学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Adsorption and co-precipitation behavior of antimony with ferrihydrite and their silica effects
(フェリハイドライトによるアンチモンの吸着・共沈挙動とシリカの及ぼす影響)

Antimony(Sb) is a natural occurring element widely dispersed in the lithosphere. Elevated antimony concentrations in aqueous environments from anthropogenic sources such as mining and smelting are becoming of global concern. In this respect ferrihydrite are known to strongly adsorb aqueous antimony species with different oxidation states, but the effect of silica on the removal characteristics is not well understood despite being a common component in the environment. A further important process, co-precipitation with ferrihydrite, does not appear to have been reported. In this study, first, the adsorption of antimonite (Sb(III)) and antimonate (Sb(V)) onto ferrihydrite were investigated as a function of initial pH, ionic strength, initial concentration and adsorbent dosage. It was further studied the adsorption process under the dissolved silica (Si) effect. Second, the surface complexation modeling was applied for the adsorption mechanism, the surface Sb(III) and Sb(V) species at different chemical conditions were evaluated. Finally, the adsorption and co-precipitation behavior of Sb(III) and Sb(V) with ferrihydrite and Si-bearing ferrihydrite was investigated.

Chapter 1 refers to the background of this study and the reviews the literature on the chemistry speciation of Sb, its distributions, the remediation from the natural environment as well as current knowledge on adsorption mechanism. This chapter describes iron oxides and hydroxides minerals such as goethite, hematite, and ferrihydrite, which are excellent scavengers for Sb adsorption due to their ubiquitous distribution in the surface, large specific surface area and unique surface characteristics. As iron minerals are closely associated with silica, one of the most common ligands present in natural environments, this could mean that silica may affect the crystallization behavior as well as the capacity of ferrihydrite to regulate hazardous element recycling.

Chapter 2 presents the literature review on surface complexation model of antimony and research objectives of this study. the drawbacks of the current using surface complexation model are identified. To gain knowledge on the adsorption mechanism of Sb on ferrihydrite, it is useful to develop a predictive model for the adsorption behaviors of Sb(III) and Sb(V) on ferrihydrite, which can predict both the adsorption effectiveness and surface speciation under variable solution conditions.

Chapter 3 refers to the adsorption of Sb on ferrihydrite and their silica effect. In this work, the X-ray diffraction (XRD) analyses of the precipitates showed two broad diffraction features at approximately 35^0 and 62^0 2θ, which are characteristics of 2-line ferrihydrite, but no significant shifts in peak positions in the ferrihydrite regardless of the Si/Fe ratios. The infrared spectra showed a sharp band at ~930 cm^{-1}, corresponding to asymmetric stretching vibrations of Si-O-Fe bonds which increased in intensity with increasing Si/Fe molar ratios. Further, the surface charge on the precipitates became more negative with increasing Si/Fe molar ratios. The adsorption experiments indicated that Sb(V) was preferentially adsorbed under acidic conditions which decreased dramatically with increasing pH while the adsorption rate of Sb(III) was independent of pH. However, the presence of Si suppressed the adsorption of both Sb(III) and Sb(V).

Chapter 4 focuses on the adsorption mechanism of Sb(III) and Sb(V) on ferrihydrite. Adsorption data were modelled using an extended triple-layer model (ETLM) to infer Sb(III) and Sb(V) adsorption reactions and equilibrium constants. The two principal reactions of Sb(III) adsorption forming bidentate binuclear inner-sphere surface species were found to be consistent with the experimental data. Solution pH and ionic strength showed little effects on the adsorption of Sb(III). The adsorption of Sb(V) was represented by the formation of a monodendate-mononuclear outer-sphere and a

bidentate-binuclear inner-sphere species. The Sb(V) adsorption on ferrihydrite decreases continuously with increasing pH and ionic strength. The predicted model speciation of Sb(V) on ferrihydrite showed that the inner-sphere species increase concomitantly with increasing pH and ionic strength and solid concentration. The outer-sphere species distribute over a wider range of pH conditions and are more important at lower ionic strengths.

Chapter 5 investigates the adsorption and co-precipitation behavior of Sb(III) and Sb(V) with ferrihydrite and Si-bearing ferrihydrite. The adsorption experiments indicated that Sb(V) was preferentially adsorbed under acidic conditions which decreased dramatically with increasing pH while the adsorption rate of Sb(III) was independent of pH. However, the presence of Si suppressed the adsorption of both Sb(III) and Sb(V). The results showed that Sb(III) and Sb(V) ions were significantly inhibited by co-precipitation with ferrihydrite even in the presence of Si by isomorphous substitution in the ferrihydrite crystal structure. Both adsorption and co-precipitation samples were analyzed by XRD for mineralogical characterization. In the adsorption samples of the Si/Fe molar ratios precipitates series, all of the XRD patterns were almost identical to that of pure two-line ferrihydrite, and any other peaks and peak shift were not observed for both Sb(III) and Sb(V) loading. While the co-precipitation samples showed that the peak of ferrihydrite around 30^0 and 60^0 gradually shifted to a lower angle with Si/Fe ratio. In addition to these noticeable features, broadening of both peaks was also observed on co-precipitation samples. They suggest that the shift and broadening can be attributed to the differences in ionic radius and charge between Fe(III) and guest Sb in ferrihydrite.

Chapter 6 presents the summary and concluding remarks as well as a short outlook for future necessities and suggestions of research. Overall, this study investigated adsorption and co-precipitation of Sb on ferrihydrite and their silica effect to gain knowledge on Sb remediation mechanism. The establishment of ETLM for antimony adsorption may help to understand not only prediction of the environmental behavior but also to provide the effective countermeasure for the contamination. This study also has important implications for determining the role of ferrihydrite in controlling the final state of Sb in the environments in which it is released. Although ferrihydrite is an excellent substance for capturing Sb, its use as a medium in a natural Si-rich system should be considered with caution because it will tend towards inhibition of Sb capture induced by the Si-rich environment. However, this may be different in the case of co-precipitation processes. In the present study, we found that silica and Sb(III) and Sb(V) can be incorporated into ferrihydrite and that these three are structurally compatible with ferrihydrite. The co-precipitation process of Sb(III) and Sb(V) would not be greatly influenced by the silica factor. Thus, Sb(III) and Sb(V) co-precipitation with ferrihydrite would be more efficient than Sb(III) and Sb(V) adsorption by ferrihydrite. This finding will be important when making predictions of the final state of Sb associated with ferrihydrite in natural Si-rich systems. In order to further develop and apply the ferrihydrite in adsorption and co-precipitation process. The efficiency of ferrihydrite to remove Sb should be studied in different water matrices since the natural environment is a more complex condition.