Effect of Surface Functional Group Coordination on As(V) Adsorption on Aluminum Hydroxide Surfaces

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Aluminum hydroxides are highly reactive minerals of widespread abundance in nature. They play important roles in regulating the environmental fate and transport of contaminants and nutrients. As a global water contaminant, arsenate fate in aquatic systems is strongly governed by adsorption to mineral surfaces. Such surfaces display multiple hydroxyl surface functional groups. On aluminum hydroxides, for example, groups occur that are coordinated to one (>AlOH) or two (>Al_2OH) underlying aluminum atoms, each of which may differ in their adsorption affinities for arsenate. The distribution of functional groups varies among distinct crystallographic faces of minerals and we thus hypothesize that arsenate adsorption behavior will show a dependence on particle morphology. To test this hypothesis, we investigated individual and competitive adsorption of arsenate and phosphate at pH 4 and 7 on two aluminum hydroxide polymorphs, gibbsite and bayerite, with distinct particle morphologies. Arsenic K-edge EXAFS measurements of select samples explored the changes in arsenate complexation mechanisms on these hydroxide minerals in the presence and absence of phosphate.

Synthetic gibbsite platelets exhibit large (001) basal surfaces bound predominantly by >Al_2OH groups. In contrast, synthetic bayerite rods expose mainly edge surfaces dominated by >AlOH groups. Macroscopic studies show both oxoanions behave similarly in individual adsorption experiments, with bayerite adsorbing more arsenate or phosphate per unit surface area than gibbsite. The addition of phosphate reduces arsenate adsorption on both minerals via competitive adsorption. Phosphate has a greater effect on arsenate adsorption to gibbsite than that to bayerite. These observations indicate that the affinities >Al_2OH groups for both oxoanions differ from that of >AlOH groups. EXAFS spectroscopy reveals that arsenate adsorbed to gibbsite has a lower coordination number of Al neighbors on average than bayerite, suggesting either a greater proportion of outer-sphere arsenate or a distinct coordination environment. These differences are largely preserved during competitive adsorption with phosphate. These results demonstrate that macroscopic and molecular-scale arsenate adsorption behavior is affected by surface functional group coordination states.