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Surface reactions of iron - enriched smectites: adsorption and transformation of hydroxy fatty acids and phenolic acids

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Iron-enriched smectites play an important role in adsorption and transformation of soil organic components. Soil organo-clay complexes, and in particular humin contain hydroxy fatty acids, which are derived from plant biopolymer cutin. Phenolic acids belong to another major group of organic acids detected in soil. They participate in various soil processes, and are of concern due to their allelopathic activity. We studied the reactivity of iron-enriched smectites (Fe(III)-montmorillonite and nontronite) toward both groups of acids. We used fatty acids-9(10),16-dihydroxypalmitic acid (diHPA), isolated from curtin, and 9,10,16-trihydroxypalmitic acid (triHPA); the following phenolic acids were used: ferulic, p-coumaric, syringic, and vanillic. Adsorption of both groups of acids was measured. The FTIR spectra of fatty acid-mineral complexes indicated inner-sphere complexation of fatty acids with iron-enriched smectites (versus outer-sphere complexation with Ca(II)-montmorillonite). The LC-MS results demonstrated enhanced esterification of fatty acids on the iron-enriched smectite surfaces (as compared to Ca(II)-montmorillonite). This study suggests that fatty acids can be esterified on the iron-enriched smectite surfaces, which results in the formation of stable organo-mineral complexes. These complexes may serve as a model for the study of natural soil organo-clay complexes and humin. The reaction of phenolic acids with Fe(III)-montmorillonite demonstrated their oxidative transformation by the mineral surfaces, which was affected by molecular structure of acids. The following order of their transformation was obtained: ferulic >syringic >p-coumaric >vanillic. The LC-MS analysis demonstrated the presence of dimers, trimers, and tetramers of ferulic acid on the surface of Fe(III)-montmorillonite. Oxidation and transformation of ferulic acid were more intense on the surface of Fe(III)-montmorillonite as compared to Fe(III) in solution due to stronger complexation on the Fe(III)-motnomrillonite surface. Our study demonstrate the importance of iron-enriched minerals for the abiotic formation of humic materials and for the transformation of aromatic (phenolic) pollutants.