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Kinetics of divalent mercury reduction by zero-valent iron: the effects of pH, chloride, and dissolved organic carbon

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ABSTRACT

The effects of pH, Cl⁻, and dissolved organic carbon (DOC) on the kinetics of Hg²⁺ reduction to Hg⁰ were investigated in anoxic Fe⁰–H₂O system. A reaction kinetic model was developed to describe separately the surface-mediated and aqueous phase Hg reduction processes. The Hg²⁺ was rapidly reduced to Hg⁰ in the presence of 2 g L⁻¹ Fe⁰ (0.42 m² L⁻¹) within 3 h although the presence of DOC significantly, about an order of magnitude, reduced the reduction kinetics. The zero-valent iron (ZVI) surface area normalized Hg²⁺ reduction rates varied between 0.5 and 2.74 m⁻² min⁻¹. In the presence of 0.1–10 mg/L DOC, the rates varied between 0.026 and 0.1 m⁻² min⁻¹. Modeling studies showed that the increase of pH and NaCl concentrations and the decrease of DOC levels increased surface-mediated Hg²⁺ reduction rate. Higher pH seemed to increase the reduction rates and this was attributed to the enhanced adsorption of Hg²⁺ to ZVI surface at higher pH. The Cl⁻ undergoes strong complexation with Hg²⁺ (i.e., HgCl⁺, HgCl₂, and HgCl⁻) and prevent the adsorption of Hg²⁺ to Fe⁰ surface and subsequent reduction. However, the enhanced corrosion and greater release of Fe²⁺ by the pitting corrosion process in the presence of Cl⁻ affected the overall Hg²⁺ reduction far more significantly, hence, increased Hg²⁺ reduction was observed in the presence of Cl⁻ in solution. The DOC seemed not only to decrease the reactivity of Hg²⁺ by rendering strong complexation but also to prevent the adsorption of Hg²⁺ to the Fe⁰ surface sthus inhibiting surface reduction.

Keywords: Zero-valent iron; Mercury reduction kinetics; Mercury-contaminated wastewater; Groundwater pollution

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