



Transport of citrate-coated silver nanoparticles in unsaturated sand

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Chemical factors and physical constraints lead to coupled effects during particle transport in unsaturated porous media. Unlike for saturated transport, studies on unsaturated transport as typical for soil are currently scarce. We investigated the mobility of citrate-coated Ag NPs in unsaturated sand (grain diameter: 0.1-0.3 mm). For three flux rates and a given pore-water ionic strength (1 mM KNO_3), the citrate-coated Ag NPs were less mobile at pH = 5 compared to pH = 9. The classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory suggests unfavorable deposition conditions at both, the air-water interface and solid-water interface. Breakthrough curves measured under quasi-steady state unsaturated flow showed retardation of the citrate-coated Ag NPs compared to inert solute (KBr). After flushing with nanoparticle-free 1 mM KNO_3 solution (pH-adjusted), retention was much lower in deeper depths compared to the surface where the particles entered the flow field. The results show a non-linear dependence of nanoparticle (NP) mobility on flux rate and water content. Especially the observed retardation similar to equilibrium sorption is in contrast to observations under saturated flow conditions. A convection-dispersion and reaction model that combines a reversible equilibrium process and a non-equilibrium interaction process reproduced the measured breakthrough curves reasonably well. From comparison between saturated and unsaturated experiments we conclude that the air-water interface is responsible for the reversible equilibrium process while the water-solid interface accounts for irreversible sorption.