Mechanisms and kinetics of organic contaminant transformation by Mn(IV) oxides

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Manganese oxides (e.g., MnO_2) are among the strongest, naturally occurring oxidants and can oxidize hazardous organic compounds containing amine or phenolic groups to potentially less hazardous species. In addition to occurring naturally, manganese oxide minerals are created during treatment of drinking water that relies on chemical oxidation and filtration to remove reduced transition metals (e.g., Fe(II) and/or Mn(II)) prior to introduction into the water distribution system. Although oxidative transformation pathways of a variety of organic contaminants by Mn oxides are relatively well understood, little is known about how the mineral surface evolves during organic contaminant oxidation. Oxidation of inorganic contaminants (e.g., As(III), Cr(III)) results in accumulation of both oxidized inorganic contaminants (e.g., As(V) or Cr(VI)) and reduced Mn (e.g., Mn(II) and Mn(III)) at the mineral surface. Accumulation of these reaction products results in decreased inorganic contaminant oxidation rates. Similarily, the organic contaminant oxidation rate decreases as reaction byproducts accumulate. For example, the rate of bisphenol A (BPA) oxidation by δ-MnO_2 decreases as Mn(III) accumulates on the mineral surface, resulting in a decrease in the average oxidation state of the Mn mineral. Interstingly, the oxidation rate continues to decrease despite stabilization of the mineral's Mn(III) content, although Mn(II) accumulation is not observed. This points to an, as yet, unidentified reaction intermediate that limits BPA oxidation. This work seeks to identify mechanisms limiting oxidation of phenols by pure, lab-synthesized Mn oxides as well as mixed Fe/Mn oxides recovered from a Mn removal system utilized for drinking water treatment. Identification of rate-limiting steps in organic contaminant oxidation by Mn oxides is critical to predicting their mobility and longevity in environmental systems. It may also allow the reuse of Mn-bearing solids that would otherwise be discarded.