

Research Group for Bioactinides Chemistry

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The research objectives of the group are to elucidate a chemical states change of actinides and lanthanides including nano-particles formation in the biological reaction environments, and to develop biological remediation system for radiocesium contaminated land areas. In the year of 2013, cobalt sorption by biogenic manganese oxides and zinc sorption during bio-oxidation and accumulation of radiocesium by *Saccharomyces cerevisiae* have been studied.

Cobalt(II) oxidation by biogenic Mn oxide produced by *Pseudomonas* sp. Strain NGY-1

It is well known that Co enrichment in natural Mn oxides is attributed to oxidative scavenging by Mn oxide. However, oxidation of Co by biogenic Mn oxide is not well known. In this study, we isolated a Mn-oxidizing bacterium (*Pseudomonas* sp.) designated as strain NGY-1, from stream water at Ningyotoge Environmental Engineering Center of the Japan Atomic Energy Agency (Kagamino-cho, Tomata-gun, Okayama Prefecture, Japan)[1]. Sorption experiments on Co were carried out using biogenic Mn oxide produced by strain NGY-1. Similar sorption experiments were also conducted using a synthetic analogue of δ -MnO₂.

Transmission electron microscopy (TEM) images give detailed information on the morphology of biogenic Mn oxide (Fig. 1). Spherical precipitates of 3–5 μ m size were found by TEM observation (Fig. 1a). Fibrous precipitates were also observed around the bacterial cells (Fig. 1b). The TEM image of the precipitates shows little geometric regularity even at a larger scale (Fig. 1c), indicating its poor crystallinity. SAED pattern of the precipitates show no clear diffraction pattern (Fig. 1d). The TEM observation suggests that the biogenic Mn oxide produced by strain NGY-1 is an aggregate of nanoscale particles.

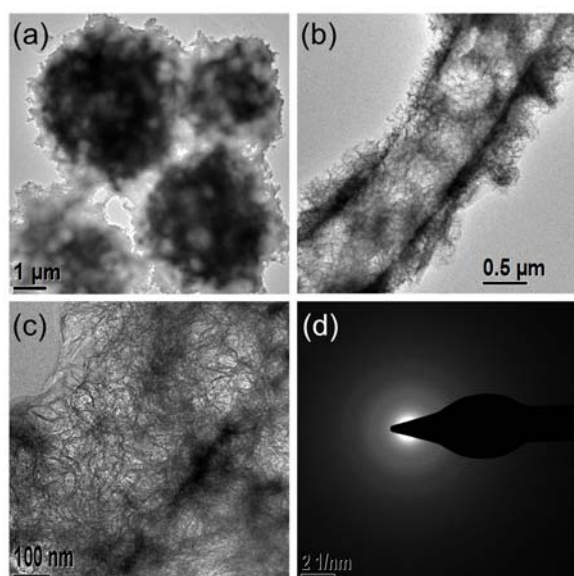


Fig. 1. (a, b and c) TEM images and (d) SAED of biogenic Mn oxide produced by strain NGY-1.

Sorption of Co on δ -MnO₂ was faster and stronger than that on biogenic Mn oxide, which was possibly due to their structural difference and/or the presence of bacterial cells in biogenic Mn oxide. X-ray absorption near-edge structure (XANES) spectra clearly demonstrated

that Co was oxidized from the divalent to the trivalent state on biogenic Mn and δ -MnO₂. The oxidation property of both the biogenic Mn oxide and δ -MnO₂ was stronger under circumneutral conditions than under acidic conditions. Linear combination fitting using divalent and trivalent Co reference materials suggested that ~90% of Co was oxidized at pH ~ 6, whereas ~80% was oxidized at pH ~ 3. Oxidation state of the biogenic Mn oxide and δ -MnO₂ was tetravalent, but Co(II) oxidation by biogenic Mn oxide was slower than that by δ -MnO₂. The difference of Co oxidation may be caused by the coexisting bacterial cells or structural differences in the Mn oxides.

Zinc sorption during bio-oxidation and precipitation of manganese

Birnessite is one of the most reactive mineral phases in the environment. It is commonly regarded as a potential scavenger of trace metals in soils, sediments, and aquatic environments [2,3]. In surface and terrestrial environments, most birnessite is considered to be of biogenic origin because the oxidation rate of Mn(II) shows up to five orders of magnitude greater in the biogenic process than in the abiotic one [2,4]. The formation and structural evolution of fungal mediate biogenic birnessite are dynamic processes.

The speciation and mobility of Zn are linked to Mn oxides [5,6]. Although the associations of Zn with the pre-formed biogenic Mn oxides are relatively well understood, the reactivity of the intermediate precipitate at the initial stage of Mn bio-oxidation appears to differ from the final precipitate. We have studied Zn sorption during precipitation of biogenic Mn oxides by contrasting Zn sorption to pre-formed biogenic Mn oxides, using the Mn-oxidizing fungus *Paraconiothyrium* sp. WL-2 [7].

A substantially higher Zn uptake was found during precipitation of biogenic Mn oxides compared to Zn sorption to pre-formed biogenic Mn oxides. This result shows that Zn was concurrently sorbed to the precipitates. The presence of Zn during Mn oxidation resulted in a biogenic Mn oxide with reduced ordering in the c-axis. The precipitate was identified by X-ray diffraction (XRD) as a layer-type Mn oxide with structural properties similar to hexagonal birnessite. Extended X-ray absorption fine structure (EXAFS) spectroscopy showed that Zn forms triple-corner-sharing tetrahedral coordination (IVTCS-Zn) complexes on the surface of birnessite, which may inhibited layer stacking of birnessite in the final products. These results indicate that the layer stacking of birnessite was inhibited by Zn loading. A Zn-containing birnessite with disordered layer stacking was formed as a final product, which showed morphology and optical property similar to MnO₂ nanosheets. These results emphasize the importance of the precipitates on Zn sorption, and provides insight regarding the dynamic interaction between Zn and Mn oxide in the process of microbiological oxidation.

References

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