

## Coupled homogeneous oxidation of Fe(II) and Mn(II)

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The oxidation of Mn(II) to form insoluble Mn(III, IV) oxides is an important process influencing the quality of drinking water and the biogeochemical cycles of major and trace elements. Whereas abiotic Mn(II) oxidation by O<sub>2</sub> requires several months to years, recent evidence suggests that reactive intermediates like superoxide radical (O<sub>2</sub><sup>-</sup>) can initiate Mn(II) oxidation in natural systems.<sup>1</sup> Although Fenton-type reactions involving Fe(II) oxidation by O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> can oxidize other redox active elements (e.g. As(III), Sb(III)) via reactive intermediates (O<sub>2</sub><sup>-</sup>, ·OH, Fe(IV)), Mn(II) oxidation in Fenton-type systems has not been documented previously.

We applied the Fe(0) electrocoagulation system, which is based on the electrolytic production of Fe(II) from Fe(0) electrodes, to investigate the co-oxidation of Fe(II) and Mn(II). EC experiments were carried out at varying Fe(II) production rates (IPR) in electrolytes containing O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> buffered at circumneutral pH with NaHCO<sub>3</sub>. We combined measurements of total and dissolved Mn and Fe throughout Fe(0) electrolysis with detailed structural analyses of the resulting nanoscale solid Mn and Fe phases using Mn and Fe K-edge X-ray absorption spectroscopy. Control experiments in homogeneous and heterogeneous (0.5 mM ferrihydrite) systems revealed negligible Mn(II) oxidation by O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> during the 90-min reaction time. By contrast, at the end of the 90-min electrolysis, 0.5 mM Fe dosed via EC at an intermediate IPR value of 5 μM Fe/min removed roughly 32% and 40% of the initial 100 μM Mn(II) in the presence of O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, respectively. This rapid Mn(II) removal of > 20 μM/h is significantly higher than typical rates of other abiotic Mn(II) oxidation pathways, such as Mn(II) oxidation catalyzed by photo-irradiated natural organic matter (8 μM/h).<sup>1</sup> We show that limiting the accumulation of aqueous Fe(II), which competes with Mn(II) for the intermediate oxidants produced in Fenton-type reactions, is the key factor governing the efficiency of Fe(II)-catalyzed Mn(II) oxidation during EC.

Our results help to elucidate a novel pathway of homogenous Fe(II)-catalyzed Mn(II) oxidation, which is essential to develop new methods of Mn(II) removal in technical systems and to predict the oxidation of Mn(II) and reactivity of Mn(III,IV) oxides in natural systems.

[1]Nico, P.; Anastasio, C.; Zamoski, R., Rapid photo-oxidation of Mn(II) mediated by humic substances. *Geochim Cosmochim Acta* **2002**, *66*, (23), 4047-4056.