

Molecular-Level Insights into the Interactions between Natural Organic Matter and Ferrihydrite Nanoparticles: Mechanisms of Adsorption and Resultant Aggregation Behavior

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Ferrihydrite nanoparticles (FNPs) are widespread in natural environments, where their colloidal stability affects contaminant transport. However, predicting their aggregation remains challenging due to the heterogeneity of natural organic matter (NOM). Here, we investigated the adsorption and aggregation of FNPs exposed to NOM fractions with different molecular weights (MW) and model organic matter (OM) isolates with varying MW and carboxyl richness. Results showed that low-MW NOM (<3 kDa) destabilized FNPs, accelerating aggregation even at high C/Fe ratios, while higher MW NOM imparted better stability through steric repulsion. Despite compositional differences, all NOM fractions formed similar adsorbed layers, suggesting that adsorbed mass and molecular size primarily controlled aggregation. To further probe these effects, we studied five model OM, including (poly)acrylic acid (PAA) and polyethylene glycol (PEG). Higher carboxyl richness led to greater adsorption ($\text{PAA}_{2k} > \text{PEGbis} > \text{PEG}$), and higher MW OM with the same carboxyl content also adsorbed more ($\text{PAA}_{25k} > \text{PAA}_{2k} > \text{AA}$). Aggregation was dictated by adsorbed OM mass: PEG and AA had negligible effects, PEGbis promoted bridging-induced aggregation, while carboxyl-rich PAA stabilized or aggregated NPs depending on coverage. These findings provide mechanistic insights into transport and fate of Fe, C elements in natural environments.