

## As(V) sorption mechanism in solution using ferrihydrite

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This study was conducted to investigate the mechanisms by which dilute As(V) co-precipitates with ferrihydrite in aqueous solutions. Co-precipitation occurs as a result of a combination of different mechanisms including adsorption, precipitation, storage or solid solution. In the present study, the co-precipitation mechanisms were divided into two categories: surface complexation and surface precipitation. Surface complexation was considered to be the two-dimensional adsorption of As(V) onto the surface of ferrihydrite, whereas surface precipitation was used to describe the three-dimensional uptake of As(V) into ferrihydrite. Surface precipitation involves ternary adsorption, storage or solid solution that occurs beyond the thermodynamic bulk precipitation range.

The objective of this study was to identify the transition point of As(V) adsorption and surface precipitation in aqueous systems using XAFS.

**Experimental**

We conducted batch experiments of co-precipitation or adsorption with ferrihydrite. The reaction time was fixed at one hour, which is the time commonly used to treat wastewater. All chemicals and solutions used in this study were of analytical grade and were purchased from Kanto Chemicals, Inc., Japan. The As(V) and Fe(III) solutions were prepared from  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , respectively. For all experiments, the pH and ionic strength were adjusted by the addition of 0.05 M  $\text{HNO}_3$ , KOH and  $\text{KNO}_3$ . Specifically, the pH was fixed at 5 or 7 and the ionic strength was fixed at 0.05. The initial concentration of Fe(III) was fixed at 0.18 mmol/dm<sup>3</sup> and the concentration of As(V) was changed to attain the target initial As/Fe molar ratio of 0.13-5. The filter residue was applied to the XAFS analysis.

Poorly crystalline ferric arsenate was synthesized as a reference material to be compared with the ferrihydrite co-precipitated with As(V)

**Results and Discussion**

Figure 1 shows a comparison of the EXAFS patterns of the co-precipitated As(V) with ferrihydrite as a function of the initial molar ratio of As/Fe at pH 5.

As shown in Figure 1, the poorly crystalline ferric arsenate (fa) showed a bumped shaped wave at a first peak. However, the XRD spectrum obtained for As(V) adsorbed ferrihydrite (ad) showed a smooth shaped wave.

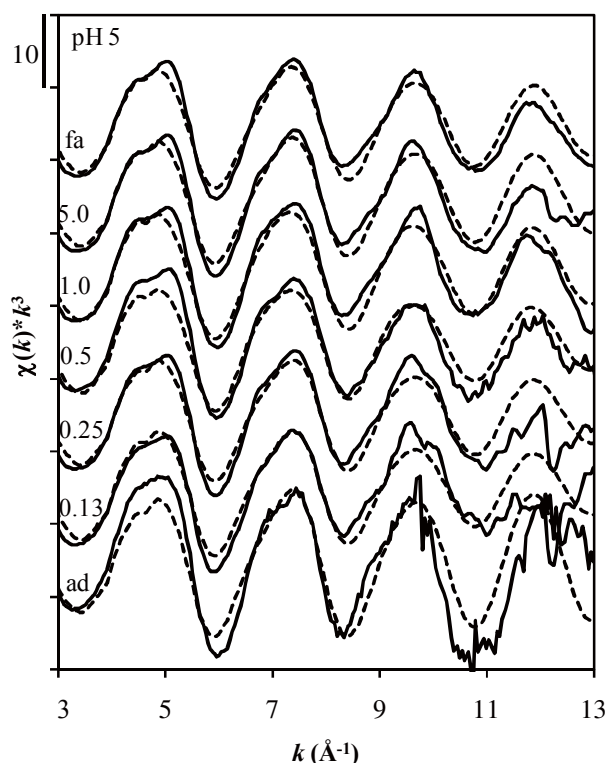


Figure 1 As EXAFS spectra of As(V) co-precipitates with ferrihydrite using an initial As/Fe ratio of 0.13 to 5.0, As(V) adsorbed ferrihydrite (ad) and poorly crystalline ferric arsenate (fa).

When the co-precipitated products were generated using an initial As/Fe ratio of 0.13 or 0.25, the EXAFS patterns were almost identical to those of As(V) adsorbed ferrihydrite, but a small bumped shape was appeared at the first peak. In these cases, the mechanism of co-precipitation of As(V) is predominantly adsorption to the surface of ferrihydrite. A bumped shape at the first peak appeared prominently with increasing initial As/Fe ratio and the EXAFS patterns of As/Fe = 5.0 were almost identical to those of ferric arsenate. These results showed that As(V) sorption mechanism in co-precipitation shifted gradually from simple adsorption of As(V) to ferrihydrite toward surface precipitation of ferric arsenate. Curve fitting results from the EXAFS patterns showed that coordination number between As-Fe bond gradually increased with increasing initial As/Fe molar ratio.

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