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Pb(II) and Zn(II) adsorption behavior onto goethites (α-FeOOH) with different specific surface areas.

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Lead (Pb) and Zinc (Zn) are potentially toxic elements (PTEs) that are released to the environment as contaminant divalent cationic species (mainly by mining activities). In soil-water systems, their mobility may be controlled by adsorption onto abundant minerals of small particle sizes, such as goethite (α-FeOOH). In this work, the adsorption of each metal cation as a function of pH was investigated onto 4 goethites with different specific surface areas (SSAs=42, 53, 76 and >80 m^2 /g) at two total concentrations ($6x10^{-4}$ and 10^{-4} mol/g), under 0.01 mol/L ionic strength. Their corresponding pH adsorption edges showed important differences among goethites, with increasing sorption per area as SSA decreased, and Pb(II) showed higher adsorption than Zn(II) in all cases under equal experimental conditions. Their behavior was adequately described using the CD-MUSIC (Charge Distribution-MultiSite Complexation) Surface Complexation Model, with independently obtained variable reactive surface site densities for the same four goethites [1, 2]. Unified acidity and electrolyte-binding constants, and variable electrostatic capacitances were previously obtained by optimizing acid-base titration data for each goethite. Metal cation adsorption data were simulated to optimize the surface complex configurations found and their corresponding affinity constants. Unified affinity parameters for all goethites were obtained considering the formation of monodentate hydroxylated complexes and bidentate non-hydroxylated complexes of each metal cation only on singly coordinated surface >OH sites, as the optimal surface configurations. These complexes vary in contribution as a function of pH, cation concentration and goethite SSA. The results obtained are very promising to start building a thermodynamic database of adsorption reactions on goethite using the CD-MUSIC model that may be used in geochemical speciation models of greater component complexity.

[1]Livi *et al.* (2017) *Langmuir* **33**, 8924-8932.

[2]Livi *et al.* (2023) *Langmuir* **39**, 556-562.