

Fe(II)-mediated Oxidation of Mn(II)

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The oxidation of Fe(II) by O₂ or H₂O₂ produces strong, short-lived oxidants (*O₂⁻, *OH, Fe(IV)). These Fenton-type reactants are widely exploited in water treatment and are implicated in the decomposition of organic matter in soils. Recent evidence has also shown that reactive oxidants (*O₂) produced in natural systems (e.g. via photochemical reactions with organic carbon) can oxidize Mn(II). However, the co-oxidation of Fe(II) and Mn(II) in Fenton-type systems has not received attention.

Our objectives in this work are to characterize the reaction products of Fe(II)-mediated Mn(II) oxidation and to determine the factors that control the Mn(II) oxidation efficiency. We employ the Fe(0) electrocoagulation (EC) system, which permits precise control over the rate of Fe(II) production and concomitant reactive oxidants. In all experiments, we investigate the co-oxidation of 200 μM Fe(II) and 100 μM Mn(II) as a function of the iron production rate (IPR), the Fe(II) oxidant (≈ 250 μM O₂ or H₂O₂), and solution pH (3.5 - 8.5). Our approach combines i) time-dependent Mn(II) removal experiments, ii) pyrophosphate (PP) extractions for measurements of Mn(III), and iii) Mn and Fe K-edge EXAFS spectroscopy.

Our results show that Mn(II) oxidation in the Fe(II)/O₂ system increases with decreasing IPR and increasing solution pH, with a maximum Mn(II):Fe(II) oxidation efficiency near 15 mol% at pH 8.5. These trends can be explained by the improved competition of Mn(II) for Fenton-type reactants under conditions that minimize aqueous Fe(II). Although Mn(II) oxidation in the Fe(II)/H₂O₂ system was also most efficient at pH 8.5 (40 mol%), a local maximum in the Mn(II):Fe(II) oxidation efficiency was observed at pH 4.5 (12 mol%). These results are consistent with the pH-dependent products of Fe(II) oxidation by H₂O₂: *OH is generated at pH < 6, whereas a more selective oxidant (e.g. Fe(IV)) forms at pH > 6. The results from PP extractions and Mn and Fe K-edge EXAFS spectroscopy show that Fe(II)-mediated Mn(II) oxidation yields Mn(III) in all samples, which is coprecipitated or structurally incorporated into lepidocrocite (O₂ system) or hydrous ferric oxide (H₂O₂ system).

Our work uncovers a new pathway of Mn(II) oxidation and will help form the basis of Mn(II) oxidation kinetic models in Fenton-type systems. While these reactions can be exploited for Mn(II) removal from water supplies, the consumption of reactive oxidants by Mn(II) must also be considered for accurate predictions of target compound oxidation in Fenton-type systems containing Mn(II).