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# Differences in Sb(V) and As(V) adsorption onto a poorly crystalline phyllosmanganate ( $\delta$ -MnO<sub>2</sub>): Adsorption kinetics, isotherms, and mechanisms

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## ABSTRACT

The environmental behavior of antimony (Sb) in soils is often considered to be similar to that of arsenic (As). Comparing the adsorption behavior of these two elements on soil minerals is important because both elements coexist in contamination areas. In this study, the differences in antimonate (Sb(V)) and arsenate (As(V)) adsorption reaction kinetics and isotherm characteristics on a poorly crystalline phyllosmanganate ( $\delta$ -MnO<sub>2</sub>) were studied. The potential mechanisms were identified using zeta potential, Fourier transform infrared spectrometry (FTIR), and X-ray photoelectron spectroscopy (XPS) analyses. The adsorption isotherm results indicated that the maximum adsorption capacity for As(V) was 1.5 times higher than that for Sb(V). The adsorption kinetics of Sb(V) and As(V) were well fitted using pseudo-first-order model, and the adsorption rate of Sb(V) and As(V) significantly depended on  $\delta$ -MnO<sub>2</sub> dosage and pH. At all tested pH values (3.0–9.0), the adsorption rate of As(V) was 4.0–7.7 times faster than that of Sb(V) at the same  $\delta$ -MnO<sub>2</sub> dosage and pH conditions. FTIR and XPS analysis confirmed that M (metal)-O was bonded with Sb(V) and As(V). The adsorption capacity and rate of As(V) were significantly higher than those of Sb(V), suggesting that  $\delta$ -MnO<sub>2</sub> had higher affinity toward As(V). The different adsorption behaviors of Sb(V) and As(V) onto  $\delta$ -MnO<sub>2</sub> should be considered in soils.

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## 1. Introduction

Antimony (Sb) and arsenic (As) belong to Group 15 elements in the periodic table. These elements are listed as priority pollutants by the United States Environmental Protection Agency and the European Union because of their high toxicity to humans, plants, and microorganisms (Filella et al., 2002; Wang et al., 2012). In Sb mining and smelting areas in China, large quantities of wastewater, mining, and smelting residue containing Sb and As and exhaust gas are discharged

into receiving environments without proper treatment (Fu et al., 2011; Liu et al., 2010), leading to pollution of groundwater, surface water, soils, and air in these areas (Fu et al., 2011; Okkenhaug et al., 2012). A previous study reported that the Sb and As contents in soils near the Xikuangshan Sb mine were as high as 5045 and 205 mg kg<sup>-1</sup>, respectively (He, 2007). Moreover, Sb and As pollution poses a serious threat to human health via drinking water and food chain (Wu et al., 2011).

Although the environmental behavior of As has been widely investigated (Nordstrom, 2002; Oremland and Stolz, 2003; Takahashi et al.,

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2004), that of Sb has received limited research attention until recent years (Filella et al., 2002; Pierart et al., 2015). The oxidation state and environmental behavior of Sb and As in soils were strongly depended on the system redox and pH. Both elements exhibit the same oxidation states ranging from –III to +V because of their identical outer electron configuration (Filella et al., 2009; Wilson et al., 2010). Sb and As most commonly occur in the +V state in the forms of antimonates and arsenates under oxic surroundings, and the +III state with antimonites and arsenites forms under anoxic environments. Previous studies indicated that inorganic As(V) and Sb(V) were the dominant species in natural unsaturated soils (Mitsunobu et al., 2006; Wilson et al., 2010). Inorganic As(V) species at pH 2.20–9.22 are presented in the forms of  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  oxyanions, whereas Sb(V) is in the deprotonated form of antimonic acid ( $\text{Sb}(\text{OH})_6^-$ ) at  $\text{pH} > 2.72$ .

In general, Sb is often considered to behave similarly to As, but the differences in chemistry and environmental behavior of the two metalloids (Sb and As) have recently gained significant attention (Fu et al., 2016a; Wilson et al., 2010; Wang et al., 2017). Soil minerals play remarkable roles in affecting the migration and transformation of Sb and As, especially for metal oxides. Several studies have investigated the adsorption behavior of Sb and As on soil Fe and Mn oxides (Fan et al., 2014; Liu et al., 2015a; Wang et al., 2016) and clay minerals (Xi et al., 2011). Mn oxides are powerful oxidizing and detoxifying agents, and they play an important role in many elemental geochemical processes (Post, 1999). Layered phyllosulfates oxides (i.e.,  $\delta\text{-MnO}_2$ ) are more reactive than Mn oxides with tunnel structures (e.g., pyrolusite and romanechite). Due to their high specific surface areas and structures with highly reactive vacancy sites, they can absorb metals and metalloids via forming inner-sphere surface complexes (Lafferty et al., 2010). The adsorption of Sb(V) and As(V) on  $\delta\text{-MnO}_2$  performs a key role in controlling the migration of Sb and As in soils, and several studies indicate that the adsorption process of Sb(V) or As(V) on  $\delta\text{-MnO}_2$  depends on environmental and chemical conditions, such as solution pH, Eh, and coexisted ions (Belzile et al., 2001; Fu et al., 2016b; Liu et al., 2015a; Zhang et al., 2014). Our recent study showed that adsorbed As(V) on  $\delta\text{-MnO}_2$  is affected by  $\delta\text{-MnO}_2$  dosage and coexisting tetracycline hydrochloride anions (Wang et al., 2015). Several studies also investigated the sole or simultaneous adsorption efficiency and potential reaction mechanism of Sb(V) and As(V) on  $\delta\text{-MnO}_2$  (Lafferty et al., 2010; Zhang et al., 2014; Wang et al., 2015). However, few studies compared the adsorption capacity and rate of Sb(V) and As(V) on  $\delta\text{-MnO}_2$  at different environmental conditions.

This study aims to investigate the comparative adsorption of As(V) and Sb(V) on  $\delta\text{-MnO}_2$ . Furthermore, the differences in As(V) and Sb(V) adsorption reaction kinetics and isotherm characteristics were studied. The effects of  $\delta\text{-MnO}_2$  dosage and solution pH on reaction kinetics were also investigated. In addition, zeta potential, Fourier transform infrared (FTIR) spectrometry, and X-ray photoelectron spectroscopy (XPS) were used to characterize the adsorption mechanisms of As(V) and Sb(V) on the  $\delta\text{-MnO}_2$  surface.

## 2. Materials and methods

### 2.1. Materials

Fresh  $\delta\text{-MnO}_2$  used in this study was synthesized in the laboratory according to the method reported by Villalobos et al., (2003). The properties of  $\delta\text{-MnO}_2$  were analyzed using X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM–EDS), and Malvern Zetasizer Nano analyzer, as reported by Wang et al., (2015). Specific surface area was determined to be  $130.8 \text{ m}^2 \text{ g}^{-1}$  via  $\text{N}_2$  adsorption using Brunauer–Emmett–Teller (BET) method.

Potassium pyroantimonate ( $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ ) (>98.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, and sodium arsenate ( $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ ) (>98.0%) was obtained from Xiya Reagent Co., Ltd., China. Other reagents were purchased from Sinopharm Chemical

Reagent Co., Ltd. Shanghai, China. Sb(V) and As(V) stock solutions at 10 mM were prepared separately in pure water, and the working solutions of Sb(V) and As(V) were serially diluted from the stock solutions.

### 2.2. Experimental design

The effects of  $\delta\text{-MnO}_2$  dosage and solution pH were investigated using the adsorption kinetic experiments. Given that the pH in Sb mine drainage ranged from 3.48 to 9.88 (Fu et al., 2016a; Zhu et al., 2009), the effect of solution pH on Sb(V) and As(V) adsorption was investigated from 3.0 to 9.0. Before adsorption experiments, the suspended  $\delta\text{-MnO}_2$  was magnetically stirred for a minimum of 12 h to be homogenized. The background electrolyte was 0.01 M KCl, and solution pH in all experiments was adjusted using 0.1 M NaOH or 0.1 M HCl. Sb(V) and As(V) working solutions (0.5 mL, 200  $\mu\text{M}$ ) were separately added to a series of centrifuge tubes containing 20 mL  $\delta\text{-MnO}_2$  suspension and then shaken on a reciprocating shaker at 220 rpm and 25 °C. Then, 5 mL samples were withdrawn at different time intervals (0, 5, 10, 15, 20, 30, 45, 60, 90, 120, 180, 300, and 480 min). The residual Sb(V) and As(V) concentrations in water were measured after filtering the samples through 0.22  $\mu\text{m}$  hydrophilic polyestersulfone membranes. All experiments were conducted in triplicates. A portion of the samples was dried for FTIR and XPS analyses.

The amounts of Sb(V) and As(V) adsorbed on  $\delta\text{-MnO}_2$  were calculated using Eq. (1):

$$Q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

where  $Q_e$  ( $\mu\text{mol g}^{-1}$ ) represents the amount of Sb(V) or As(V) adsorbed on  $\delta\text{-MnO}_2$ ,  $V$  (mL) is the volume of the suspension,  $C_0$  ( $\mu\text{M}$ ) and  $C_e$  ( $\mu\text{M}$ ) are the initial and equilibrium concentrations of Sb(V) or As(V) in the supernatant, respectively, and  $m$  (g) is the mass of  $\delta\text{-MnO}_2$ .

The experiments for developing adsorption isotherms were performed at an initial pH of 7.0 and 25 °C. The initial Sb(V) and As(V) concentrations ranged from 1 to 200  $\mu\text{M}$  (1, 5, 10, 25, 50, 100, and 200  $\mu\text{M}$ ), whereas the content of  $\delta\text{-MnO}_2$  was  $300 \text{ mg L}^{-1}$ . After 480 min, equilibrium was supposedly reached, and the residual concentrations of Sb(V) and As(V) in solution were measured accordingly. Langmuir (Eq. (2)) and Freundlich (Eq. (3)) adsorption isotherm models were used to fit the Sb(V) and As(V) adsorption processes.

$$Q_e = \frac{k_1 Q_m C_e}{1 + k_1 C_e} \quad (2)$$

$$Q_e = k_f C_e^n \quad (3)$$

where  $Q_m$  ( $\mu\text{mol g}^{-1}$ ) is the maximum Sb(V) or As(V) adsorption capacity of  $\delta\text{-MnO}_2$ , whereas  $k_1$ ,  $k_f$ , and  $n$  represent the adsorption constants of Langmuir and Freundlich models. The units of  $k_1$  and  $k_f$  are  $\text{L } \mu\text{mol}^{-1}$  and  $\mu\text{mol}^{1-n} \text{ g}^{-1} \text{ L}^{-1}$ , respectively.

### 2.3. Analytical methods

The speciation of Sb, As, Mn, and O in solid samples was determined using XPS coupled with an Axis Ultra DLD spectrometer (Kratos, Shimadzu, Japan). The XPS data were measured using Al K $\alpha$  X-ray source, and the pressure in analytical chamber was less than  $6 \times 10^{-8}$  Pa. High resolution spectra for Sb 3d, As

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