Structural controls on Cu^{2+} sorption behavior in biogenic birnessite

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Birnessite is widely spread in various natural environments, and plays an important role in controlling the geochemical behaviors of heavy metal contaminants, such as Cu^{2+}. The formation of natural birnessite can be mainly attributed to the catalytic oxidation by microorganisms. This biogenic birnessite are typically featured by a large inter-layer space, a high Mn average oxidation state (close to +4) and high vacancy abundance. Those unique structural features would sensitively determine the uptake mechanisms of Cu^{2+}, e.g. the sorption amount, sorption sites and local coordination structures. Our study focuses on Cu^{2+} sorption mechanism and local structures in biogenic birnessite produced by *Pseudomonas putida* strain MnB1, and further discusses its influence on the sustaining structural performance of birnessite.

As revealed by X-ray diffraction (XRD) analysis, the biogenic birnessite owns a large interlayer space of ~9.17 Å. Linear combination fitting on the Mn K-edge X-ray absorption near-edge structures (XANES) spectrum and fitting on the Mn $2p_{3/2}$ spectra of the X-ray photoelectron spectroscopy (XPS) together indicate a low content of Mn(III/II) as ~7-13%. The Langmuir adsorption model is used to depict Cu^{2+} sorption behavior onto birnessite and predicts a maximum sorption amount of ~0.24 (μmol Cu/μmol Mn), which is larger than the experimental results of ~0.17. Structural model fitting on the Cu K-edge extended X-ray absorption fine structures (EXAFS) spectrum implies the proclivity for Cu^{2+} to adsorb above Mn vacancy or be incorporated into the vacancy. This could be related to the low fraction of Mn(II/III) and large interlayer space, favoring the accommodation of the inner-sphere Cu-complexes. Theoretically, the vacancy incorporation of Cu^{2+} is energetically unstable, which could explain the overestimation of the maximum Cu^{2+} sorption amount as predicted by Langmuir model. The location of Cu^{2+} above or inside vacancy could possibly promote the transformation of birnessite towards tunneled-type Mn oxides.