

Organo-mineral interactions in *Pseudomonas putida*-birnessite assemblages: Impact on mineral reactivity

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The ability of microorganisms to precipitate biogenic birnessite nanoparticles is widely spread in the bacterial and fungal trees of life, with this process accounting largely for the formation of birnessite in nature. Birnessite minerals occur typically as nanoparticles that exhibit significant chemical and structural disorder. Furthermore, the mineral is embedded within a biomass matrix composed of microbial cells and extracellular polymeric substances, where the biomass not only provides reactive surfaces but can mediate electron transfer reactions. The overarching question guiding our research is: *How do nanoscale properties and admixing with microbial biomass modify the reactivity of Mn oxide minerals?*

In this study, we investigate the biomass-birnessite composites of *Pseudomonas putida* GB-1 biomass and δ -MnO₂ nanoparticles. We characterized the structure and composition of the mineral fraction using X-ray diffraction, Mn K-edge X-ray absorption spectroscopy and wet-chemical methods. To characterize the biomass fraction, we employed FTIR spectroscopy and size-exclusion chromatography analysis of the extracellular polymeric substances. Finally, we measured Ni(II) sorption isotherms at pH 6 and Ni K-edge EXAFS spectra to determine the extent and mechanism of Ni sorption in the biomass-mineral composites and in biomass-only and mineral-only systems. This approach provided direct and indirect evidence for the extent of organo-mineral interactions in the composites, as well as a direct measure of sorption reactivity in the composites relative to biomass-only and mineral-only systems.

We found that admixing of mineral nanoparticles with biomass reduced the reactivity of the edge sites of birnessite particles towards Ni(II) through the attachment of organic moieties to the mineral particles and/or modification of the assemblage surface charge properties. In addition, the interaction of biomass components with MnO₂ particles leads to partial Mn(IV) reduction and biomass oxidation, which is manifest as a decrease in the fraction of reactive vacancies in the mineral fraction and an increase in the sorption capacity of the biomass. The mechanisms identified in our work have wide implications in understanding organic matter-mineral interactions, which are central to metal attenuation and elemental cycling in soils.