

Mixed-valent Manganese Oxide Modified Activated Carbon (MOMAC) Amendments for Mercury Contaminated Sediment

EDWIN RIVAS MERAZ, SAMUEL J TRAINA, MARC
BEUTEL AND PEGGY A. O'DAY

University of California Merced

Presenting Author: erivasmeraz@ucmerced.edu

Manganese oxides (MnOx) are among the strongest naturally occurring oxidants and greatly influence elemental biogeochemical cycles through system redox poisoning. Combining MnOx with common sediment amendments such as activated carbon creates a novel, cost-effective, and practical approach for remediation of sediments polluted with redox-sensitive contaminants. For example, manganese oxide modified activated carbon (MOMAC) can be applied to mercury (Hg)-contaminated sediments to create a redox buffer that disfavors production of neurotoxic methylmercury (MeHg), which is generated through anaerobic microbial pathways, while AC binds Hg and MeHg species to the sediment through sorption. However, AC functional groups can be oxidized by high-valent Mn during synthesis and produce mixed-valent Mn phases that can affect the redox buffering capacity. This study compared the relative fractions of Mn species and Mn(II), (III), and (IV) oxidation states present in MOMAC against homogeneously precipitated MnOx. Mn speciation was estimated by linear combination fits of Mn K-edge XANES and EXAFS with reference spectra. Relative percentages of Mn(II), (III), and (IV) oxidation states were determined by fits of Mn2p_{3/2} spectra collected with X-ray photoelectron spectroscopy (XPS) and corroborated with iodometric titrations. Changes to carbon functional groups relative to unreacted AC were also quantified by analysis of C1s XPS. Synthetic MnOx was mostly Mn(IV) (as δ -MnO₂ and Ca-birnessite) and a minor (~10%) manganite (Mn(III)OOH) fraction. MOMAC XAS fits were similar across different loadings, but had higher manganite (24-41%) fractions and a minor hausmannite (Mn(II),Mn(III)₂O₄) component compared to MnOx. Lower fractions of Mn(IV) in MOMAC were also evident in XPS but had higher fractions of Mn(II) relative to XAS results. The higher Mn(II) fraction shown in XPS may be due to the surface sensitivity of XPS that is capturing residual sorbed Mn(II) from synthesis. The iodometric titration results showed lower Mn average oxidation states in MOMAC compared to MnOx. Fits to the C1s peak showed an increase of oxygenated functional groups in MOMAC. The presence of mixed-valent Mn oxides in MOMAC may have an advantage in buffering redox compared to MnOx, which is predominantly Mn(IV), but requires further studies to optimize the oxidative capacity and longevity of this novel amendment.