

Exploring contaminant adsorption on the surface of nanoscale particles: A combined experimental and theoretical approach.

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Naturally occurring iron and aluminum oxyhydroxide nanoparticles with Keggin-type structural features are considered some of the most effective materials for adsorption of toxic heavy metals, radionuclides, and oxyanions. While the adsorptive capabilities of these particles have been established, identification of the specific reactivity factors and a mechanistic understanding of the adsorption process is lacking. To gain insights into these processes, polyaluminum Keggin-type species with diameters between 1-2 nm can be utilized as geochemical model compound and probed using both experimental and theoretical methods. In the current study, the well known Al_{30} molecule has been chosen as a model compound to investigate the adsorption of heavy metal (Cu^{2+} , Zn^{2+}) cations and phosphate anions. Al_{30} nanoparticles with adsorbed contaminants were crystallized and their structural characteristics were determined using single crystal X-ray diffraction. Density Functional Theory (DFT) was utilized to determine the relative stability of the experimentally determined molecules and provide a more detailed understanding of the reaction mechanisms. For the heavy metal cations, the DFT energetics associated with step-wise reaction schemes indicated that the counter-ion present in solution plays an important role in the adsorption process. For the phosphate anion, the adsorption process is exothermic, but the reaction mechanism is quite different. In addition the energetics of the anion adsorption can be tuned by introducing of organic functional groups, suggesting the presence of organic matter can also impact contaminant uptake on nanoparticle surfaces.

