

The limitations of observed first order rate constants: a case study on As(III) depletion by Mn oxides

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Arsenic (As) contamination of drinking water is a threat to public health around the world. Manganese(III/IV) (Mn) oxides play a role in controlling As fate in groundwater by sorbing As and oxidizing more mobile and more toxic As(III) to less mobile and less toxic As(V). While this redox reaction has been the subject of extensive research, results across studies are inconclusive and often contradictory. The depletion of aqueous As(III) by Mn(III/IV) oxides is biphasic, with reported first order rate constants ranging seven orders of magnitude. To demonstrate potential causes of inconsistencies between studies, two datasets from batch reactions of As(III) with δ -MnO₂ were reanalyzed. The observed first order rate constants for As depletion are time-dependent and do not fit pure kinetic rate models. A single dataset yields rate constants ranging from 3.0 to 25.0 hr⁻¹ ($R^2 > 0.80$), depending on the cut-off time of the initial rate. These rate constants were calculated using the linearized form of the first order rate law. Not forcing this equation through the origin ($\ln(C/C_0) = 0$ at $t = 0$) removes the assumption of a kinetic fit and results in rate constants approximately 50% lower than those forced through the origin. Observed first order rate constants are valuable in obtaining relative depletion rates within a study, but there are significant limitations when generalizing across studies on oxyanion depletion in the presence of Mn oxides. To better predict depletion rates, mechanistic modeling that accounts for differences in reactivity between Mn(III) and Mn(IV) as well as the sorption and desorption of As(III), As(V), and Mn(II) is needed.