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Assessing redox properties of birnessite minerals using ABTS

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Manganese oxide minerals are critical players in a number of biogeochemical processes and have the potential to be used for inorganic and organic pollutants oxidation due to the high adsorption capacities and high reduction potentials of these oxides. Layer-type MnO_x (birnessite) show a range of particle sizes (nm to µm), Mn^{III} content/location (0 to 30% as layer and/or interlayer Mn^{III}), and the presence of vacancy sites (0 to 20%). However, studies that link redox reactivity and mineral structure and composition are lacking.

We investigated the redox properties for a suite of Mn oxides by reacting them with 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) to form oxidized $ABTS^{\bullet+}$. The $ABTS^{\bullet+}$/ABTS redox couple presents several advantages from an experimental viewpoint: fast one electron transfer, pH-independent redox speciation, strong absorbance in the visible of $ABTS^{\bullet+}$ and in the UV of ABTS, and overall net negative charges of both species that should minimize adsorption to like-charged birnessite. Thus, mass and electron balances can be followed accurately in Mn oxide-ABTS systems by spectrophotometry. We measured the initial oxidation rates of ABTS in minerals suspensions at pH 5 and 7 what suggest that the reactivity of the oxides correlates with Mn^{III} content and crystallographic location and specific surface area to a lesser extent. In addition, we used the ratio of $ABTS^{\bullet+}$ to ABTS at apparent equilibrium to estimate the reduction potential of the ABTS-MnO_2 suspensions.

The redox state of the minerals was also characterized before addition of ABTS and after one hour of reaction using sodium pyrophosphate (PP) to extract solid-phase Mn^{III} and form Mn^{III}-PP complexes ($\lambda = 254$ nm). Our measurements suggest that reaction with ABTS promotes additional Mn oxidation and reduction reactions, leading to non-stiochiometric accumulation or depletion of Mn^{III} in the minerals based on initial mineral structure and composition.

Our study links particle size and Mn^{III} content/crystallographic location to the mineral redox properties of birnessite. These results will improve our understanding of the role of Mn oxides in the transformation dynamics of natural organic molecules and pollutants, which may allow for control and design of Mn oxides with specific redox reactivities.