

Impact of δ -MnO₂ on the chemical speciation of cations in aqueous solution

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Among manganese oxides, birnessite (δ -MnO₂) was found to be the most existing form in soils and sediments. It is a lamellar compound consisting of layers of edge shared MnO₆ octahedra. These layers are negatively charged and are stacked together. Depending on the synthesis conditions, the birnessite symmetry differs. When prepared in alkaline medium, birnessite presents triclinic symmetry. The hexagonal homologue is obtained in acidic medium. For both structures, the negatively charged layers are compensated with hydrated interlayers cations providing a cation exchange capacity to these solids. The ion exchange is assumed to take place through a diffusion mechanism in the interlamellar space and neither the solid nor the exchangeable cations should be involved in any chemical transformations. In contrast, it has been proved that birnessite possesses a strong oxidizing capacity as it can oxidize several elements: As(III) to As(V), Se(IV) to Se(VI), Co(II) to Co(III) and Cr(III) to Cr(VI). Birnessite also oxidizes organic molecules and inorganic complexes such as glyphosate, Cu-citrate or dye molecules. In marine and sediments, the conversion of combined nitrogen to dinitrogen is traditionally assumed to take place via the coupled bacterial nitrification-denitrification process or through the anaerobic ammonium oxidation. However, in Mn-rich media, the existence of an alternative abiotic pathway that may take place via chemical process is suggested.

Thereby, the cationic exchange and the oxidative capacities of birnessite might be considered in nitrogen cycle and in the speciation of different cations in sediments containing manganese oxide.