NOM and AQDS enhance the electron transfer between Fe(III)reducing bacteria and Fe(III) minerals over cm-distances

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Natural organic matter (NOM) can act as an electron shuttle, promoting extracellular electron transfer. Reduction of NOM by Fe(III)-reducing bacteria (FeRB) facilitates the transfer of electrons to Fe(III) minerals in a second abiotic step. The addition of NOM can significantly increase Fe(III) mineral reduction rates and enables reduction of Fe(III) minerals by microbes at a distance. However, the spatial scales over which electron transfer is possible and the mechanism of NOM electron shuttling, i.e., by diffusion of reduced and re-oxidized NOM molecules or by electron hopping through the redox-active network of the NOM, remain undercharacterized.



Figure 1. Schematic illustration of agarose-solidified electron shuttling experimental setup.

We conducted agarose-solidified electron shuttling experiments, separating FeRB (Shewanella oneidensis MR-1 or Geobacter sulfurreducens) from Fe(III) minerals (ferrihydrite or goethite) by 2.5 cm, with either NOM (Pahokee Peat Humic Acid or Suwanee River NOM) or anthraquinone-2,6-disulfonate (AQDS) in between as electron shuttles (Figure 1). We found that in the absence of NOM Fe(III) reduction did not occur. Ammendment with NOM led to Fe(III) reduction, and increasing concentration resulted in faster reduction. The extent and rate of reduction varied with the type of FeRB, Fe(III) mineral and NOM. Experiments with AQDS showed that the rate and extent of electron shuttling correlate with the concentration of quinone functional groups. However, concentrations above 5 mM did not yield faster electron shuttling rates. We developed a diffusion-reaction model simulating AQDS-mediated extracellular electron transfer aiming at identifying the rate limiting step, and used the model to test competing mechanisms explaining the enhancement of long-distance electron transfer by NOM and NOM-like compounds.