

Ligand-limited oxidation of ciprofloxacin by Mn(III)

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Mn (III) species play critical roles in determining the environmental fate of antibiotics released into natural systems. Their reactivity, however, is strongly influenced by complexation reactions with (in) organic ligands. This study investigates the impact of Mn (III) complexation with pyrophosphate (PP), a model environmental ligand, on the redox-driven degradation of ciprofloxacin (CIP), a widely used antibiotic and environmental contaminant. Spectroscopic analysis and thermodynamic modeling revealed that Mn (III)-PP complexes initially dissociate into MnOH²⁺ species, which then undergo disproportionation to form MnO₂ colloids. Both dissociation and disproportionation processes had comparable trends at pH 4 and 7, with reactivities that were strongly dependent on Mn (III):PP ratios. The progress of CIP oxidation by Mn compounds was sigmoidal over time, with an initial lag phase which can be attributed to Mn (III)-PP complex dissociation and disproportionation steps. CIP degradation was predominantly governed by pH, which altered the redox potential of the Mn (III)/Mn (II) couple, as confirmed by cyclic voltammetry data. These findings indicate that ligand complexation, such as with PP, enhances Mn (III) stability and mitigates dissociation and disproportionation reactions. This work thereby provides significant insights into the speciation and redox activity of Mn (III) in natural environments, and their implications for pollutant degradation in contaminated water systems.