Iron-mediated oxidation of 2methoxyhydroquinone under acidic conditions: Kinetic and mechanistic insights

XIU YUAN¹, JAMES A. DAVIS² AND PETER S. NICO³

Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

¹xiuyuan@lbl.gov

²jadavis@lbl.gov

³psnico@lbl.gov

Despite the biogeochemical significance of the interactions between natural organic matter (NOM) and iron species, considerable uncertainty still remains as to the exact processes contributing to the rates and extents of these redox reactions. Investigations on reactivity of low-molecular-weight quinones, which are believed to be key redox active compounds within NOM, towards iron species, could provide considerable insight into the kinetics and mechanisms of reactions involving NOM and iron [1] [2]. In this study, we investigated the oxidation of 2-methoxyhydroquinone (MH₂Q) by ferric iron (Fe(III)) under acidic conditions in the absence and presence of oxygen. While Fe(III) was capable of stoichiometrically oxidizing MH₂Q under anaerobic conditions, catalytic oxidation of MH_2Q was observed in the presence of O2 due to further cycling between oxygen, semiquinone radicals, and iron species. A detailed kinetic model was developed to describe the predominant mechanisms, which indicated the mono-dissociated anion of MH₂Q was the key species accounting for the pH dependence of the oxidation. The generated radical intermediates, namely semiquinone and superoxide, are of great importance in reaction chain propagation. The kinetic model should provide critical insight into the thermodynamic and kinetic characteristics of mineral-organic interactions and assist in understanding and predicting the factors controlling iron and organic matter transformation and bioavailability in aquatic systems.

[1] Uchimiya, M. and A. T. Stone (2006). *Environ. Sci. Technol*, **40**: 3515-3521. [2] Yuan, X., et al. (2013). *Environ. Sci. Technol*, **47**: 8355-8364.