

Synthesis of bio-Mn oxide and recovery of critical metals by the incubation of Mn-oxidizing microbial community using deep seawater

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Ferromanganese crusts are seafloor mineral resources rich in critical metals such as Co, Ni, Mo, and rare earth elements. The accumulation of these critical metals in ferromanganese crust is attributed to the high adsorption capacity of their constitute minerals, Fe and Mn oxides, which adsorb various trace elements from seawater (Hein et al., 2013). Although ferromanganese crusts are considered potential future resources, their exploration remain challenging due to their occurrence in deep-sea environments. On the other hand, Mn oxides can be formed in various settings through microbial activity. In this study, we aimed to replicate the formation of Mn oxides and the concomitant accumulation of critical metals “on land” using microbial activity. For this purpose, we cultured marine oligotrophic Mn-oxidizing bacteria using deep seawater, which is nutrient-rich but low in organic matter.

The cultivation of Mn-oxidizing microbial community and the synthesis of bio-Mn oxides were conducted using a Down-flow Hanging Sponge (DHS) bioreactor. This reactor keeps the polyurethane sponge suspended in the air, allowing for a continuous supply of medium (Imachi et al., 2022). A deep sea sediment sample was used as the inoculum (Kato et al., 2017). Filtered Muroto deep seawater (0.1 μm membrane) supplemented with dissolved Mn^{2+} , was supplied to the DHS bioreactor at a controlled flow rate of 1.1 L/day.

Initially, the Mn^{2+} consumption rate was less than 5%. However, after 20 days, the consumption rate gradually increased, ultimately reaching near-complete oxidation after approximately 330 days. As the cultivation continued, biofilm covered the sponge surface, which caused a decrease in the Mn^{2+} consumption rate. When the biofilm was removed, the Mn^{2+} consumption rate increased again. This observation suggests that excessive biofilm formation may hinder Mn oxidation activity. Black precipitates were observed on the sponge surface, alongside biofilm formation. X-ray diffraction analysis identified these precipitates as birnessite ($\text{MnO}_2 \cdot n\text{H}_2\text{O}$). These results demonstrate that (i) Mn-oxidizing bacteria can be selectively cultivated and (ii) bio-Mn oxides can be synthesized using deep seawater. Future research will focus on quantifying the concentration of critical metal adsorbed on the Mn oxides.

Keywords: biomineral, bio-Mn oxides, Adsorption