

Fenton reactions in presence of fungal metabolites and iron oxides

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Both ectomycorrhizae and saprotrophic fungal metabolites have proven capable of initiating a Fenton ($\text{H}_2\text{O}_2 + \text{Fe}^{2+} + \text{H}^+ \leftrightarrow \text{H}_2\text{O} + \text{Fe}^{3+} + \cdot\text{OH}$) or Fenton-like reaction during decomposition of wood and soil organic matter [1,2]. Previous studies have typically involved systems containing dissolved Fe(III) to generate the Fenton reaction. However, in oxic soils Fe(III) is primarily found in the solid state as minerals. Thus, both mineral dissolution and Fe reduction is needed to trigger the Fenton reaction, and the extent and rate of these reactions are dependent on the physicochemical properties of the Fe(III) minerals. The aim of this study was to investigate the extent and rate of a Fenton or Fenton-like reaction initiated by fungal metabolites in heterogeneous systems containing iron oxides. We investigated the reactions between synthesized ferrihydrite or goethite with 2,6-dimethoxyhydroquinone (DMHQ), a stable analogue to common secondary metabolites produced by the brown-rot fungi, and with crude metabolite extracts produced by the ectomycorrhizae *Paxillus involutus*. This was examined by relating in-situ IR spectroscopy to the solution content of total Fe, measured by ICP-AES, Fe(II), measured by the ferrozine assay, and hydroxyl radical, detected by the TPA probe, at different time scales by conducting a series of systematic experiments at a pH range from 3 to 8.

Results will be presented showing that 2,6-DMHQ can initiate a Fenton or Fenton-like reaction in systems containing H_2O_2 and iron oxides. In systems without H_2O_2 no $\cdot\text{OH}$ can be detected but an increase in Fe(II) and of total Fe concentrations in solutions were pronounced within the first 4 h of reaction, followed by a marked decrease. A slow heterogeneous Fenton-like reaction was also indicated in presence of iron oxides and in absence of 2,6-DMHQ. Furthermore, we will show that crude metabolites can produce Fe(II) and dissolve Fe in both the ferrihydrite and goethite systems, the latter, however, to a lesser extent. The results of this study provide a better understanding of the reactions between fungal metabolites and mineral surfaces at naturally relevant conditions, and give a new perspective on how these reactions define organic matter decomposition.

[1] Rineau et al. (2012), *Environ Microb*, 14, 1477-1487 [2] Korripally et al. (2013), *Appl Environ Microb*, 79, 2377-2383.