Reconstitution of cutin monomers on smectite surfaces

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Cutin biopolymer and its common building blocks 9(10),16 dihydroxy palmitic acid (diHPA) are commonly found in soil organic matter and in particular in humin fraction. However, little information is available on the reactions of cutin monomers and fatty acids with clays.

Adsorption and reconstitution of cutin monomers were measured with Na^{+}-, Ca^{2+}- and Fe^{3+}-Wyoming montmorillonite (SWy1, CaWy1 and FeWy1) and on nontronite (NAu2). The isotherms of adsorption of cutin monomers on smectites were fitted by a dual mode model of sorption, which combines site specific adsorption mechanism (Langmuir –type part) and linear part related to smectite interlayer penetration and multilayer adsorption of cutin monomers on clay surfaces. The diHPA specific adsorption affinity was 5-10 times higher for the iron-enriched smectites (FeWy1 and NAu2) as compared with CaWy1 and SWy1. Based on FTIR data we suggest that diHPA forms inner-sphere complexes with FeWy1 and NAu2 surfaces but not with SWy1 and CaWy1. XRD measurements showed expansion of the interlayer spacing of smectites by up to 0.45 nm with increase in diHPA loading. This indicates the diHPA penetration into smectite interlayers. All montmorillonite samples induced esterification and oligomerization of the monomers. Esterification was more pronounced for the iron-enriched smectites (FeWy1 and NAu2). Atomic Force Microscopy (AFM) analysis of monomer-smectite complexes demonstrated the coverage of smectite surfaces with monomers, and increased hydrophobicity of organo-clay complexes as compared with cutin monomers.

Esterification and polymerization of monomers of cutin on surfaces of smectites results in the formation of natural soil organo-mineral complexes, in particular, humin.