



Lab-based assessment of critical metal adsorption by biotic and abiotic hydrous manganese oxides

Tashane J. Boothe¹, Rosemary C. Capo¹, Brian W. Stewart¹, Benjamin C. Hedin²,
Travis A. Olds³, Carla E. Rosenfeld³

¹Department of Geology and Environmental Science, University of Pittsburgh, Pittsburgh, PA 15260

²Hedin Environmental, 195 Castle Shannon Blvd., Pittsburgh, PA 15228

³Carnegie Museum of Natural History, Pittsburgh, PA 15213

Extended Abstract

The global demand for technology and energy critical minerals is expected to increase in the coming years (Alonso et al. 2012). Developing new and sustainable sources of these metals will stabilize supply and alleviate the potential pollution produced by traditional mining. Acid mine drainage (AMD) treatment precipitates are a potential source of critical metals, including Ni, Mn, Co, and rare earth elements (REE) (Cravotta, 2008; Ayora, et al., 2016; Stewart et al., 2017; Vass, et al., 2019). Hydrous manganese oxides (HMO), common constituents of AMD treatment precipitates, are known to be very efficient at sorbing and concentrating trace metals (Tan et al., 2010; Hedin et al., 2019; 2023). However, more work is needed to understand how the biogeochemical conditions within AMD treatment systems influence HMO formation and their ability to adsorb and concentrate critical metals.

In this study we performed bench-top experiments to investigate the sorption of critical metals (La, Nd, Ce, Gd, Pr, Dy, Yb, Y, Co, and Ni) by biotically- and abiotically-precipitated HMO. The biotic HMO was produced through the oxidation of $MnCl_2$ by two species of Mn-oxidizing fungi, *P. sporulosa* and *Stagonospora sp.*, and the abiotic HMO (δ - MnO_2 and H^+ birnessite) were synthesized through chemical oxidation of aqueous $MnCl_2$. The efficiency of critical metal uptake by these HMO was assessed by conducting time series analyses of dissolved metal concentrations over 31 days and by characterizing the HMO minerals.

Scanning electron microscopy shows that HMO produced by *Stagonospora sp.* and *P. sporulosa* are closely associated with fungal biomass and hyphae. X-ray diffraction shows that both biotic and abiotic HMO were initially poorly crystalline, but abiotic HMO transformed to more crystalline HMO phases over the 31 days of the experiment. Biotic HMO and/or fungal biomass facilitate rapid adsorption of REE. After 6 hours, greater than 99% of both LREE and HREE were removed from solution (Fig. 1). The LREE were preferentially adsorbed, and the Ce anomaly was weak or absent. Biotic HMO also adsorbed 80-90% of dissolved Co and 50-60% of dissolved Ni from solution over 31 days. Energy-dispersive X-ray spectroscopy confirms that critical metals become associated with both HMO and fungal biomass. Abiotic HMO adsorbed REE at a slower rate, with maximum adsorption occurring after 4 days. After 31 days, 75-80% and 50-70% of LREE and HREE, respectively, were adsorbed. However, abiotic HMO only adsorbed 5-10% of Co and Ni over the same timeframe.

This study shows that biotic HMO are very efficient at adsorbing critical metals. Fungal biomass also plays an important role in this process. Abiotic HMO may be susceptible to mineral transformation and dissolution under certain conditions, and this can potentially reduce their capacity to adsorb some critical metals. AMD treatment systems that produce HMO through microbial oxidation (passive systems) are therefore likely viable targets for critical metal recovery.

Keywords: HMO, critical metals, REE, cobalt, nickel, fungi, acid mine drainage

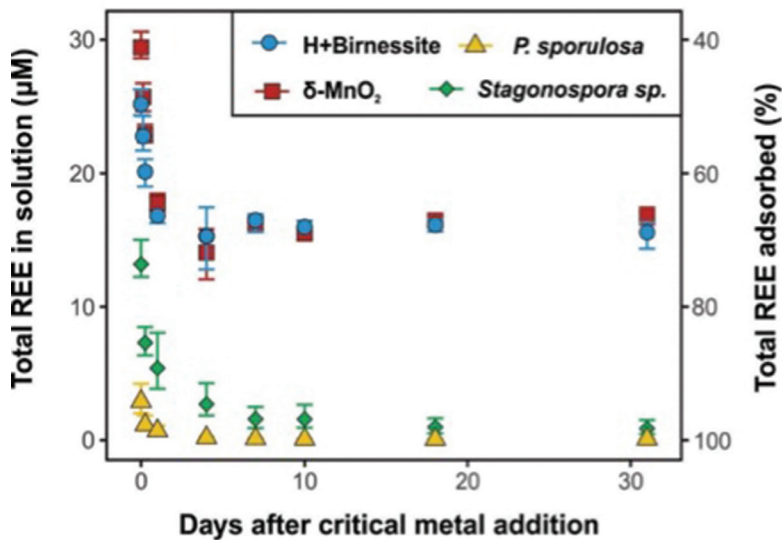


Figure 1 Change in total REE concentration over 31 days after the addition of critical metals in the presence of biotic HMO produced by *Stagonospora sp.* and *P. sporulosa*, and abiotic HMO δ -MnO₂ and H⁺ birnessite

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