

ARSENIC-GIBBSITE INTERACTIONS USING ADSORPTION STUDIES, VIBRATIONAL SPECTROSCOPY AND MECHANISTIC MODELING

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Because of its toxicity, arsenic is of considerable environmental concern. Arsenate and arsenite ions, for example are highly toxic species, which may be present in aquatic environments as a result of geothermal activities, contamination by pesticides and dissolution of mine wastes. Of the various sources of As in the environment, drinking water probably poses the greatest threat to human health.

The mobility of arsenic in the environment depends on the mineralogy of the soil and on adsorption-desorption. The major arsenic adsorbants in natural systems are the hydroxides of iron. In this study, adsorption properties of As(V) at gibbsite-water interface was determined by pH and pAs titrametric methods in combination with vibrational spectroscopy and molecular modeling methods. The effect of electrolyte concentration on As(V) adsorption at a given pH was not significant, and thus the formation of an inner sphere complex is revealed. As(V) adsorption on gibbsite was a significantly rapid process and was found to reach optimum adsorption after a maximum 2 hour equilibrium period.

The FTIR spectrum of As(V)-treated gibbsite showed six peaks in the OH stretching region: the peaks at 3396 and 3378 cm^{-1} in bare gibbsite being shifted to 3380 and 3372 cm^{-1} respectively, whilst the signal at 3520 cm^{-1} is lost. Disappearance of the signal at 3520 cm^{-1} provides strong evidence for an As(V)-surface direct bonding. However, solely based on IR spectral data, it is difficult to discuss the surface nature of complex or the number of Al atoms that bond to arsenate polyhedra. Further evidence for the stability of a bidentate binuclear complex of As(V)-gibbsite is derived from molecular model calculations. Analysis of As(v) adsorption data with the charge distribution multisite ion complexation model (CD-MUSIC) shows that the formation of the surface complex is accompanied by a redistribution of charge in the interfacial region due to the binding structure in which anion partially coordinates with the surface. Interestingly, during the energy minimization step the As(V) monodentate complex always converges to the bidentate mode, which demonstrates that the former surface configuration is not stable, at least from a theoretical viewpoint. Hence, it is concluded that the most stable As(V)-gibbsite configuration is a bidentate-binuclear complex.