

An experimental investigation on arsenic sorption and release by Mn-dioxides.

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Models for arsenic cycling in surface environments generally involve goethite as a major arsenic host and its reductive dissolution being the dominant process of releasing arsenic from sediments and soils to groundwater. Although experiments showed high arsenic sorption capability for Mn-oxides, they were far less addressed than goethite. With this project, we synthesized three Mn-dioxides using arsenic-containing solutions. The products were analyzed with an arsenic sequential extraction procedure (SEP) to quantify total arsenic sorption capacity and adsorption/co-precipitation proportions and to reveal their arsenic release potentials.

Among the three synthesized MnO_2 , the low-crystallinity birnessite ($\delta\text{-MnO}_2$) had the highest arsenic sorption capacity that increased from 3.6 to 2140 $\mu\text{g As/1 g Mn}$ with solution arsenic increasing from 0.1 to 50 ppm. The values for the synthesized hollandite ($\alpha\text{-MnO}_2$) were ~50% lower. Meanwhile, the arsenic adsorption:co-precipitation proportion of the hollandite remained at ~40:60, whereas that of the low-crystallinity birnessite increased from 0:100 to 40:60 with co-precipitated As/Mn ratios of ~0.0001–0.003, mostly < 0.0001 . In contrast, the high-crystallinity birnessite was characterized by a low adsorption capacity with nearly nil co-precipitated arsenic. Opposing to the SEP designation, all the three synthesized MnO_2 were hardly decomposed by the HCl extraction. Although the subsequent oxalic acid extraction completely dissolved the hollandite after three repetitions, it only recovered $< 65\%$ of bulk Mn from the birnessite. Stronger ascorbic acid designated for goethite extraction in SEPs was required to completely dissolve the birnessite. Arsenic release rate was not in proportion to the dissolution rate of the MnO_2 hosts. About one-third of the co-precipitated arsenic in the hollandite persisted until the third repetition of the oxalic acid extraction that dissolved the final 10–15% Mn. In contrast, over 90% of co-precipitated arsenic in the low-crystallinity birnessite was released during the first and second repetitions of the oxalic acid extraction that recovered only ~60% of Mn. Being shown to have high arsenic co-precipitation capacities and release rates via reductive dissolution, the low-crystallinity birnessite possibly plays a more crucial role than goethite in arsenic cycling for its higher redox potential, provided with certain quantities in sediments/soils.