

Long-Term Nanoparticle Transport and Deposition Behavior in Saturated Porous Media: Coupled Effects of Hydrodynamic and Solution Chemistry

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Comprehensive understanding of the transport and deposition of COOH-functionalized latex colloid particles in subsurface is required to evaluate their latent negative impact on the soil and water environment. This study aims to systematically explore the coupled effects of hydrodynamic and solution chemistry conditions on the long-term transport and deposition kinetics of nanoparticles (NPs) in saturated porous media. Column transport experiments were carried out at various solution ionic strengths (IS), ion types (monovalent and divalent), and flow velocities utilizing negatively charged carboxyl-modified latex NPs of two different sizes (50 and 100 nm) using acid washed medium sized river sand. Most experimental studies of NP deposition in porous media have focused on the initial clean bed deposition. In this study the experiments were designed to obtain the long-term breakthrough curves (BTCs) in order to unambiguously determine the full deposition kinetics and the fraction of the solid surface area (S_f) that was available for NP deposition. The experimental evidence accessible in the literature on the dependency of S_f on physiochemical and hydrodynamics factors, especially for NP are very narrow. The BTCs exhibited a bimodal shape with increasing solution IS; e.g., BTCs were initially delayed, then they rapidly increased, and then slowly approached the influent particle concentration. Most research were conducted in the presence of monovalent electrolyte. In this study we compared the effect of monovalent (NaCl) and divalent (CaCl₂) solution chemistry. NP deposition was much more prominent in the presence of Ca²⁺ than Na⁺ at any given solution IS. Deposition dynamics of NPs was successfully simulated using a two-site kinetic model that accounted for irreversible deposition and blocking (e.g., a decreasing deposition rate as the available site filled) on each site. Results showed that S_f values were controlled by the coupled effects of flow velocity, solution chemistry, and particle size. Data analyses further demonstrated that only a small fraction of solid surface area contributed in NP deposition even at the highest IS (60 mM NaCl and 3mM CaCl₂) and lowest flow velocity (1 m/day) tested. Consistent with previous studies conducted with clean sand, our results imply that NP deposition occurred because of physicochemical interactions between the negatively charged COOH groups on the NPs and nanoscale physical and/or chemical heterogeneities on the sand surfaces that produced localized nanoscale favorable sites. Furthermore, our results suggest that the NP interactions with the collector surfaces tended to strengthen with increasing contact time. This new approach in modelling will help to predict the long term nanoparticle deposition in porous media with respect to particle size, pore water velocity and solution chemistry.