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Recovery of Rare Metals from Contaminated Seawaters by Biogenic Manganese Oxides with a Mn(II) Oxidizing Enzyme Activity.

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Summary

In this study, we examined the oxidation of Mn(II) and sequestration of Co(II), Cd(II), Ni(II) and Zn(II) by biogenic manganese oxides (BMOs), formed by the Mn(II)-oxidizing fungus *Acremonium strictum* KR21-2 in artificial seawaters (ASWs) at pH 7.0. In ASWs, Mn(II) was readily oxidized to insoluble Mn oxides by newly formed BMOs with the conversion efficiency of > 90% during the repeated treatment experiments. The kinetics of Mn(II) oxidation in ASWs slightly slowed with the treating times probably due to the inhibitory effect by chloride ions while Na^+, SO_4^-, and NO_3^- did not affect the Mn(II) oxidation kinetics. Sequestration efficiencies of newly formed BMOs were >99% for Mn(II) and >85% for Co(II), Zn(II), and Ni(II) while only 55.6% of Cd(II) was sequestered in ASWs probably because of predomination of anionic complexes of Cd(II) with Cl^- ions such as $[CdCl_3]^-$ and $[CdCl_4]^{2-}$ in ASWs. Inactivation of Mn(II) oxidizing enzyme(s) in BMOs (by heating or deaeration) caused less Mn(II) oxidation as well as lower sequestration efficiencies for Cd(II), Zn(II), and Ni(II), suggesting the important role of Mn(II) oxidizing activity on metal sequestrations. High sequestration efficiency for Co(II) by BMOs was maintained even after inactivation of Mn(II) oxidizing activity, indicating that abiotic Co(II) oxidation to insoluble Co(III) is the main path for Co(II) sequestration. Cr(III) was readily oxidized to Cr(VI) by newly formed BMOs at pH 6.0, indicating the indirect oxidation of Cr(III) through Mn(II/IV) redox cycles on BMOs. In anaerobic condition, most of Cr(III) was sequestered on BMOs without the oxidative transformation to Cr(VI).