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Photoreductive dissolution of schwertmannite induced by oxalate and the mobilization of adsorbed As(V)

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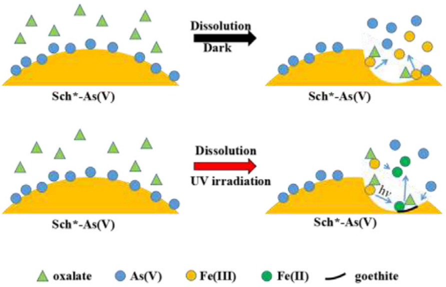
HIGHLIGHTS

- Dissolved Fe(II) produced during the dissolution of Sch under UV irradiation.
- Oxalate has different role in the dissolution of Sch in the dark and under UV irradiation.
- UV irradiation resulted in the mobilization of As(V) declined obviously in the presence of oxalate.

GRAPHICAL ABSTRACT



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ABSTRACT

Schwertmannite (Sch), a poorly crystalline iron mineral, shows high sorption capacity to As(V). In this study, the effects of UV irradiation and oxalate on the dissolution of pure Sch, Sch with adsorbed As(V) [Sch*-As(V)] and subsequent mobilization of As(V) were investigated at pH 3.0. Under UV irradiation, the dissolved Fe(II) took the majority of the total dissolved Fe during the dissolution of Sch and Sch*-As(V). In the presence of oxalate, Fe(III)-oxalate complexes formed on Sch [or Sch*-As(V)] could be converted into Fe(II)-oxalate by photo-generated electrons under UV illumination, and more total dissolved Fe produced compared to that without oxalate. In the dark, total dissolved Fe reached the maximum value (42.64 mg L^{-1} for Sch) rapidly and existed as Fe(III) predominately. In addition, UV irradiation has almost no effect on the mobilization of As(V) in Sch*-As(V) in the absence of oxalate. However, in the presence of oxalate, UV irradiation resulted in the mobilization of As(V) declined by 14–36.5 times compared to that in the dark. This study enhanced our understanding on the mobilization of As(V), and UV irradiation could contribute to the immobilization of As(V) on Sch in the aquatic environments containing oxalate.

1. Introduction

Arsenic (As) is a toxic contaminant in natural aquatic environments and originates from both natural processes, such as geothermal sources, weathering of As-bearing minerals, microbial activities, and anthropogenic activities (Smedley and Kinniburgh, 2002). Concentrations of arsenic in drinking water in many regions worldwide are higher than the World Health Organization

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(WHO) recommended safety limit of 10 μg L^{-1} (WHO, 1993), which puts a severe threat to the health of millions of people. In natural environments, As exists in a variety of valent states and in numerous organic and inorganic forms. Arsenate [As(V)] is a predominant inorganic specie in oxygen-rich environments and primarily exists as $H_2AsO_4^-$ and $HAsO_4^{2-}$ in natural aquatic environments since the pK_a values for arsenic acid are $pK_{a1} = 2.3$, $pK_{a2} = 6.8$, and $pK_{a3} = 11.6$ (Rasheed et al., 2017; Mohan and Pittman, 2007).

Iron (hydr)oxides are present in the environment as a wide range of minerals, most commonly goethite (α-FeOOH), ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$), lepidocrocite (γ-FeOOH) and schwertmannite [$Fe_8O_8(OH)_{8-2x}(SO_4)_x$, $1.0 \le x \le 1.75$] (Smedley and Kinniburgh, 2002; Cornell and Schwertmann, 2003). Owing to their great abundance and strong binding affinities to arsenic, iron (hydr)oxides are probably the most important adsorbents for the immobilization of arsenic in natural environments (Cornell and Schwertmann, 2003). Sunlight irradiation can lead to the photoreductive dissolution of iron minerals in photic water and soil surfaces (Sulzberger and Laubscher, 1995; Borer et al., 2005, 2009a, 2009b; Banwart et al., 1989). Two reaction steps are involved in this photoreductive dissolution process: (i) photoreduction of Fe(III) at the (hydr)oxides surface and (ii) subsequent release of surface-bound Fe(II) into solution (Banwart et al., 1989). Previous study has demonstrated that two mechanisms are known to potentially account for the formation of surface Fe(II) in natural waters: (i) electrons and holes are generated under irradiation via the charge transfer between lattice O(-II) and Fe(III) in iron (hydr)oxides, and then the photo-induced electrons will result in surface Fe(III) reduction (that is, the mechanism of semiconductor); (ii) ligand-to-metal charge transfer (LMCT) in photo-active surface Fe(III) complexes contribute to the formation of surface Fe(II) (Borer et al., 2005). The detachment of surface Fe(II) which determines the overall dissolution rate is of great importance in the photoreductive dissolution reaction of iron (hydr)oxides (Waite and Morel, 1984).

Dissolved organic matter (DOM) can affect the fate of As via different mechanisms (Sundman et al., 2014). Interactions between As and DOM are believed to occur mainly through Fe-bridges in ternary DOM-iron-As complexes (Lin et al., 2004; Redman et al., 2002; Sharma et al., 2010). DOM could effectively promote the reductive dissolution of iron minerals (Borer et al., 2005, 2009a, 2009b; Banwart et al., 1989). Siderophores [Desferrioxamine B (DFOB) and Aerobactin], for example, can accelerate the photoreductive dissolution of lepidorocite. At pH = 3, lepidocrocite dissolved 91 times faster in the presence than in the absence of DFOB (Borer et al., 2009b). DOM also competes with As(III/V) for binding sites on mineral surface (Redman et al., 2002). Oxalate is commonly found in natural environments (concentration varies from 2.5×10^{-5} to 4.0×10^{-3} M) and has a great contribution to photoreductive dissolution of iron (hydr)oxides (Reichard et al., 2007). Fe(III)/oxalate systems in atmospheric waters, in iron-rich surface waters, and possibly on soil surfaces are of interest in the degradation of pollutants. Wu et al. (2012) revealed that after 5 min UV irradiation 25 mg L^{-1} dissolved Fe(II) was yielded in the system of Sch (0.2 g L^{-1}) and oxalate (2 mM) at pH 4.0. In addition, 97% of methyl orange with the initial concentration of 50 mg L^{-1} was removed after 40 min UV irradiation. However, little attention has been paid to the photochemical reactions of the ternary As(V)-iron (hydr)oxides-oxalate system. Under light illumination, the effects of oxalate on the mobilization of As(V) adsorbed on iron minerals have not been studied, and the mechanism involved in the immobilization of the released As(V) by the newly-formed secondary iron minerals is also not clearly understood.

Acid-mine drainage (AMD) is polluted water with low pH and high concentrations of heavy metals and other toxic elements (Cheng et al., 2009). Nordstrom and Alpers (1999) reported that As(V) concentration could even reach 850 mg L^{-1} in an acid seep at Iron Mountain, California. Sch, a poorly crystalline Fe(III)-hydroxysulfate mineral, commonly found in AMD, is a good adsorbent for As(III) and As(V) (Bigham et al., 1994; Jönsson et al., 2005; Regenspurg et al., 2004). Our recent study suggested that the maximal adsorption capacity of As(V) on Sch could reach 182.86 mg g^{-1} Sch (Song et al., 2015). In the present study, we will further investigate oxalate and the amount of As(V) loading on the photoreductive dissolution of Sch with (and without) adsorbed As(V) and the mobilization of As(V).

2. Experimental section

2.1. Materials

All laboratory glasswares were repeatedly rinsed with deionized water before use. All reagents were of analytical grade, and all solutions were prepared with deionized water. $NaH_2AsO_4 \cdot 7H_2O$ (Merck, purity > 99.0%) and oxalate (Tianjin Bodi Chemical Co., Ltd., Tianjin, P.R. China, purity>98.0%) were used as As(V) and oxalate sources, respectively.

2.2. Synthesis of Sch and Sch*-As(V)

Synthetic schwertmannite was prepared according to the method by Kumpulainen et al. (2008). In this method, 500 mL preheated deionized water was mixed with 2.6 g $Fe_2(SO_4)_3$ in a round-bottomed flask with a mechanical stirrer. The flask was placed in a water bath at 85 °C for 1 h. The obtained solid was then centrifuged at 4200 rpm for 5 min, washed three times with deionized water and freeze-dried before use.

As(V) adsorption experiments were conducted at pH 3.0

Table 1
Adsorption capacity of Sch to As(V) at pH 3.0.

Species	As(V) adsorption (mg g^{-1})
Sch*-As(V)-1	97.0
Sch*-As(V)-2	128.7
Sch*-As(V)-3	147.9

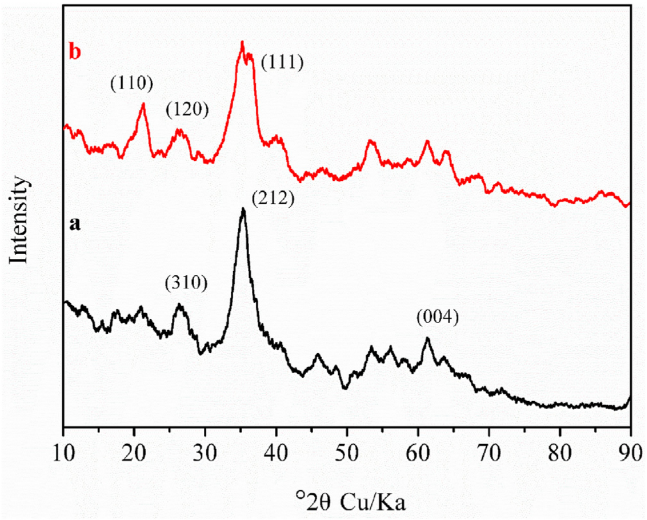

Fig. 1. XRD patterns of the synthetic Sch (a) before and (b) after the photoreductive dissolution in the presence of oxalate.