Photoreductive Dissolution of Schwertmannite with Incorporated As(V) Induced by Oxalate and the Mobilization of As(V)

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Abstract

Schwertmannite (Sh), a poorly crystalline iron (hydr)oxide that usually appears in acid mine drainage, plays a significant role in the immobilization of As(V). In this study, the effects of UV irradiation and oxalate on the dissolution of Sh with structurally incorporated As(V) [Sh–As(V)] and the subsequent mobilization of As(V) were investigated at pH 3.0. In the dark, more total dissolved Fe was produced (the maximum value was 33.2 mg/L) in the suspensions of Sh–As(V) with oxalate than in those without oxalate. UV irradiation slightly enhanced the mobilization of As(V) for the system of Sh–As(V)-1 and Sh–As(V)-2 in the absence of oxalate compared with that in the dark. However, in the presence of oxalate, UV irradiation caused the concentration of mobilized As(V) to decline by 630–875% compared with that in the dark. This study enhanced our understanding of the mobilization of As(V) and demonstrated that UV irradiation could contribute to the immobilization of As(V) on Sh in aqueous environments containing oxalate.

Keywords Schwertmannite · Photoreductive dissolution · Oxalate · As(V) · Mobilization

Introduction

Arsenic (As) is a toxic contaminant that is mainly present in inorganic forms as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)] in aqueous environments [1]. Various health issues including skin lesions, circulatory disorders, and diverse cancers are correlated with long-term intake of water with arsenic [2, 3]. Considering the severe toxicity of arsenic, the World Health Organization reduced the guideline for arsenic in drinking water from 50 to 10 µg/L in 1993 [4]. The existence of arsenic in drinking water results from the dissolution of As-bearing minerals, microbial activities, geochemical reactions, and drainage of As-rich sewage generated from anthropogenic activities such as agriculture, metallurgy, and mining [1, 5].

Iron (hydr)oxides are found in natural environments as an impressive array of minerals, most commonly goethite

(α -FeOOH), ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), lepidocrocite (γ -FeOOH), and schwertmannite [$\text{Sh}; \text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_x$, $1.0 \leq x \leq 1.85$] [6, 7]. On account of their natural abundance and surface absorptivity, iron (hydr)oxides play a significant role in attenuating the concentration of arsenic in natural environments through adsorption and precipitation. As a result, dissolution of iron (hydr)oxides is of great importance to the mobilization of arsenic.

Sunlight irradiation can lead to the light-induced dissolution of iron (hydr)oxides in photic water and soil surface [8–12]. Two reaction steps are involved in this photoreductive dissolution process: (1) photoreduction of Fe(III) on the surface of iron (hydr)oxides and (2) subsequent release of surface-bound Fe(II) into solution [9]. Previous studies demonstrated that two mechanisms are known to potentially account for the formation of surface Fe(II) in natural water: (1) Electrons and holes are generated under irradiation via the charge transfer between lattice O^{2-} and Fe(III) in iron (hydr)oxides, and photo-induced electrons will result in surface Fe(III) reduction (i.e., the mechanism of semiconductor); (2) ligand-to-metal charge transfer in Fe(III) complexes formed on photoactive surface contributes to the formation of surface Fe(II) [9]. Dissolved organic matter can effectively promote the reductive dissolution of iron minerals containing arsenic [9–12]. Siderophores [desferrioxamine

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B (DFOB) and aerobactin] can accelerate the light-induced dissolution of lepidocrocite. Lepidocrocite dissolves 91 times faster in the presence than in the absence of DFOB at pH 3 [12].

Oxalate (concentration varies from 2.5×10^{-5} to 4.0×10^{-3} mol/L) is usually detected in natural waters. Meanwhile, oxalate has a remarkable contribution to the dissolution of iron (hydr)oxides [13]. During the past decade, intensive studies of irradiated iron (hydr)oxide–oxalate systems, which exist in natural aqueous environments and on soil surface, have been carried out. Many kinds of environmental pollutants can be degraded in such systems due to the photo-Fenton-like reaction [14–18]. Wu et al. [18] revealed that 5 min of UV irradiation yields 25 mg/L dissolved Fe(II) in the system of schwertmannite (1 g/L) and oxalate (4.4 mmol/L) at pH 4.0. In addition, 97% of methyl orange with the initial concentration of 50 mg/L can be removed after 40 min of UV irradiation.

Nevertheless, studies related to the photochemical reactions of the ternary As(V)–iron (hydr)oxide–oxalate system are limited. Under light illumination, the effects of oxalate on the mobilization of As(V), which is adsorbed onto and structurally incorporated into iron minerals, have not been studied. Moreover, the mechanism involved in the immobilization of the released As(V) by residual minerals or newly formed secondary iron minerals is not clearly understood.

Acid mine drainage (AMD) involves polluted water with low pH and high concentrations of heavy metals and other toxic elements [19]. Nordstrom et al. [20] reported that the As(V) concentration can reach 850 mg/L in an acid seep at Iron Mountain, California. Sh is a poorly crystalline metastable mineral that usually appears in AMD. [21, 22]. Sh can immobilize a large amount of As(V) [23]. Our recent study suggested distinctions in reactivity between Sh with adsorbed As(V) [Sh*–As(V)] and Sh with structurally incorporated As(V) [Sh–As(V)] [24]. The present research focused on the photochemical reactions of the ternary As(V)–Sh–oxalate system. We aimed to investigate the effect of oxalate and the amount of structurally incorporated As(V) on photoreductive dissolution of Sh–As(V) and the mobilization of As(V) involved in this process.

Experimental Section

Materials

All laboratory glassware was repeatedly rinsed with deionized water before use. $\text{NaH}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$ (Merck, purity > 99.0%) and oxalate (Tianjin Bodi Chemical Co., Ltd., Tianjin, China, purity > 98.0%) were used as As(V) and oxalate sources, respectively.

Synthesis of Sh and Sh–As(V)

Sh was prepared following the procedures reported by Loan et al. [25]. In this method, preheated deionized water (500 mL) was mixed with $\text{Fe}_2(\text{SO}_4)_3$ (2.6 g) in a round-bottomed flask with a mechanical stirrer. The flask was then placed in a water bath at 85 °C for 1 h.

The process of preparing Sh–As(V) by the co-precipitation method was basically the same as that of preparing Sh. However, a certain amount of As(V) was added to the water in advance and warmed up to 85 °C, and the reaction time was 2 h. After the suspension cooled to room temperature, it was centrifuged at 4200 r/min for 5 min. The obtained solid was washed with distilled water for three times and then freeze-dried.

The contents of As(V) in the synthetic Sh–As(V) were determined by the following methods. First, 0.015 g of Sh–As(V) solid was dispersed in 150 mL of NaCl solution (0.1 mol/L) at pH 3.0. Second, 0.264 g of ascorbic acid was added to the mixture. The suspension was electromagnetically stirred for 24 h to guarantee that Sh–As(V) was completely dissolved. After the dissolution reaction, the suspension was centrifuged at 12,000 r/min for 5 min, and the supernatant was used to determine the As(V) concentration.

Photochemical Experiment

(Photo)dissolution experiments were carried out in an XPA-7 photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China). A 300-W Hg lamp was used as the light source. The wavelength was mainly 365 nm, and the power was 2.5 mW/cm^2 . Before the experiments, the lamp was turned on for 5 min to guarantee stable irradiating intensity during the experiment period. Sh–As(V) was dispersed in 15 mL NaCl solution (0.1 mol/L) at pH 3.0. In Sh–As(V) dissolution, 2 mmol/L oxalate in 15 mL NaCl solution (0.1 mol/L) with the same pH was mixed with the Sh–As(V) suspension. After mixing, the initial concentrations of Sh–As(V) and oxalate were 0.1 g/L and 1 mmol/L, respectively. During the photoreactions, the suspensions were stirred with a magnetic stirrer at 800 r/min. A steady flow of cooling water was used to maintain a constant temperature of about 25 ± 1 °C. In addition, photodissolution experiments of Sh–As(V) in the absence of oxalate were carried out for comparison. In the duration of the dissolution experiments, solution samples of 1.0 mL were pipetted every 30 min and centrifuged at 12,000 r/min for 5 min. The supernatant was applied to determine the concentrations of As(V), dissolved Fe(II), and total Fe. Experiments in the dark were conducted at the same

conditions. All the experiments in this section were conducted in duplicate, and the average values were recorded.

Analytical Methods

The As(V) concentration was detected by a molybdate blue method [26], and the detection limit for As(V) in this study was 0.005 mg/L. Dissolved Fe(II) concentration was detected by a modified ferrozine method. To eliminate the interference of Fe(III), 0.05 mol/L NaF was added to mask Fe(III) in Fe(II) determination. The total dissolved Fe was determined by reducing total Fe(III) to Fe(II), and dissolved Fe(II) was measured by the ferrozine method without the addition of NaF solution [27]. We demonstrated the phase composition of iron (hydr)oxides by applying X-ray diffraction (XRD, Rigaku D/max 2200/PC). The Fourier transform infrared (FTIR, Nicolet 670, Thermo Fisher Scientific) spectrum was utilized to determine the variety of iron (hydr)oxides.

Results and Discussion

Characterization of Synthetic Sh–As(V)

In this study, Sh–As(V)-*i* (*i* = 1, 2, or 3) represented Sh with various amounts of structurally incorporated As(V). Specifically, the amount of structurally incorporated As(V) was 142.0, 128.0, and 64.0 mg/g for Sh–As(V)-1, Sh–As(V)-2, and Sh–As(V)-3, respectively (Table 1).

Figure 1 shows the XRD pattern of synthetic Sh, in which all diffraction peaks were in accordance with rhomb-centered hexagonal Sh (JCPDS Card No. 47-1775). Specifically, the diffraction peaks at 2θ of 26.3°, 35.2°, and 61.3° were indexed to be (310), (212), and (004) planes of pure Sh, respectively [22]. XRD patterns of Sh–As(V) were similar to those of Sh (data not shown).

FTIR analyses of Sh–As(V) are shown in Fig. 2. The peak at 825 cm⁻¹ was assigned to the As–O stretching vibration of As–O–Fe coordination [28].

Table 1 Content of structurally incorporated As(V) into Sh

Species	Content of As(V) (mg/g)
Sh–As(V)-1	142.0
Sh–As(V)-2	128.0
Sh–As(V)-3	64.0

Effect of UV Irradiation on the Mobilization of As(V) in Sh–As(V) in the Absence of Oxalate

Figure 3 shows the concentrations of total dissolved Fe and Fe(II) during the dissolution of Sh–As(V) in the absence of oxalate in the dark. Total dissolved Fe increased slightly and leveled off at 1.66, 2.11, and 4.23 mg/L after 120 min for Sh–As(V)-1, Sh–As(V)-2, and Sh–As(V)-3, respectively (Fig. 3a). Under UV irradiation, the total dissolved Fe continued to increase during the whole experimental period (Fig. 4a). After 240 min, dissolution of Sh–As(V) resulted in 4.98, 5.43, and 7.85 mg/L total dissolved Fe, and these values were nearly double of the amounts in the dark (Fig. 4a). In addition, the vast majority of them was dissolved Fe(II) (Fig. 4b). This result indicated that the photoreductive dissolution of Sh–As(V) could proceed in the absence of organic ligands under acidic condition. A previous study demonstrated that 6 h of UV irradiation of lepidocrocite suspensions (25 mg/L) at pH 3.0 in the absence of organic ligands resulted in the formation of 6.13 μmol/L total dissolved Fe, and 90% of them presented as Fe(II) [11].

Fig. 1 XRD pattern of the synthetic schwertmannite (Sh)

Fig. 2 FTIR analyses of Sh–As(V)

Fig. 3 Dissolution experiments in the dark with suspensions of 0.1 g/L Sh-As(V) at pH 3.0 and 0.1 mol/L ionic strength (NaCl) in the absence of oxalate. **a** total dissolved Fe, **b** dissolved Fe(II), and **c** As(V) were measured

In the absence of oxalate, the mobilization of As(V) during the dissolution of Sh-As(V) in the dark and under UV irradiation is shown in Figs. 3c and 4c, respectively. In the dark, the concentration of As(V) varied slightly at 0.4, 0.4, and 0.6 mg/L for Sh-As(V)-1, Sh-As(V)-2, and Sh-As(V)-3, respectively (Fig. 3c). Under UV irradiation, the final concentration of aqueous As(V) declined apparently with the decrease in the As(V) content in Sh-As(V), which was 1.4, 0.8, and 0.6 mg/L for Sh-As(V)-1, Sh-As(V)-2, and Sh-As(V)-3, respectively (Fig. 4c). Compared with the results in the dark, UV irradiation enhanced the mobilization of As(V) for the systems of Sh-As(V)-1 and Sh-As(V)-2 in the absence of oxalate. However, the final concentration of aqueous As(V) was equal in the dark and under UV irradiation for Sh-As(V)-3, even though more minerals dissolved under UV irradiation.

Effect of UV Irradiation on the Mobilization of As(V) in Sh-As(V) in the Presence of Oxalate

Dissolution experiments of Sh-As(V) in the presence of oxalate showed a significant formation of total dissolved Fe

(Figs. 5, 6). As oxalate mixed with Sh-As(V), the total dissolved Fe reached 4.98, 2.86, and 13.73 mg/L for Sh-As(V)-1, Sh-As(V)-2, and Sh-As(V)-3, respectively (Fig. 5a). These results demonstrated that the dissolution reaction of oxalate with Sh-As(V) was fast [18]. When the suspensions were in the dark, two stages were found in the variation in total dissolved Fe: A rapid increase was observed within the first 30 min, and the curves leveled off after 90 min (Fig. 5a). In the presence of oxalate, the dissolution of all three Sh-As(V) samples resulted in highly similar total dissolved Fe concentrations (~32.95 mg/L) (Fig. 5a). Therefore, in the dark, the differences in amount of structurally incorporated As(V) had almost no effect on the dissolution of Sh-As(V) in the presence of oxalate.

However, for experiments under UV irradiation, the total dissolved Fe exhibited different trends (Fig. 6a). When the amount of structurally incorporated As(V) was relatively low [for Sh-As(V)-3], the total dissolved Fe initially decreased and leveled off at 5.73 mg/L after 60 min of UV irradiation. However, when the amounts of structurally incorporated As(V) were high, such as Sh-As(V)-1 and Sh-As(V)-2 in the present study (Fig. 6a), the total

Fig. 4 Dissolution experiments under UV irradiation with suspensions of 0.1 g/L Sh-As(V) at pH 3.0 and 0.1 mol/L ionic strength (NaCl) in the absence of oxalate. **a** total dissolved Fe, **b** dissolved Fe(II), and **c** As(V) were measured

dissolved Fe initially increased and peaked within the first 30 min. Subsequently, they decreased and leveled off at 4.22 and 2.87 mg/L for Sh-As(V)-1 and Sh-As(V)-2, respectively (Fig. 6a). After 240 min of UV irradiation, pH of the suspensions increased from 3.0 to 6.0. Lan et al. [14] reported that the dissolved Fe(III)/Fe(II) significantly declines in irradiated goethite/oxalate systems. This observation was also attributed to the quick rise in pH from 3.5 to 6.0.

The mobilization of As(V) during the dissolution of Sh-As(V) in the dark and under UV irradiation in the presence of oxalate is shown in Figs. 5c and 6c, respectively. In the dark, As(V) increased within the first 60 min and then leveled off at 12.6, 10.8, and 7.0 mg/L for Sh-As(V)-1, Sh-As(V)-2, and Sh-As(V)-3, respectively (Fig. 5c). Under UV irradiation, As(V) released from the dissolution of Sh-As(V) reached the maximum values after the addition of oxalate, decreased within the first 60 min, and leveled off at 2.0, 1.4, and 0.8 mg/L for Sh-As(V)-1, Sh-As(V)-2, and Sh-As(V)-3, respectively (Fig. 6c).

Proposed Mechanism of Sh-As(V) Dissolution and As(V) Mobilization

On the basis of the above discussion and previous studies [10, 14–16], the possible mechanisms of Sh-As(V) dissolution induced by oxalate and As(V) mobilization in the absence and presence of UV irradiation were proposed (Scheme 1). Iron oxide–oxalate complexes of $[\equiv \text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_n]^{(2n-3)-}$ are formed by the adsorption of oxalate on the surface of Sh-As(V) [Eq. (1)]. The symbol $\equiv$ is a shorthand notation of the surface lattice of an Fe(III) (hydr)oxide. Under UV irradiation, $[\equiv \text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_n]^{(2n-3)-}$ was excited to form $[\equiv \text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)_{(n-1)}]^{4-2n}$ and a series of radicals including oxalate radical $(\text{C}_2\text{O}_4)^{\cdot-}$, carbon-centered radical $(\text{CO}_2)^{\cdot-}$, and superoxide ion $\text{O}_2^{\cdot-}$ [Eqs. (2)–(4)]. Fe^{3+} reacted with $\text{O}_2^{\cdot-}$ to form O_2 and Fe^{2+} [Eq. (5)]. Reduction of Fe(III) could also occur in the solution under UV irradiation according to Eq. (6). In the dark, accompanied with the dissolution of Sh-As(V) in the presence of oxalate, structurally incorporated As(V) was released into the solution. [The maximum concentration of dissolved As(V) was 12.6 mg/L

Fig. 5 Dissolution experiments in the dark with suspensions of 0.1 g/L Sh–As(V) at pH 3.0 and 0.1 mol/L ionic strength (NaCl) in the presence of oxalate. **a** total dissolved Fe, **b** dissolved Fe(II), and **c** As(V) were measured

(Fig. 5c).] However, under UV irradiation, the mobilization of As(V) in the system of Sh–As(V) was hindered. At the end of the dissolution experiment, the maximum concentration of dissolved As(V) was 2.0 mg/L (Fig. 6c), which could be attributed to the re-adsorption of the released As(V) on residual Sh.

Conclusions

This study revealed the effects of UV irradiation and oxalate on the dissolution of Sh–As(V). Under UV irradiation, Fe(III) oxalate complexes formed at the surface of Sh–As(V) could be converted into Fe(II) oxalate. UV irradiation slightly enhanced the mobilization of As(V) for the systems of Sh–As(V)-1 and Sh–As(V)-2 in the absence of oxalate compared with that in the dark. However, in the presence of oxalate, UV irradiation caused the released As(V) to decline by 630–875% compared with that in the dark. This study enhanced our understanding of As(V)

Fig. 6 Dissolution experiments under UV irradiation with suspensions of 0.1 g/L Sh-As(V) at pH 3.0 and 0.1 mol/L ionic strength (NaCl) in the presence of oxalate. **a** total dissolved Fe, **b** dissolved Fe(II), and **c** As(V) were measured

Scheme 1 Proposed mechanisms of Sh dissolution and As(V) mobilization in Sh-As(V)

mobilization and proved that UV irradiation could improve the immobilization of As(V) on Sh in aqueous environments including oxalate.

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