

Quantifying Fe oxide – aqueous Fe(II) reduction potentials using mediated electrochemical analyses

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Iron (Fe) (oxyhydr)oxides are important redox-active phases in the environment that influence the global cycling of major elements (such as C, N, and P), nutrient bioavailability, and the fate and transport of environmental contaminants. Despite their importance, Fe redox processes have proven to be both experimentally and conceptually difficult to study. In experiments, Fe oxide suspensions do not reach redox equilibrium with working or redox electrodes. Conceptually, Fe oxide and aqueous Fe(II) interactions are known to be complex and can involve several possibly irreversible processes, including sorption, interfacial electron transfer, and reductive dissolution.

Here, we demonstrate that the experimental challenges associated with measuring reduction potential (E_H) values of Fe oxide – aqueous Fe(II) redox couples can be overcome using novel mediated electrochemical analyses. Electron transfer mediators facilitate electron transfer between suspended oxide particles and electrodes, allowing for rapid redox equilibration to occur. Experiments were conducted in batch reactors containing goethite or hematite particles under different solution conditions (i.e., pH, dissolved Fe(II) concentrations). Using this approach, standard reduction potential (E_H^0) values were determined for both oxides. The measured standard reduction potential values are in good agreement with estimated values in previous works. Experiments are currently underway to investigate the reversibility of electron transfer to and from the Fe oxides.

This study demonstrates that mediated electrochemical analyses can be effectively used to analyze interfacial redox couples, and values collected here can be used to improve estimates of contaminant degradation rates and extents in aquatic systems.