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Restructuring of polygalacturonate on alumina upon hydration - effect on phosphate sorption kinetics

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In soils, hydration of organic coatings is expected to affect the immobilization of oxyanions by hydrous Fe and Al oxides. We hypothesized that the hydration of polygalacturonate (PGA) coatings on alumina (Al_2O_3) increases their permeability for phosphate. Pure and PGA-coated alumina were equilibrated in deionized water for two and 170 hours at pH 5 and 20˚C before studying (i) their porosity with N_2 gas adsorption and ^{1}H-NMR relaxometry, (ii) structural changes of PGA-coatings with differential scanning calorimetry (DSC), and (iii) the kinetics of phosphate sorption and PGA desorption in batch experiments. Scanning electron micrographs revealed that PGA molecules formed three-dimensional networks with pores ranging in size from $<$10 nm to several hundred nanometers. Our NMR results showed that the water content of intraparticle alumina pores decreased upon PGA sorption, indicating a displacement of pore water by PGA. Contrary, the amount of water in interparticle alumina pores increased strongly after PGA addition and was attributed to water in pores of PGA and/or in pores at the PGA-alumina interface. The flexibility of PGA molecules and the fraction of a PGA gel phase increased within one week of hydration, implying restructuring of PGA. Hydration of PGA coatings increased the amount of instantaneously sorbed phosphate by 84%, showing that restructuring of PGA enhanced the accessibility of phosphate to external alumina surfaces. Despite the fact that the efficacy of phosphate to displace PGA was higher after 170 hours than after two hours, a higher phosphate surface loading was required after 170 hours to set off PGA desorption. Our findings imply that the number of PGA chain segments directly attached to the alumina surface decreased with time. We conclude that

hydration/dehydration of polymeric surface coatings affects the sorption kinetics of oxyanions, and may thus control the sorption and transport of solutes in soils.