Adsorption and desorption of Sb(III) on goethite

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Abstract: The present study examined the effect of pH and ionic strength on Sb(III) adsorption on goethite and desorption of Sb(III) binding to goethite. Adsorption of Sb(III) is favored by low pH and high ionic strength. Desorption of Sb(III) from Sb(III) treated goethite is dependent on the adsorption suspension pH and increased with increasing the original suspension pH.

1. Introduction
Antimony(Sb) have many applications in modern industry such as increasing the hardness of alloys in lead-acid batteries, functioning as a flame retardant, and being used in the clarification of glass products and is consequently widely distributed throughout the environment. Recent years, some researchers focused on the Sb pollution in the environment considering its potential carcinogenicity to humans.

Sb(III) and Sb(V) are the most stable species in the environmental samples under the natural oxidizing and reducing conditions, respectively. Sb(III) exists as Sb(OH)₃ and Sb(V) should occur as a negatively charged complex, Sb(OH)₆⁻ in the pH range of 2 to 11 in aqueous solution. The toxicity of Sb depends strongly on its oxidation state and Sb(III) is ten times more toxic than Sb(V) [1]. Elevated Sb concentration has been detected near Sb mining and smelting areas [2] although its value is generally below 1 mg/kg and 1 ug/L in natural soils and waters in the unpolluted environments, respectively [3]. Speciation analyses of Sb in aquatic systems and soil systems have shown that Sb(V) predominates and Sb(III) is only found at low concentrations under oxic conditions [4-6]. The reason for this may be that Sb(III) sorbs more strongly to mineral surface than Sb(V) and this strong adsorption results surface oxidation of sorbed Sb(III). Humic acid, a natural occurred organic matter, can also bind Sb and oxidize Sb(III) to Sb(V) [7,8].

Recent studies have demonstrated that iron oxide in the natural soils and sediments is the most important host of Sb and Sb(III) sorbs more strongly to surfaces than Sb(V) [9,10]. Goethite is a common iron oxide existed in natural environment. The purpose of this study was to investigate the adsorption of Sb(III) on goethite under various environment conditions and the desorption of Sb(III) from goethite.

2. Materials and Methods
The goethite used in this study was obtained from Sigma-Aldrich, with a 15.8 m²/g specific surface area determined by BET method using N₂. All chemicals were of at least analytical grade and used without further purification. Double distilled water was used throughout. All experiments were performed in at least duplicate. Sb(III) stock solution was prepared from potassium antimonyl tartrate. Batch adsorption of Sb(III) at different pH and ionic strength was examined by shaking goethite suspension in a series of 50 mL polythene centrifuge tubes containing 500 mg goethite in 20 mL of 1
mg/L Sb(III) for 24 hours at 298 K. The pH of the suspensions was adjusted ranging from 3 to 10 with 0.1 M NaOH/HCl after addition of the Sb solution. Ionic strength was maintained by adding NaCl. Desorption was performed for goethite which were treated with Sb(III) solution between pH 3 and 10. The Sb(III) treated goethite was resuspended in 20 mL 0.1 M MgSO₄ for 12 hours at 298 K. After shaking, the tubes were centrifuged and filtered. The concentrations of Sb(III) in the filtered supernatants were determined by hydride generation atomic fluorescence spectrometer (AFS-230, Beijing Haiguang Instrument Co., China). The pH of the suspensions was measured by a basic PB-10 pH meter (Sartorius, Germany), calibrated with commercial pH 4.0, 7.0 and 10.0 buffers.

3. Results and Discussion

The effects of both solution pH and ionic strength on the adsorption of Sb(III) on goethite are shown in Figure 1. It is obvious that Sb(III) adsorption on goethite was strongly dependent on pH and decreased with increasing pH between pH 3 and 10 in 0.005, 0.05 and 0.1 M NaCl solutions respectively. In an earlier study, the similar pH-dependence curves of Sb(III) adsorption on hydrous oxides of Mn, Fe, and Al were shown in an pH range of 4 to 9 in the presence and absence of NaAc and with Sb(III) from Sb₂O₃ and potassium antimonyl tartrate respectively[11]. Another research on Sb(III) adsorption on goethite reported that maximum Sb(III) adsorption was found at pH values of 3 to 5 and Sb(III) adsorption decreased weakly at both pH values below 3 and above 5, and >80% of Sb(III) was adsorbed between pH 1 and 12[12]. In highly and mildly acidic media, the amount present as Sb(OH)₄⁻ increases and this cation formation would explain the phenomenon that Sb(III) adsorption decreased at low pH values in Leuz’s work[12] due to the increased goethite positive charge. Whereas at high pH values, adsorption of Sb(III) decreased due to sorbed Sb(III) oxidation to Sb(V) and Sb(V) desorption which had been addressed by Leuz et al[12]. According to Thanabalasingam and Pickering[11], the effect of pH on Sb(III) adsorption is more related to the chemical form of the adsorbate species than to the changes in net surface charge of mineral because the trend of pH dependence curves of Sb(III) adsorption on MnOOH, FeOOH, and Al(OH)₃ was similar in a pH range of 3 to 9. There were two most notable differences in experimental conditions used by Leuz et al. and Thanabalasingam et al. which may resulted the above different explanations for the effect of pH on Sb(III) adsorption by Leuz et al. and by Thanabalasingam et al. Firstly, Leuz et al. took a wide pH range of 1 to 12 to conduct the experiment while Thanabalasingam et al. did not test the effect of pH on Sb(III) adsorption under the highly acidic conditions. Secondly, surface oxidation of Sb(III) to Sb(V) was considered and examined by Leuz et al. Leuz et al. measured the concentrations of Sb(III) both in solution and on goethite surface after Sb(III) adsorption experiment, corresponding results showed that 35, 50, and 90% of Sb(III) adsorbed on goethite were oxidized within 7 days at pH 3, 5.9 and 9.7 respectively. However, no significant amounts of Sb(V) were determined in solution at pH below 7.3. These observations investigated that Sb(V) from surface oxidation of Sb(III) inclined to bind to the goethite surface under acidic and neutral media and easily escape into the solution at high pH. The observed enhanced amount of Sb(V) desorption at high pH is generally expected because of the decreasing positive charge on the goethite. In addition, Sb(V) ions is likely to form oligomers such as Sb₁₂(OH)₆₄⁻ under acidic conditions which is more favored for Sb(V) adsorption compared with Sb(V) monomers.

Above pH 5, the influence of ionic strength on the adsorption of Sb(III) was strong and resulted in a higher adsorption of Sb(III) at higher ionic strength as shown in figure 1. A different result on ionic strength effect on Sb(III) adsorption to goethite was shown, which shown that ionic strength had no influence on Sb(III) adsorption in 0.01 and 0.1 M KClO₄ solutions over a wide pH range and proposed that Sb(III) formed inner-sphere surface complexes at the goethite surface[12]. This result may be due to the combination of high Sb(III) adsorption capacity of goethite and a very low Sb(III) addition. A explanation for the phenomenon observed in the present study is that ionic strength had a profound effect on the oxidation of adsorbed Sb(III) on goethite, which consequently showed significant effect on Sb(III) adsorption. Leuz and Johnson[11] found that the rate coefficients for Sb(III) oxidation with H₂O₂ were indeed influenced by ionic strength and increased at pH 10 and 12 with increasing ionic
strength. However, there has no any research on the effect of ionic strength on Sb(III) oxidation in the presence of minerals till the present. A previous study revealed that As(III) oxidation in clay minerals suspensions did not depend on ionic strength\cite{14}.

![Desorption of Sb(III) from goethite](image)

**Figure 1.** Effect of pH and ionic strength on the adsorption of Sb(III) on goethite with reaction conditions: $T=298\pm1K$, initial Sb(III) concentration=1 mg/L, $m/v=0.5$ g/20 mL, reaction time=24 h.

![Desorption of Sb(V) from goethite](image)

**Figure 2.** Desorption of Sb(V) from goethite with reaction conditions: $T=298\pm1K$, $m/v=0.5$ g/20 mL, 0.1 M MgSO$_4$ extraction solution, reaction time=12 h.

The desorption of adsorbed Sb(III) from Sb(III) treated goethite is shown in Figure 2. The fraction of Sb(III) recovery was strongly dependent on the original suspension pH. A maximum desorption of Sb(III) was observed when the adsorption was conducted at pH 9.8. Significant amount of adsorbed Sb(III) was oxidized to Sb(V) on the goethite surface in the pH range of 3 to 10. While Sb(V) is more easily released into solution from mineral surface at high pH values as demonstrated by McComb et
A similar research on As(III) adsorption and stability at the clay mineral-water interface reported the similar experimental results about As(III) desorption.

4. Conclusions
In this study, we investigated the effect of pH and ionic strength on Sb(III) adsorption and desorption of Sb(III) from Sb(III) treated goethite. Sb(III) adsorption decreased with increasing pH in a pH range of 3 to 10 and increased with increasing ionic strength above pH 5. Desorption experiment shows that Sb(III) inclined to escape into the solution from goethite surface at high adsorption pH values. The observed desorption phenomenon may be that Sb(III) sorbs strongly to goethite, but that also results in Sb(III) surface oxidation and Sb(V) desorption particularly at high pH values.

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