Binding of heavy metals at the interface of mineral-microorganism complexes

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Clay minerals, bacteria and humic substances produce mineral-organic composites in soils and associated environments. The mechanisms of the binding and competitive adsorption of heavy metals on bacteria-associated clay mineral complexes have been poorly understood. Batch sorption, ITC, EXAFS and μ-XRF were applied to investigate the binding characteristics of Cd and its competition with Pb on montmorillonite (Mont)-humic acid(HA)-bacteria composites. Additive sorption and non-additive Cd(II) sorption are observed for the binary Mont-bacteria and ternary Mont-HA-bacteria composite, respectively. In the ternary composite, the coexistence of HA and bacteria inhibits Cd adsorption, suggesting a "blocking effect" between humic acid and bacterial cells. Large positive entropies, and linear combination fitting of the EXAFS spectra for Cd adsorbed onto Mont-bacteria and Mont-HA-bacteria composites, demonstrate that Cd is mostly bound to bacterial surface functional groups by forming inner-sphere complexes. The decreased coordination of C atoms around Cd and the reduced adsorption enthalpies and entropies for the binary mixtures suggested the transformation of bidentate Cd-carboxyl complexes into monodentate ones. Stronger competition was observed on clay mineral than on bacteria–clay composite due to more non-specific sites for heavy metal adsorption on clay mineral. Both competing heavy metals tended to react with bacterial fractions in the composite, which was verified by the higher correlation of Cd (and Pb) with Zn ($R2 = 0.41$) elemental distribution than with Si ($R2 = 0.10$). The competitive adsorption exhibited a lower entropy change (ΔS) at the metal-sorbent interfaces compared with single-metal adsorption. The understanding on the binding mechanism of Cd at the bacteria–mineral interfaces from a molecular and thermodynamic view would have an environmental significance for predicting the chemical behavior of heavy metals in complex mineral–organic systems.