



Adsorption of antimony onto iron oxyhydroxides: Adsorption behavior and surface structure



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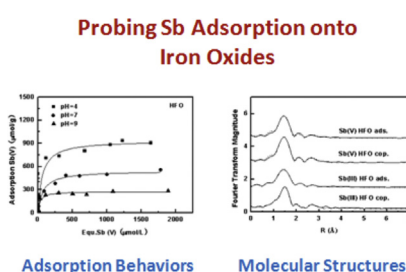
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HIGHLIGHTS

- Antimony adsorption depended on the Sb species, pH, and the type of iron oxides.
- Sb(V) adsorption favored at acidic pH, Sb(III) adsorption optimized in wider pH.
- Antimony was adsorbed onto the iron oxides by the inner-sphere surface complex.
- Bidentate mononuclear (²E) was the dominant form of Sb incorporated into HFO.
- XAFS and XPS indicated Sb(III) adsorbed was slowly oxidized to Sb(V).

GRAPHICAL ABSTRACT



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ABSTRACT

Antimony is detected in soil and water with elevated concentration due to a variety of industrial applications and mining activities. Though antimony is classified as a pollutant of priority interest by the United States Environmental Protection Agency (USEPA) and Europe Union (EU), very little is known about its environmental behavior and adsorption mechanism. In this study, the adsorption behaviors and surface structure of antimony (III/V) on iron oxides were investigated using batch adsorption techniques, surface complexation modeling (SCM), X-ray photon spectroscopy (XPS) and extended X-ray absorption fine structure spectroscopy (EXAFS). The adsorption isotherms and edges indicated that the affinity of Sb(V) and Sb(III) toward the iron oxides depended on the Sb species, solution pH, and the characteristics of iron oxides. Sb(V) adsorption was favored at acidic pH and decreased dramatically with increasing pH, while Sb(III) adsorption was constant over a broad pH range. When pH is higher than 7, Sb(III) adsorption by goethite and hydrous ferric oxide (HFO) was greater than Sb(V). EXAFS analysis indicated that the majority of Sb(III), either adsorbed onto HFO or co-precipitated by FeCl₃, was oxidized into Sb(V) probably due to the involvement of O₂ in the long duration of sample preservation. Only one Sb–Fe subshell was filtered in the EXAFS spectra of antimony adsorption onto HFO, with the coordination number of 1.0–1.9 attributed to bidentate mononuclear edge-sharing (²E) between Sb and HFO.

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1. Introduction

Antimony (Sb) is widely used in industry, such as flame retardants, catalyst in plastics, pigment in paints, additives in glassware and ceramics, and alloys in ammunition and battery producing plants [1–3]. It is one of the most exploited metalloids with a world production about 1.4×10^5 tons each year, resulting in elevated Sb concentrations in many soils and waters, especially around mining and smelter areas [4–9]. Sb concentration up to 0.5% in soil [4] and 6 mg L^{-1} in well water [9] was reported in the world largest antimony mine, Xikuangshan in Hunan province, China.

The toxicity of antimony species is similar to arsenic with trivalent compounds being ten times more poisonous than pentavalent species [10]. Antimony has been increasingly identified as a toxic heavy metal with implication in cancer development [10–13]. It is considered as a pollutant of priority interest by Environmental Protection Agency of the United States [14] and European Union [15].

In spite of the widespread usage and the substantial toxicity, little is known on the environmental behaviors of antimony in soil and aquatic system [5,7,16]. Both Sb(III) and Sb(V) appear to adsorb strongly to iron oxides, which thereby strongly influence the speciation, mobility and fate of antimony in the environment [17–21]. As the major antimony-carrying phase, iron hydroxides were reported to adsorb 40–75% of the total antimony retained in soil [22,23]. Strong evidence of Sb binding preferentially to iron oxides was further provided by the extended X-ray adsorption fine structure (EXAFS) measurements of soils from shooting ranges in Switzerland [5] and Ichinokawa mine in Japan [7]. On the other side, the ferric coagulation had been proved to be an effective technology to remove antimony from the aqueous systems, although the mechanism details were still unclear [24,25].

Compared with the extensive studies of adsorption of arsenic onto iron oxides, there have been relatively few investigations addressing the property and mechanism of antimony binding to these iron minerals. With similar trend as As(V), the adsorption of Sb(V) onto the iron oxides is favored at lower pH and decreases dramatically with increasing pH [17,18,23]. Sb(III) is strongly bound by goethite in a broad pH range 2–10 [18]. However, previous studies had not yet compared Sb(III) and Sb(V) adsorption capability exerted by different typical iron oxide minerals at different pHs, which is essentially important for the evaluation of environmental mobility of Sb species. The modeling fits had been applied in the adsorption edges, including a modified triple-layer model (TLM) for Sb adsorption to goethite [18], and diffuse-layer model (DLM) for Sb removal by ferric chloride coagulation [25]. Moderate agreement between the modeling fits and experimental data was obtained, although with significant discrepancy at relatively lower or higher pH [18,25].

In natural sediments, both crystalline (i.e., goethite, akaganéite, lepidocrocite, and hematite, magnetite) and amorphous iron oxide minerals can coexist. Based on Fe content, crystalline solids can be 2 to >10 times more abundant than amorphous solids [26]. The relative affinity of these different iron oxides for Sb species will greatly determine their distribution and mobilization in the environment. However, the adsorption isotherms of Sb(III) and Sb(V) on the iron oxides have only been depicted in the Sb(V) adsorption onto goethite [18]. Therefore, the evaluation of antimony mobility during the phase transformation of iron oxides is currently not accessible due to the lack of information on the affinity and adsorption densities of different iron oxides for Sb species.

The surface structure of Sb(III) and Sb(V) binding with the iron oxides is still unclear [5,7,18]. The local structure of Sb species in ferrihydrite and goethite has been studied using EXAFS. Both Sb(V) and Sb(III) are adsorbed onto iron oxyhydroxides by the

formation of an inner-sphere surface complex [5,7,27–29]. Mitsunobu et al. [30] proposed the formation of bidentate binuclear complex with double corner linkage (^2C) between Sb(V) and ferrihydrite. However, an alternative complex form of bidentate-mononuclear surface complex with edge linkage (^2E), was extracted in Sb(V) adsorption onto goethite [5]. The structural incorporation of Sb(V) into ferrihydrite, goethite, and natural iron oxyhydroxides from Sb contaminated soil was likely to occur [30]. Within one week, Sb(III) adsorbed on goethite was partly oxidized, and the oxidation rate tends to increase with increasing pH [18].

The first objective of this study was to compare the relative affinity of Sb(III) and Sb(V) for different iron oxide minerals, including hydrous ferric oxide (HFO), goethite, akaganéite, lepidocrocite, and hematite. Secondly, this study compared and modeled Sb(III) and Sb(V) adsorption edges on two common iron oxide minerals, HFO and goethite, at different pHs. The comparison of adsorption capability would benefit the prediction of Sb environmental mobility, which was mainly determined by the species of Sb, the phase of iron oxides, and acid–base condition. Finally, EXAFS and X-ray photon spectroscopy (XPS) spectra were used to illustrate the mechanism and speciation of antimony retained on the as-synthesized HFO.

2. Materials and methods

2.1. Antimony adsorption experiments

Chemicals and materials in details were provided in the supporting information. The adsorption experiments were carried out with a background electrolyte of 0.01 M KClO_4 for Sb(V) or 0.2 M NaCl for Sb(III). Adsorption of Sb(V) and Sb(III) onto iron oxides (0.4 g L^{-1}) was initiated by the addition of antimony stock solutions into solid suspensions. Both the Sb(III) stock solution and the solid suspensions were purged with N_2 gas for 10 min before adsorption experiments. The pH of the suspension was adjusted with HCl (or HClO_4) and KOH during the experiment. Suspensions were mixed on a rotary shaker (110 rpm) for 24 h at 20.5°C . The final pH measured at the end of the experiment is reported. After the reaction, the suspensions were centrifuged.

2.2. Adsorption isotherm

Antimony adsorption isotherms onto goethite, akaganéite, lepidocrocite, and hematite, magnetite, and HFO were performed at $\text{pH } 4 \pm 0.1$, 7.0 ± 0.1 and 9 ± 0.1 for Sb(III) and Sb(V). After the centrifugal separation, the supernatant was poured out, and the slurry was dissolved in 2 M HCl. The Sb concentrations in both the supernatant and the slurry were analyzed. The data of antimony adsorption were fitted with Langmuir isotherm model. The Langmuir adsorption isotherm is expressed as an equation of the type:

$$q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (1)$$

where C_e is the equilibrium concentration of antimony in solution ($\mu\text{mol Sb L}^{-1}$), q_e is the equilibrium adsorption capacity ($\mu\text{mol Sb g}^{-1}$ sorbent), Q_{\max} is the maximum adsorption capacity ($\mu\text{mol Sb g}^{-1}$ sorbent), and b is constant ($\text{L } \mu\text{mol}^{-1}$). A nonlinear regression (Origin 7.0) was used to obtain the isotherm model parameter.

2.3. Adsorption edges

Antimony adsorption edges (adsorption vs. pH) were obtained at two initial Sb(V) or Sb(III) concentrations (50 and $100 \mu\text{mol L}^{-1}$ of Sb(V) or Sb(III) for goethite, 100 and $200 \mu\text{mol L}^{-1}$ of Sb(V) or Sb(III) for HFO). In a pH range of 3–12, the suspension pH values

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