fe plaque, rather than the change of the amount of Fe plaque. The change of mineral composition in Fe plaque may be induced by the SO_4^{2-} released from schwertmannite structure (Fig. S6). Under anaerobic conditions, SO_4^{2-} can be microbially reduced to S^{2-} via sulfate-reducing process, which can readily react with

Fe ions to produce Fe–S precipitates (Burton et al., 2014; Xu et al., 2019). In fact, in anaerobic environments with high sulfur content, such as sediments and flooded soil, the sulfuration of ferric (hydr)oxides often occurs (Zhang et al., 2022), which is closely related to the retention of P. When the sulfuration of ferric (hydr)oxides was enhanced, that is, a large amount of FeS/FeS₂ is produced, the retention capacity of ferric (hydr)oxides to P was sharply reduced (Rozaan et al., 2002). Furthermore, Fe–S minerals have low zero charge points and do not adsorb P at neutral pH (Bebie et al., 1998). In the present study, the pH value of soil solution was maintained in the neutral range (Fig.S5b). Based on the above results, it can be inferred that the addition of schwertmannite probably caused the sulfuration of ferric (hydr)oxides on the Fe plaque, thus reducing the retention capacity of P. The XPS

results (Figs. 4 and 5) also confirmed the formation of sulfide in Fe plaque in the treatments with schwertmannite amendment, regardless of alone or along with Pi fertilization, in which S^{2-} component appeared in XPS S 2p spectrum and meanwhile the proportion of Fe–S compounds slightly increased compared with that of treatments with Pi fertilization alone. Therefore, amending the As-contaminated soil with schwertmannite can reduce the retention of P by Fe plaque via changing the proportion of mineral species in Fe plaque, which is beneficial to improve the utilization efficiency of P by rice plants.

4.3. Pi fertilization along with schwertmannite amendment has greatly reduced grain As and meanwhile improved rice growth

Several previous studies reported that P application can enhance the mobility of As in paddy soils to increase the risk of As accumulation in rice grains (Lee et al., 2016; Lei et al., 2014; Wu et al., 2022; Yang et al., 2020). In the present study, the As content in tissues of rice plants has not been increased by amending the As-contaminated paddy soil with 75–300 mg/kg Pi alone, even though the release of As from soil particles has indeed been promoted. Furthermore, amending the paddy soil with 600 mg/kg Pi alone has significantly reduced the grain As ($P < 0.05$) and meanwhile improved rice growth (Fig. 6). In fact, As and Pi share the same transport pathway from soil to roots and from roots to shoots in rice plants (Garbinski et al., 2019; Muehe et al., 2014), which may explain why the high dose of Pi fertilizer can inhibit the absorption of As by rice plants (Jiang et al., 2014; Lei et al., 2014). We also found that As showed a significant negative correlation with P in grains ($R^2 = 0.5723$, Fig. S9), and the application of Pi fertilizer significantly reduced the translocation factor of As from roots to rice grains (Table S3). These results clearly showed that the transport of As and P in rice plants are antagonistic. It is often argued that arsenite is the main chemical species of As in flooded paddy soil and the uptake of arsenite should not be affected by P (Bogdan and Schenk, 2009; Irtelli and Navari-Izzo, 2008). However, rice roots create niches for microaerophilic arsenite-oxidizing bacteria (Hu et al., 2015a; Maisch et al., 2019; Zhang et al., 2015), where arsenite can be microbially oxidized to arsenate and then compete with phosphate for transport in rice. Additionally, the dilution effect resulted from the increased shoot biomass by Pi application might also contribute to the reduced As content in rice tissues, even though this effect should be relatively minor.

Although amending As-contaminated paddy soils with high dose of Pi fertilizer may reduce the accumulation As in rice to some extent, it seems unfeasible in practice. It mainly due to the facts that the high dose of Pi can cause P pollution, and the usefulness of Pi fertilization in reducing grain As is very limited. By contrast, amending the As-contaminated soil with Pi fertilizer and schwertmannite together has drastically reduced As content in rice grains by 50.35%–69.01% ($P < 0.05$) (Fig. 6d) and significantly improved rice growth by providing much more bioavailable P. Therefore, using schwertmannite to remediate As-contaminated paddy soils can achieve the dual goals of effectively reducing grain As and maintaining the utilization efficiency of Pi fertilizers, which is superior to conventional Fe(III) oxides/hydroxides. The present study demonstrated that schwertmannite can be used as an excellent remediation material to immobilize As in flooding paddy soil, reduce As absorption by rice, and maintain the utilization efficiency of P fertilizer. However, the phase transformation of schwertmannite in paddy soils and its associated effect on the chemical and microbial processes related with As, S and Fe changes in soils should be further investigated. Besides, the present research is limited to pot experiments, and thus the feasibility of using schwertmannite to remediate flooding As-contaminated paddy soils should be further verified by field experiments.

5. Conclusion

The present study reported for the first time the feasibility of using

schwertmannite to remediate As-contaminated paddy soil. It was found that amending As-contaminated paddy soil with schwertmannite and Pi fertilizer together can effectively reduce the mobility of soil As and meanwhile increase the availability soil P. The schwertmannite amendment along with Pi fertilization reduced the retention of P by Fe plaque on rice roots via changing the iron mineral composition of Fe plaque, which was beneficial for improving the utilization efficiency of Pi fertilizer. In particular, amending As-contaminated paddy soil with schwertmannite and Pi fertilizer together has greatly reduced the content of As in rice grains and significantly improved the growth of rice plant. All these findings suggested that remediating As-contaminated paddy soils with schwertmannite can achieve the dual goals of effectively reducing grain As and maintaining the utilization efficiency of Pi fertilizers.

Credit author statement

Ru Wang: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization. Yinglin Guo: Methodology, Formal analysis, Investigation. Yang Song: Methodology, Formal analysis, Investigation. Yuting Guo: Methodology, Formal analysis, Investigation. Xiaomeng Wang: Writing - review & editing, Visualization. Quan Yuan: Writing - review & editing, Visualization. Zengping Ning: Writing - review & editing, Visualization. Chengshuai Liu: Writing - review & editing, Visualization. Lixiang Zhou: Conceptualization, Supervision, Funding acquisition. Guanyu Zheng: Conceptualization, Validation, Formal analysis, Writing - review & editing, Visualization, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2023.121383>.

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