

Fe(II)-Fe(III) Oxide Redox Chemistry and its Impact on Contaminant Reduction Investigated using Mediated Electrochemistry

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As the most abundant transition metal on the Earth's surface, iron plays a particularly important role in environmental biogeochemistry, facilitating the redox transformation of a range of environmental contaminants. This is advantageous as redox transformations often render environmental contaminants easier to degrade or less toxic. Many microorganisms also gain energy or assimilate iron by reducing or oxidizing iron, with these processes more broadly affecting the biogeochemical cycling of iron and associated elements such as carbon, sulfur, phosphorus and trace metal contaminants such as arsenic.

The redox chemistry of Fe(II)-Fe(III) oxides are difficult to measure experimentally due to poor physical contact between the working electrode and solid suspensions and a low concentration of aqueous Fe(III) ions. Mediated electrochemistry is employed here to avoid these difficulties to obtain reliable reduction potential measurements for the Fe(II)-Fe(III) oxide systems. Mediators facilitate the efficient transfer of electrons between the solid Fe oxide substrate and the working electrode without the need for physical contact. Using this method, silica is found to have a profound effect on 4-chloronitrobenzene reduction kinetics, as is Fe(III) oxide particle size. These effects are partially related to changes induced to the Nernstian behavior of these Fe(II)-Fe(III) oxide systems, where thermodynamics is found to be a significant driving force of 4-chloronitrobenzene reduction kinetics.