

RESEARCH ARTICLE

Remediation of arsenic contaminated soil by sulfidated zero-valent iron

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HIGHLIGHTS

- Sulfidation significantly enhanced As(V) immobilization in soil by zerovalent iron.
- S-ZVI promoted the conversion of exchangeable As to less mobile Fe-Mn bound As.
- Column test further confirmed the feasibility of sulfidated ZVI on As retention.
- S-ZVI amendment and magnetic separation markedly reduced TCLP leachability of As.

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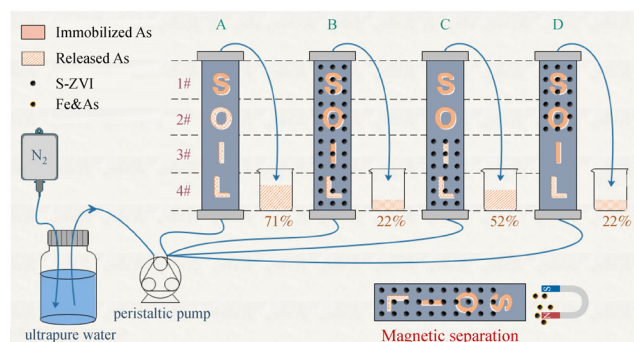
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GRAPHIC ABSTRACT



ABSTRACT

In this study, the influences of sulfidation on zero-valent iron (ZVI) performance toward As(V) immobilization in soil were systemically investigated. It was found that, compared to unamended ZVI, sulfidated ZVI (S-ZVI) is more favorable to immobilize As(V) in soil and promote the conversion of water soluble As to less mobile Fe-Mn bound As. Specifically, under the optimal S/Fe molar ratio of 0.05, almost all of the leached As could be sequestered by >0.5 wt.% S-ZVI within 3 h. Although the presence of HA could decrease the desorption of As from soil, HA inhibited the reactivity of S-ZVI to a greater extent. Column experiments further proved the feasibility of applying S-ZVI on soil As(V) immobilization. More importantly, to achieve a good As retention performance, S-ZVI should be fully mixed with soil or located on the downstream side of As migration. The test simulating the flooding conditions in rice culture revealed there was also a good long-term stability of soil As(V) after S-ZVI remediation, where only 0.7% of As was desorbed after 30 days of incubation. Magnetic separation was employed to separate the immobilized As(V) from soil after S-ZVI amendment, where the separation efficiency was found to be dependent of the iron dosage, liquid to soil ratio, and reaction time. Toxicity characteristic leaching procedure (TCLP) tests revealed that the leachability of As from soil was significantly reduced after the S-ZVI amendment and magnetic separation treatment. All these findings provided some insights into the remediation of As(V)-polluted soil by ZVI.

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1 Introduction

Arsenic (As) contamination in soils has been reported in many countries because of its wide use in various products and uncontrolled release during a series of human activities such as the use of arsenical pesticides and herbicides, combustion of fossil fuels, and ore mining and smelting

operations (Al-Abed et al., 2007; Bitema et al., 2007). As it is well known that arsenic is toxic to humans and animals, it has been regarded as one of the most health hazardous carcinogens by the International Agency for Research on Cancer (IARC) (Anders et al., 2004). Under oxic conditions, arsenic exists mainly in As(V) oxidation state as the arsenate oxyanion (HAsO_4^{2-} , H_2AsO_4^-), while under anoxic conditions, arsenic is commonly present as As(III) oxidation state as the arsenite molecule (H_3AsO_3) (Al-Abed et al., 2007; Bitema et al., 2007). Due to its high mobility and bio-availability, soil arsenic may transport to

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the groundwater and eventually the food chain through biotic and abiotic processes under environmental conditions (Jones et al., 1997; Macur et al., 2001). There is substantial evidence that arsenic can be ingested through food, for example, it can be accumulated in crops planted in As-contaminated soil (Das et al., 2004; Zavala and Duxbury, 2008). Therefore, there is an urgent demand to develop efficient, reliable, and economical technologies for remediation of As-contaminated soil.

Due to the excellent adsorption ability of iron oxides toward arsenic (Jung et al., 2009), many studies have proven that zero-valent iron (ZVI) can be employed for remediation of As-contaminated soil through the adsorption and/or co-precipitation processes (Bang et al., 2005; Bitema et al., 2007; Mak et al., 2009; Peng et al., 2017). According to this removal mechanism, the sequestration of As by ZVI could be improved by the growth and accumulation of iron (hydr)oxide minerals which are generated during the corrosion of ZVI. From another perspective, however, despite the formation of more iron oxides that could increase the surface area for arsenic sequestration, breakdown of the passivating oxide film on ZVI surface may be necessary to guarantee sustained dissolution of ZVI. Actually, in most cases, due to the presence of the pre-existing iron oxide film, the reactivity of traditional ZVI is low and it will decline further with the accumulation of passive iron oxides (Dou et al., 2010). Therefore, the traditional iron particles are generally not effective in As sequestration either from water or soil. To overcome this drawback, some strategies have been proposed over the past two decades, such as pretreatment with a weak magnetic field (Sun et al., 2014) or reduced sulfur species (Su et al., 2016; Fan et al., 2017), decreasing iron particle size to nanoscale (Comba et al., 2011), coupling ZVI with other materials (e.g., Cu (O'Carroll et al., 2013), activated carbon (Dou et al., 2010)), and assisting with chemicals (Fe^{2+} (Tang et al., 2014), oxidants (Guo et al., 2015)).

Among these approaches, sulfidation pretreatment is prevailing in recent years and is considered to be one of the most favorable methods to improve ZVI performance in terms of both reactivity and selectivity (Su et al., 2016; Fan et al., 2017). Sulfidation of ZVI is generally achieved by the reaction of ZVI particles and low valent sulfur species (e.g., S, Na_2S , and $\text{Na}_2\text{S}_2\text{O}_4$) in aqueous-solid phase or solid-solid phase (Fan et al., 2017). As a consequence, sulfidated ZVI (S-ZVI) is typically characterized as a Fe^0 core and a FeS_x shell. It was reported that the FeS_x shell was much more active than the iron oxide film, which can facilitate the electron transfer from Fe^0 core to the target contaminants and/or the accumulation of specific contaminants onto ZVI surface (He et al., 2018). Su et al. (2016) found that, compared to unamended nanoscale ZVI (nZVI), sulfidated nZVI was more efficient in Cd^{2+} removal from water, in which a maximum Cd^{2+} removal capacity of 85 mg/g was obtained under oxygen-limited

conditions. It was proposed that, under anoxic conditions, Cd removal at low S/Fe molar ratios is mainly through adsorption and complexation, while the formation of $\text{Fe}_{1-x}\text{Cd}_x\text{S}$ phases became dominant at high S/Fe molar ratios. By using microscale ZVI, Huang et al. (2018) also revealed that sulfidated ZVI could significantly accelerate the antimonite (Sb(III)) sequestration rates from 0.0012 to 0.018 min^{-1} via adsorption and coprecipitation. All these studies highlighted the advantages of sulfidation on the decontamination performance of ZVI in aqueous phase. Nevertheless, few studies have been carried out to examine the feasibility of S-ZVI in remediating the heavy metal (loid) (especially As) contaminated soils, despite ZVI based technology is also a commonly used means for soil remediation as mentioned above.

For remediation of heavy metal(loid) contaminated soil, although many methods could enhance the stabilization of heavy metal(loid)s and minimize their release from soil, their total amounts would not be reduced through these immobilization processes (including ZVI), from the perspective of eliminating the environmental risk of heavy metal(loid) completely. Thus, there may still exist a concern about the transformation of the immobilized metal(loid)s which may become available again with the fluctuation of soil redox conditions. To solve this challenge, several studies have proposed that the combination of ZVI sequestration and magnetic separation could remove the heavy metal(loid)s from soil (Phenrat et al., 2019; Zhou et al., 2020). In a recent study, we also found that S-ZVI could enhance soil Cr(VI) immobilization and more importantly, combining with a magnetic separation process, the immobilized Cr could be retrieved from soil (Guan et al., 2019). However, the recovery efficiency of Cr by magnetic separation was not very efficient where only 9.5%–33.6% of the total Cr could be removed. Therefore, the long-term stability of residual heavy metal(loid)s after S-ZVI treatment and magnetic separation still needs further investigations.

Accordingly, taking As(V) as a probe, the objectives of this study were to (i) evaluate the effects of sulfidation on ZVI performance toward soil As(V) immobilization under different operating conditions; (ii) investigate the transformation of the As forms after S-ZVI amendment; (iii) explore the As migration under intensive leaching conditions in column tests and its retention in stabilized soil upon the changeover of redox conditions; and (iv) examine the feasibility of using magnetic separation to retrieve As from S-ZVI treated soils.

2 Materials and methods

2.1 Materials

Analytical grade chemicals were used as received in this study. All solutions were prepared with deionized water

from a Milli-Q system. The microscale ZVI particles (a mean diameter of 46.2 μm) employed in this work was purchased from Alfa Aesar Chemicals Company (Shanghai, China). S-ZVI was prepared following a ball-milling method used in our previous study (Guan et al., 2019). Briefly, the elemental sulfur and iron particles with different molar ratios were mixed evenly and placed into a planetary ball mill (Boyuntong Instrument Technology, Nanjing, China) followed by being milled for 4 h at a mixing rate of 500 r/min. The ball-milled ZVI without adding elemental sulfur, noted as ZVI^{bm} , was also fabricated for comparison. All the obtained ZVI^{bm} and S-ZVI samples were freeze-dried for 24 h and stored in a N_2 -filled glovebox (Mikrouna, China).

2.2 Soil preparation

The raw soil sample used in this work was obtained from a paddy field in Shanghai, China. The physiochemical properties of raw soil are given in Table S1. Before use, the raw soil material was washed three times to remove the soluble compounds and suspended solids, and then air-dried, homogenized, and screened through a 2-mm mesh. Thereafter, the soil was spiked with two levels of As(V) (105.5 and 749.1 mg/kg As(V) using $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$). Noted that, after the As(V) spiking process, the mixture was mechanically stirred for about one week and then air-dried for another one week.

2.3 Batch experiments

Unless otherwise specified, batch tests were carried out in a range of 50-mL glass vials. Two grams of As(V)-laden soil was weighed into the vials and mixed with 10 mL ultrapure water. Adjustment of initial soil pH with NaOH and HCl was only made during the experiments examining the pH effect on S-ZVI performance. To initiate the reaction, different amounts of iron particles were dosed into the mixtures. Then, the reactors were placed on a water bath shaker at 220 oscillation/min at $25 \pm 1^\circ\text{C}$. Periodically, four vials were sacrificed for analysis. In specific, at each sampling time point, several vials were centrifuged at 5000 r/min for 10 min, afterward, the supernatant solution was filtered through a 0.22 μm syringe filter and acidified to $\text{pH} < 2.0$ with HNO_3 before aqueous As determination. For solid phase, it was collected and dried in a vacuum freeze dryer, finely grounded, and stored in a N_2 -filled glovebox before the determination of As forms.

To fully reflect the performance of S-ZVI on As fractionation and release from As(V)-contaminants soil, column experiments were also conducted using a series of column reactors with an inner diameter of 20 mm and a length of 200 mm. Filter screens were equipped at the top and bottom of the column to minimize the loss of fine particles. For one column, it was filled with As(V)-laden soil alone as a control (soil = 60 g, denoted as column A),

while the other three ones were filled with a mixture of soil and 5.0 wt.% S-ZVI (soil = 60 g, S/Fe = 0.05, denoted as column B, C, and D, respectively). It should be noted that, although the amounts of S-ZVI were the same in the three column treatments, column B was filled with thoroughly mixed soil and S-ZVI samples while S-ZVI was mixed with soil either at the bottom half (column C) or at the top half of the column (column D). Deoxygenated ultrapure water was introduced to the columns in an up-flow mode using a peristaltic pump at a flow rate of approximately 0.75–0.90 mL/h (He et al., 2010; Krol et al., 2013). The pore volume (PV) of the packed soil column was about 18 mL. During the tests, aqueous samples were collected at designated time intervals and then filtered through a 0.22 μm syringe filter. One part of the filtrate was used for pH and ORP measurement immediately. Another was acidified to $\text{pH} < 2.0$ with HNO_3 and analyzed for As concentration. At the end of the experiment, the undisturbed solid samples were retrieved from the columns, cut into four equal parts (denoted as 1#, 2#, 3#, and 4#, respectively, from outlet to inlet), and freeze-dried for subsequent analysis. In addition, the relative long-term As mobility in S-ZVI treated soil (collected from column B) was also explored by leaching with water under both oxic (open to the air) and anoxic (move the reactors to a glove box filled with nitrogen) conditions.

To further minimize the risk of soil As, a magnetic separation process used in our prior study (Guan et al., 2019) was also employed in this work to recover the As-bearing iron particles after S-ZVI treatment. Briefly, by moving a permanent magnet (~ 100 mT) back and forth, the iron-contained particles could be gradually separated from the treated soils. Then the collected solid samples were divided into two subsamples. One subsample was immediately acidic digested for analysis of the retrieved total As and Fe; the other was used to assess the leaching of As from the solid residual with the toxicity characteristic leaching procedure (TCLP).

2.4 Analytical methods

The total As and Fe in the filtrate were measured using a graphite furnace atomic absorption spectrometer (GF-AAS, Thermo iCE3300). For determining the contents of As and Fe in the solid phase, a microwave digestion process was employed before AAS analysis. The As forms in soil before and after S-ZVI treatment were analyzed by the well-defined Tessier's method (Tessier et al., 1979).

3 Results and discussion

3.1 As(V) immobilization by S-ZVI

Figure 1 shows the effect of iron particles on As immobility and the transformation of As fractionation at

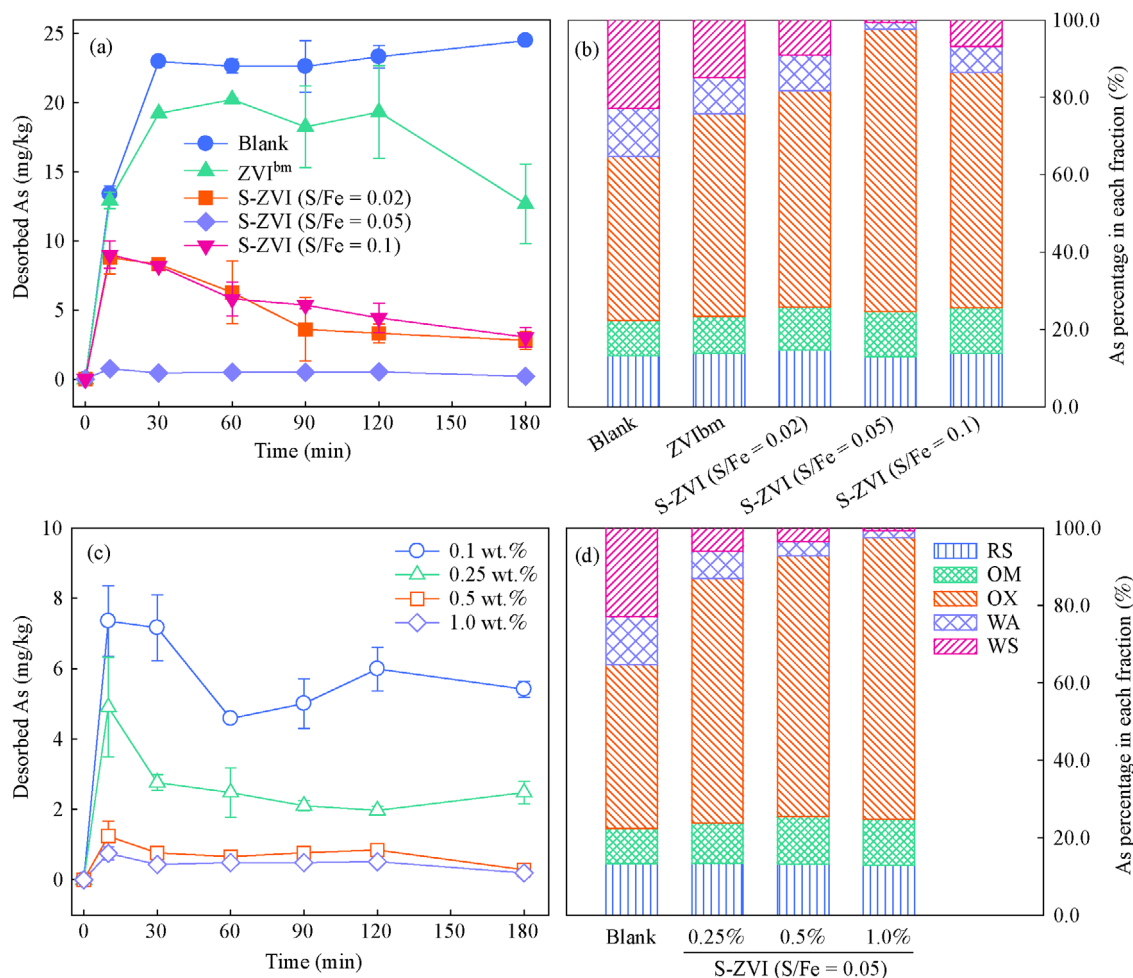


Fig. 1 Effect of sulfidation on the performance of ZVI in remediating As-laden paddy soils in terms of the desorption (a, c) and speciation (b, d) of As. Reaction conditions: initial As in soil = 105.5 mg/kg, soil/solution = 2 g/10 mL, iron loading = 1.0 wt.% for Figs. (a) and (b). S/Fe molar ratio = 0.05 for Figs. (c) and (d), $T = 25^{\circ}\text{C}$, incubation time = 15 d for Figs. (b) and (d).

different S/Fe molar ratios and iron dosages. It can be seen that in the control experiment without iron particles, As rapidly desorbed from soil and reached a maximum of 24.5 mg/kg (accounted for 23.2% of the pre-loaded As) (Fig. 1(a)). Furthermore, after the introduction of 1.0 wt.% ZVI^{bm} particles, the desorption of As was still significant at the very beginning of the experiment, despite the leached As could be partially immobilized with elapsing time. In comparison, upon the addition of S-ZVI, the desorption of As from soil was markedly inhibited where only 8.3% (8.8 mg/kg As) of the pre-loaded As could be leached in the presence of 1.0 wt.% S-ZVI (S/Fe ratio of 0.02), indicating S-ZVI was more favorable than unmodified ZVI in immobilizing As. Moreover, as demonstrated in Fig. 1a, the S/Fe molar ratio could also impact the S-ZVI performance. Specifically, when elevating the S/Fe molar ratio from 0.02 to 0.05, negligible As was observed in the leachate even at the first 10 min, which suggested that the corrosion of S-ZVI was very fast and thus could provide sufficient adsorption sites for soluble As. The performance

of S-ZVI toward As immobilization was deteriorated, however, when the S/Fe molar ratio was further increased from 0.05 to 0.1. During the remediation process, although the soil pH varied slightly in general (Fig. S1), the pH values in S-ZVI system with S/Fe of 0.05 increased to a higher level compared to the other iron systems, further suggesting the highest reactivity of S-ZVI was achieved at S/Fe molar ratio of 0.05. A similar effect of S/Fe on S-ZVI decontamination process has also been reported in our previous work (Guan et al., 2019) and several other studies (Fan et al., 2013; Han and Yan, 2016), which was proposed to be related with the decreased contact of FeS_x with Fe^0 core at high S/Fe molar ratios (Bhattacharjee and Ghoshal, 2018). It should be noted that, As may also be sequestered by the reduced S species in S-ZVI particles through the formation of low-solubility metal sulfide phases. However, the declined As immobilization efficiency with increasing S contents indicated that this pathway should not play a dominant role in this study. Instead, As adsorption and/or coprecipitation removal by iron (hydr)oxides, the products

of iron corrosion, still prevailed in the S-ZVI system. Nonetheless, further investigation is needed to elucidate the potential interaction between S and As species.

To further assess the remediation performance of S-ZVI, the transformation of As fractionation in contaminated soil after treatment was determined using a Tessier's sequential extraction procedure (Tessier et al., 1979). According to this method, the heavy metal(loid) forms in soil can be partitioned into five fractions: water soluble (WS), weakly-adsorbed (WA), Fe-Mn oxides-bound (OX), organic matter/sulfide-bound (OM), and residual fraction (RS). Among these forms, the first two are relatively less stable and of greater concerns during the remediation process. As shown in Fig. 1b, in the control experiment without adding iron particles, the fractions of WS, WA, OX, OM, and RS were 22.9%, 12.5%, 42.3%, 9.0%, and 13.3% respectively. Noted that, since the spiked As level in these experiments was low (105.5 mg/kg) and the pre-existing Fe in the tested soil was relatively high (27.2 g/kg), the dominant As form was found to be OX bound in the untreated soil. Nevertheless, as mentioned above, lots of As could still be desorbed from soil due to the presence of WS and WA bound arsenic. After incubation with 1.0 wt.% ZVI^{bm} for 15 d, the WS and WA fractions declined slightly to 14.9% and 9.3%, respectively, which further implied the reactivity of unmodified Fe⁰ particles was limited. However, in comparison, both the fractions of WS and WA could decrease to less than 2% after incubation of only 1 d (Fig. 1(b) and Fig. S2) when soil was amended with S-ZVI (S/Fe molar ratio of 0.05). Correspondingly, OX, the relatively more stable fraction, increased from 42.3% to >70%.

Under the optimal S/Fe molar ratio of 0.05, the influence of S-ZVI dosage on As remediation in soil was further explored in this study. As illustrated in Fig. 1(c), with the decrease of S-ZVI dosage from 1.0 wt.% to 0.1 wt.%, the efficiency of As immobilization decreased obviously. In specific, almost all of the leached As could be sequestered by >0.5 wt.% S-ZVI within 3 h, whereas only 78.0% of the leached As were immobilized by 0.1 wt.% S-ZVI within 3 h and the soluble As kept almost constant during the following 15 d. Accordingly, from another perspective, more water soluble As was left in soil after treatment with low S-ZVI dosages (Fig. 1(d)). Obviously, this ineffective As(V) immobilization at low S-ZVI dosages should be ascribed to the fact that less adsorption sites could be provided during the process.

3.2 Effect of operating conditions

In the contaminated-soil, there are not only target pollutants but also many co-existing solutes, such as minerals and organic matters, which may affect both the rate of iron corrosion and the subsequent As(V) immobilization. Therefore, in order to explore the applicability of S-ZVI, tests were performed under different operating

conditions, including different initial pH, the presence of MnO₂ (a model mineral), and humic acid (HA) (a model organic compound), and the results were demonstrated in Fig. 2 and Fig. S3.

Acting as potential adsorbents for arsenic, minerals in soil could minimize the leaching of As. Indeed, as shown in Fig. 2(a)–2(b), the addition of MnO₂ could decrease the desorption of As from soil. However, it should be noted that the adsorption ability of the pre-synthesized MnO₂ minerals was much lower than S-ZVI, where 10.8 mg As/kg was still leached from soil with the presence of 0.5 wt.% MnO₂. Organic matter, especially HA, can affect the chemical transformation and migration of heavy metal(loid)s by complexing with heavy metal(loid) ions. It was reported that HA could readily form complexes with metal cations, and further form ternary complexes with arsenic through metal bridging mechanisms, thus increasing the mobility of arsenic (Redman et al., 2002; Buschmann et al., 2006). As demonstrated in Fig. 2(c), the introduction of HA could slightly eliminate the As release from soil, which might be caused by the adsorption and complexation of As with HA. Moreover, HA could also affect the iron corrosion process. As depicted in Fig. 2(d), at the beginning of the reactions, the presence of 2.0 wt.%–5.0 wt.% HA inhibited the reactivity of S-ZVI, and thus about 7.8 mg As/kg was leached from soil. Nevertheless, with elapsing time, most of the desorbed As could be immobilized again at 3 h. A similar phenomenon was also observed by Rao et al. (2009), and they found that in groundwater, the production of iron precipitates was hindered by the formation of soluble Fe-humate and thus decreased the removal rate of arsenic by Fe⁰.

pH is also an important factor influencing both the iron corrosion and As adsorption behavior. As illustrated in Fig. 2(e), without S-ZVI, the desorbed As concentrations generally increased as the increasing pH values, which was in agreement with the pH adsorption trend of As(V) on soil minerals. As aforementioned, the content of Fe in soil is 27.2 g/kg and the fraction of the corresponding Fe-Mn oxides-bound arsenic is 42.3%. Many studies have reported that the surface of minerals such as Fe/Mn oxides will become more positively charged at low pH values and thus favor the adsorption of negatively charged arsenate oxyanions. An increase of pH levels, however, will decrease the positive charge surface of minerals and thereby deteriorate the contact with arsenate oxyanions and minerals. Also, the increasing amounts of OH⁻ could compete with arsenate oxyanions for adsorption sites (Sun et al., 2014). Consequently, compared with the scenario at pH 8.2, less As was released from the soil when pH was decreased to 4.0, whereas more As was leached at pH 12.0. Upon S-ZVI was introduced, as shown in Fig. 2(f), at pH 4.0 and 8.2, negligible As was released from soil while 27.1 mg As/kg was released at pH 12.0. This suggested that the performance of S-ZVI at high pH values was still limited. Several studies have proved that a low pH could

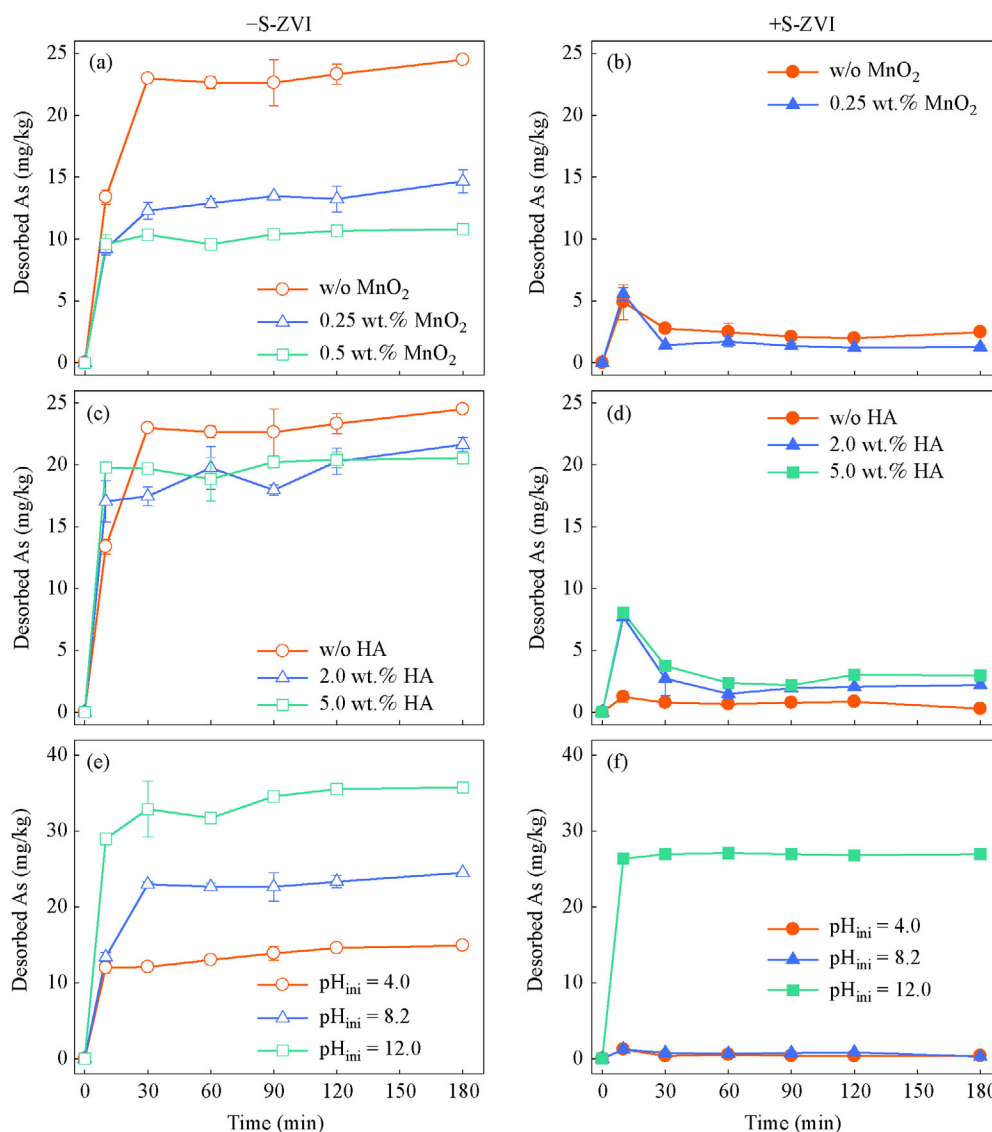


Fig. 2 Effect of S-ZVI addition on the desorption of As from As-laden paddy soils under different operating conditions (soil/solution = 2 g/10 mL, S/Fe molar ratio = 0.05, S-ZVI = 0 or 5 g/kg (0.5 wt.%), $T = 25^{\circ}\text{C}$).

accelerate iron corrosion but a high pH could deteriorate the performance of ZVI because the mass transfer was inhibited by the passive oxide film (Dong et al., 2010; Bae and Lee, 2014).

3.3 Effect of S-ZVI on the mobility of As(V) in continuous flow column systems

To fully reflect the S-ZVI performance toward As(V) immobilization in soil, the retention effect of S-ZVI amendment was investigated by leaching with water in a column test. Note that, a high As concentration level, i.e., 749.1 mg/kg, was used in the column experiments. Figures 3 and S4 showed the concentration trends of dissolved As, pH, and the oxidation-reduction potential (ORP) in the

column effluents. It was found that in column A without S-ZVI, As in the leachate increased rapidly and 55.5% of the total As could be released from soil in the first 10 PV and the cumulative released As reached as high as 71.4% eventually. In contrast, upon the addition of S-ZVI, the As mobility was effectively minimized. For instance, in column B packed with S-ZVI homogeneously throughout the column, the As leaching rate was relatively slow and only 22.6% of As was released from soil. In addition, it was interesting to find that S-ZVI could also effectively reduce As release from soil when it was only filled in the top half of the column (outlet side, column D). However, when S-ZVI was packed in the bottom half of the column (inlet side, column C), more As could be leached from soil and this should be associated with the limited Fe migration

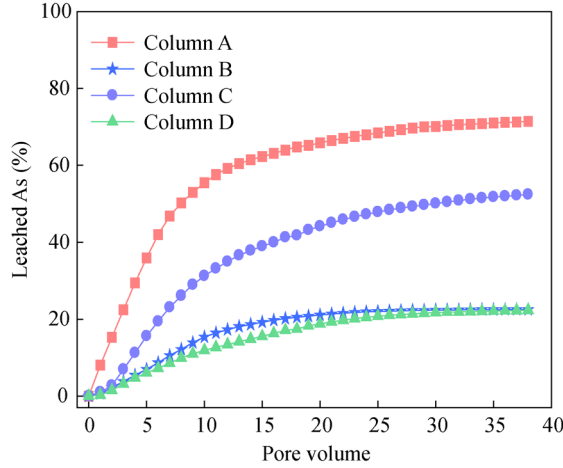


Fig. 3 Cumulative As desorption in the effluents of different columns: (A) without S-ZVI, (B) filled S-ZVI homogeneously throughout the column, (C) filled S-ZVI in the bottom half of the column, (D) filled S-ZVI in the top half of the column. Reaction conditions: the flow rate of pure water = 0.75–0.90 mL/h; S-ZVI = 3 g; soil dosage = 60 g; $T = 25^{\circ}\text{C}$.

under circumneutral pH conditions. Given above, for the successful application of S-ZVI in soil remediation, S-ZVI should be well mixed with soil or located at the downstream side of As migration.

Furthermore, Figure 4 illustrates the fractionation and spatial distribution of As in soil after reaction. It was found that, at the start of the tests, the dominant form of As in soil was the water soluble fraction that accounted for 56.5% of the total As, and the fractions of the other forms were WA (15.0%), OX (17.0%), OM (2.2%) and RS (9.3%), respectively. For the control column A, consistent with the aqueous-phase data, it showed a significant loss of solid-phase As, where most of the readily mobile WS and WA As disappeared at the end of the reaction. In column B, although some of the WS and WA As were washed up by water, most of them were immobilized by S-ZVI and the solid-phase As at the end of the experiment were determined to be mainly present as OX (44.6%–73.2%) and RS (8.1%–14.9%) fractions. Similarly, for column D, some of the water-soluble As could be converted to more stable OX and RS forms. It should be noted that there was still a markable loss of As in the bottom soil of column D, despite the mobilized As could be partially immobilized and accumulated in the upper layer when they came into contact with S-ZVI, as depicted in Fig. 4. For column C, however, the amendment with S-ZVI did not show an effective As(V) immobilization as observed in columns B and D. Substantial amounts of the soil As could be leached from this column, and much greater As depletion was found in the part close to the outlet, compared to its counterpart close to the inlet. Given soluble As were

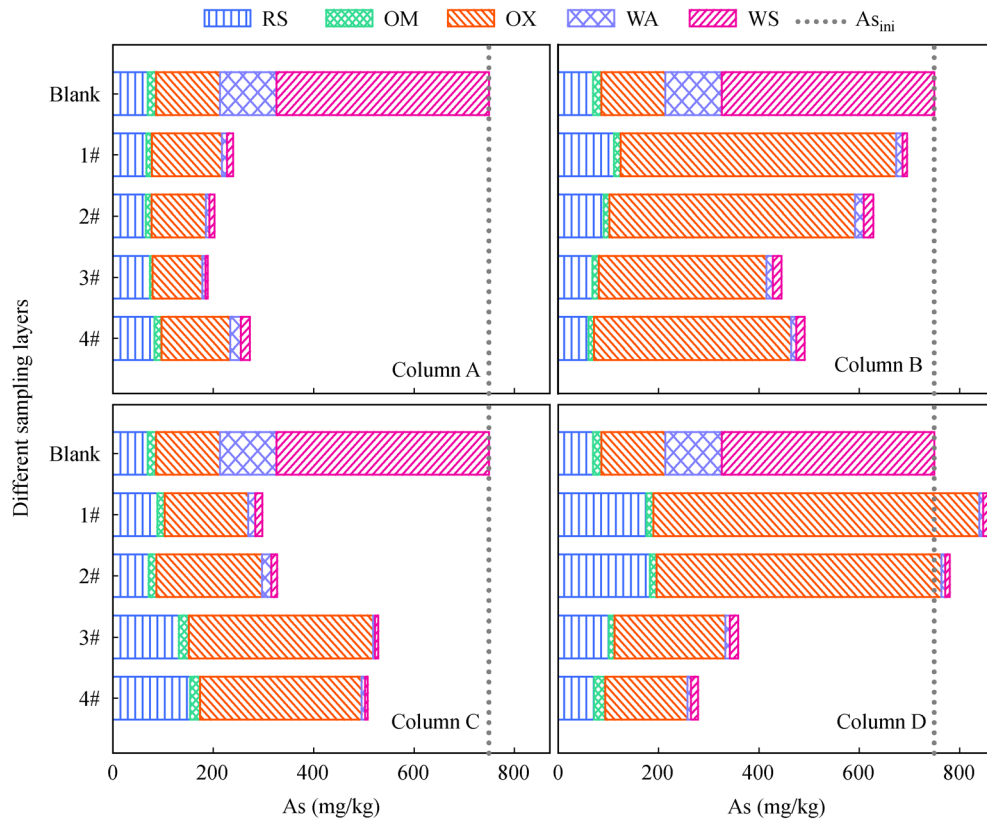


Fig. 4 The spatial distribution and speciation of As at the end of the column experiments.

mainly sequestered by the iron (hydr)oxides, this As distribution trend further suggested that the Fe species released from S-ZVI corrosion could not efficiently migrate along the column, and thus could not prevent the As leaching significantly.

3.4 Long-term stability of As in soil after S-ZVI remediation

In a long time-scale, the redox environment of soil may change due to rainfall, microbial metabolism and/or human activities (Kögel-Knabner et al., 2010). For example, in the paddy field, when soils are flooded periodically, O_2 can be gradually consumed by microorganisms and thus lead to the change of soil redox environment from oxic to anoxic conditions. More importantly, during the processes of flooding and drainage, the speciation and solubility of As in soil could also be altered due to the changes of the soil redox environment (Wang et al., 2019). Hence, the long-term stability of S-ZVI treated soil was evaluated in this section by simulating the changeover of anoxic/oxic conditions. Note that the S-ZVI treated soil collected from column B was employed here for the test.

As demonstrated in Fig. 5(a), in the first 15 days, the concentrations of aqueous As increased progressively and the cumulative amount of As reached a plateau of ~ 3.60 mg/kg; thereafter, the release of As leveled out in the following 15 days. This result suggested that the stabilized As by S-ZVI could remobilize to solution when the soils were subjected to anoxic conditions. However, it was worthy to note that the amount of the released As was relatively small where only 0.7% of the total As was remobilized from soil during a 30 d incubation period. From this perspective, the S-ZVI remediated soil As(V) seems to hold a strong tolerance to the anoxic environment. On the other hand, when the soils were exposed to oxic conditions at 30 d, most of the released As could be immobilized again, as demonstrated in Fig. 5(a).

Obviously, it can be inferred that this phenomenon should be mainly associated with the evolution of Fe(III) (hydr)oxides. To confirm this, the dissolved Fe in leachate and also the suspension pH (Fig. S5) were monitored during the desorption test. As shown in Fig. 5(a), a similar variation trend of leached Fe was indeed observed, and more importantly, there was a linear positive relationship between As leaching and Fe dissolution (Fig. 5(b)). This implied that it may be the reductive dissolution of As-bearing Fe(III) (hydr)oxides under anoxic conditions accounted for the release of As. As illustrated in Fig. S5, despite the variation degree was small (increased first from 8.3 to 8.7 at 30 d, and then decreased to 8.4), the suspension pH could also change in a similar manner with that of As and Fe, which may serve as an indicator of the dissolution of Fe(III) (hydr)oxides. On the other hand, the reduction of As(V) to As(III) may occur at O_2 -free conditions, and this transformation could also cause As remobilization since the relatively weak adsorption affinity between Fe(III) (hydr)oxides and As(III) (Bang et al., 2005).

3.5 Recovery of As from soil by magnetic separation

The aforementioned findings revealed that S-ZVI could not only immobilize As(V) effectively but also exhibit a good remediation stability over 30 days. However, given this kind of immobilization methods could not reduce the total As contents in soil, concern remains as to the potential detrimental effects of the adsorbed As. Hence, in order to further minimize the risk of As, the feasibility of applying magnetic separation to separate the trapped As by iron oxides from soil was explored in this study. As mentioned in our previous study (Guan et al., 2019), to achieve efficient As recovery from soil, the degree of iron corrosion is critical since it could not only influence the As sequestration but also determine whether the As-bearing iron particles are still magnetic enough. Hence, the

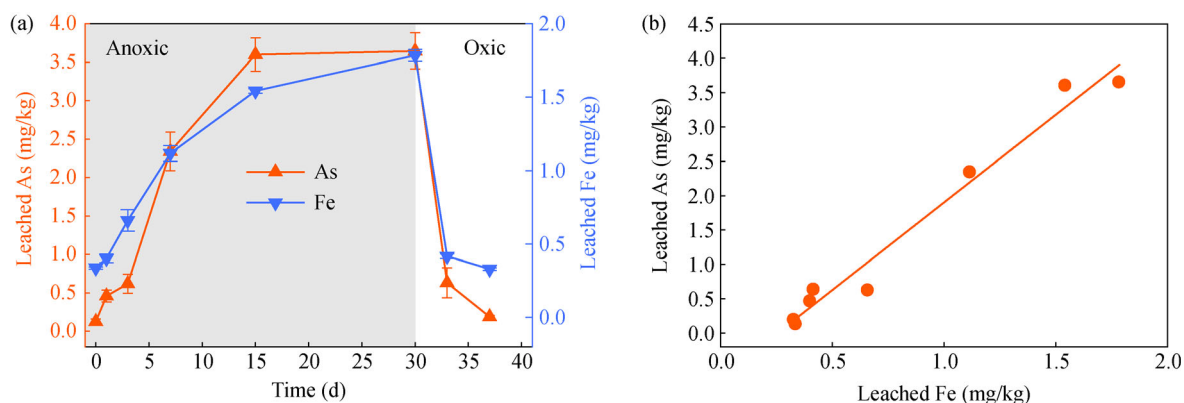


Fig. 5 Effect of the changeover of anoxic and oxic condition on the release of As from the S-ZVI treated soils in pure water. Reaction conditions: Soils were collected from Column B, $As_{tot} = 578.9$ mg/kg, $Fe_{tot} = 180.0$ g/kg, soil/solution = 1 g/10 mL.

influence of some key factors, such as S-ZVI dosages, liquid/soil (L/S) ratio, and reaction time, on As separation from soil were examined.

As depicted in Fig. 6, under the tested S-ZVI dosages, the contents of retrieved As increased with the increasing of iron loadings. Specifically, when L/S was 10 and the reaction time was 24 h, the retrieved As increased from 17.6 mg/kg to 52.6 mg/kg with the S-ZVI dosage increased from 0.25 wt.% to 1.0 wt.%. Likewise, a high L/S ratio generally favored the As recovery, regardless of the iron dosages and reaction time. It was reported that the presence of As(V) could depress the iron corrosion (Sun et al., 2014). Indeed, as shown in Fig. S6, although the amounts of retrieved total Fe were comparable at each L/S ratio, more unreacted Fe^0 was observed in the cases of low L/S ratios. Hence, it can be inferred that the As immobilization were less efficient at lower L/S ratios, which resulted in the relatively lower As recovery. With respect to the influence of incubation time, opposite trends could be obtained depending on the S-ZVI dosages. Specifically, at a low iron dosage (e.g., 0.25 wt.%), a longer reaction time deteriorated the As recovery from soil. However, at a relatively high iron dosage (e.g., 1.0 wt.%), increasing the reaction time from 3 h to 24 h enhanced the As recovery from

16.7%–24.2% to 30.9%–49.9%. This phenomenon may be ascribed to the amounts of unreacted Fe^0 and the distribution of As in solid samples at the end of the reaction.

After S-ZVI treatment and magnetic separation, TCLP tests were further employed to assess the As leachability from the stabilized soil. As illustrated in Fig. 7, As leachability was effectively minimized by the combination of S-ZVI amendment and magnetic separation, where the leached As was determined to be 2.1–6.2 mg/kg (accounting for 2%–6% of the spiked As) in the case of 0.25 wt.% S-ZVI. Moreover, with the increase of iron dosage, As leachability was further reduced where the released As could reach as low as 0.4 mg/kg, suggesting that the residual As in soil was present in more geochemically stable forms.

4 Conclusions

This study systematically explored the feasibility of applying sulfidated ZVI to remediate As(V) contaminated soil in both terms of remediation efficiency and long-term stability. As expected, batch testes showed that sulfidation

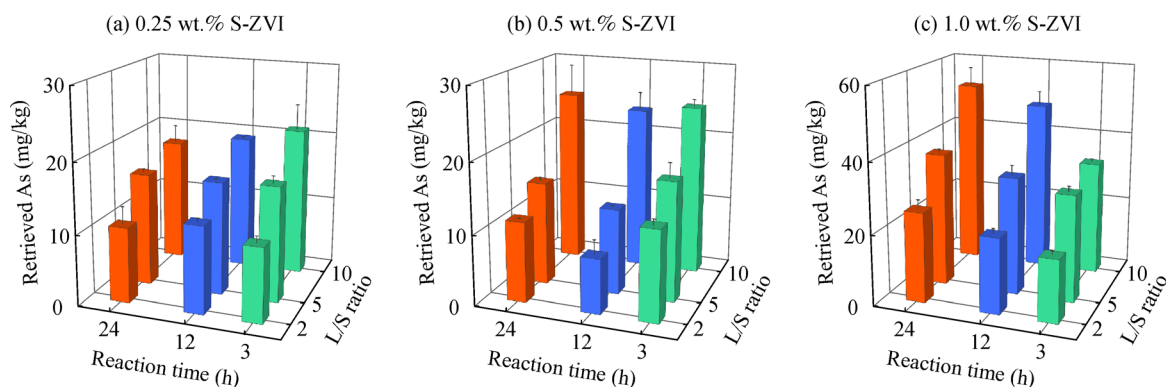


Fig. 6 Effect of operating conditions on the recovery of As from S-ZVI treated soils by magnetic separation ($\text{As}_{\text{tot}} = 105.5$ mg/kg).

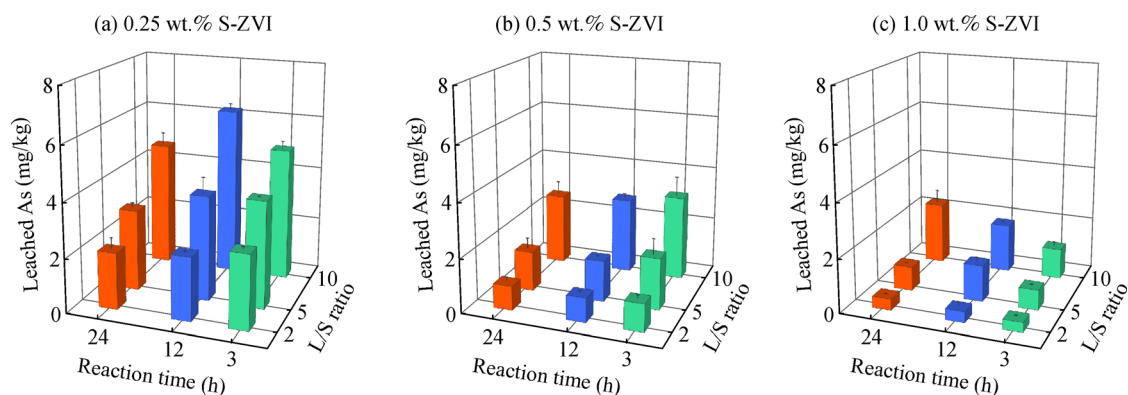


Fig. 7 TCLP leachability of As from soils treated by S-ZVI and magnetic separation ($\text{As}_{\text{tot}} = 105.5$ mg/kg).

treatment remarkably improved the performance of ZVI toward soil As(V) immobilization by accelerating the corrosion of ZVI. Moreover, almost all of the water-soluble arsenic species could be transformed into the more stable Fe-Mn oxides-bound As after S-ZVI treatment. The presence of MnO₂ minerals in soil could decrease the leaching of As from soil to some extent and thus may enhance the As(V) immobilization by S-ZVI. However, the addition of HA slightly diminished As immobilization since it could deteriorate the corrosion of ZVI. By combining the S-ZVI treatment and magnetic separation, 16.7%–49.8% of the immobilized As could be removed from soil. Taking advantage of the continuous flow columns, the superiority of S-ZVI on As retention was further confirmed where only 22.6% of the spiked As was leached from soil while the leached As could reach as high as 71.4% in the control test. Furthermore, it was found that S-ZVI remediated soil As(V) seems to hold a strong tolerance to the anoxic environment where only 0.7% of As remobilized from the soil during a 30 d incubation period. All results indicated that S-ZVI was a promising material for the remediation of As(V)-contaminated soil.

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