MECHANISTIC, SPECTROSCOPIC AND MOLECULAR MODEL PROBING OF THE ARSENIC – GIBBSITE INTERFACE

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Because of its toxicity, arsenic is of considerable environmental concern. Its solubility in nature is strongly influenced by adsorption – desorption processes. Majority of arsenic adsorption in natural systems indicate iron hydroxides as main sorbents. Relatively few studies have focused on adsorption properties at the gibbsite – water interface. In this work, I have characterized, systematically, the gibbsite – water interface by pH and pAs titrametric methods in combination with vibration spectroscopy and molecular modeling methods.

Analysis of As(V) adsorption data with the charge distribution multisite ion complexation model (CD-MUSIC) show 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. In principle four surface structures are suggested i.e. bidentate binuclear complex, bidentate mononuclear complex, monodentate mononuclear complex, and monodentate binuclear complex. The vibration spectroscopic data have confirmed that As(V)-surface complex is bidentate binuclear complex. Semi-empirical molecular methods using MOPAC and PM3 were used to optimize the geometry of this surface complex resulting inter-atomic distances of As(V)-Al, As(V)-O as 3.21 A° and 1.67 A °respectively.

Analysis of As(III) adsorption data such as ionic strength dependence, kinetic data and adsorption isotherms suggest that As(III) is outer spherically bonded weakly to surface sites. No considerable pH change in the As(III) treated samples assumed that there is no proton exchange upon As(III) adsorption on gibbsite. Calculated relative abundance of As(III) species using ECOSAT program and corresponding thermodynamic data have shown only H_3AsO_3 is the most dominant throughout the pH range considered. Two surface configurations are suggested i.e. bidentate binuclear complex and monodentate mononuclear complex. Analysis of As(III) adsorption data with the charge distribution multisite ion complexation model (CD-MUSIC) show that the possible surface configuration is a bidentate binuclear complex. Semi-empirical molecular methods using MOPAC and PM3 calculations predicted that the distance between two adjacent $>AlOH^{1/2-}$ sites is 2.80 A°. The terminal –OH groups of As $(OH)_3$ reside at a 3.10 A° distance apart.