Lead and cadmium sorption onto magnetite: similarities and differences

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Pb(II) and Cd(II) sorption onto synthetic magnetite (mixed valence iron oxide - Fe_3O_4) with specific surface of 3 m^2/g (BET) are studied at room temperature in reductive conditions (Ar/CH_4: 90/10), in 0.1 M $NaNO_3$ electrolyte. The studied parameters before and after reactions are: lead and cadmium concentrations and their speciations in solutions, iron concentrations variations in solutions, pH, E(h) and z (oxidation number of magnetite to maghemite). The sorption processes are studied as a function of pH (4.5–9.4), sorption density (0.6 nmol–8.0 $\mu mol/m^2$ for Pb(II); 2.0 nmol–2.0 $\mu mol/m^2$ for Cd(II)) and $[Pb]_{eq}$ (80 nM–45 mM) or $[Cd]_{eq}$ (2 nM–6 mM).

Recent study by Peterson *et al.* (1996) about chromium sorption on magnetite has shown heterogeneous redox reaction at the aqueous chromium/solid interface. They observed a reduction of mobile Cr(VI) to strongly-chemico-adsorbed Cr(III) in agreement with an oxidation in the solid of Fe^{2+} to Fe^{3+} by electron transfer. Very few other studies on sorption of metallic cations onto magnetite have been published. However this mixed valence iron oxide with its sorption capacities, its electrochemical characteristics (fast electronic transfer without structure changes) and its magnetic properties should be in the future an important element for the heavy metals decontamination of industrial and urban sludges and waters. Magnetite has the advantage on usual solid phases used for heavy metals sorption that water can be very efficiently cleared from a magnetite suspension by the use of magnetic field (Dixon (1985)).

Results

Acid titrations performed on magnetite showed a high capacity of this mineral for the adsorption of H^+ (or loss of OH^-) with a pH_{zpc} of 9.4 ± 0.1. The notable difference between this value and those obtained by Milonjic *et al.* (1983), should be due to the opposite reaction conditions such as absence or presence of oxygen in solution and in ambient atmosphere. The sorption experiments are performed with the same ratio solid/solution (180 m^2/l) than acid titration in order to compare pH evolution of sorption reactions to pH variations without metallic cations in solution. The lead and cadmium sorption isotherms displayed in Fig. 1 point out several distinct facts: (1) the general shapes of the curves are very similar with a high affinity of these metals for the magnetite, and important retention capacities of this iron oxide for lead and cadmium cations. (2) Despite low pH of initial solution before addition of magnetite compared to pH_{zpc}, therefore giving a positive charged surface, the adsorption of the metallic cations is significant. This fact indicates that chemical attractions are higher than electrostatic repulsions. (3) The affinity of cadmium for first sorption sites on magnetite is stronger than in the case of lead. (4) The retention capacity of magnetite for Pb(II) is four times higher than capacity for Cd(II). (5) For lead, a particular point at $[Pb]_{ads} = 10^{-5.6}$ mol/m^2 of solid is observed with an important isotherm bound. At this step, a beginning of iron loss by the oxide mineral toward the solution is observed with releasing of one to three H^+ for one Fe. (6) For cadmium, this phenomena is not noticed. However, a particular point at $[Cd]_{eq} = 10^{-3.9}$ M is observed with an increasing adsorption of H^+ onto magnetite and minimum of the $(H^+_{adsorbed}/H^+_{(pHzpc-pHeq)})$ ratio versus Cd sorption. This trend is not detected for lead. Specific features of lead and cadmium sorption onto

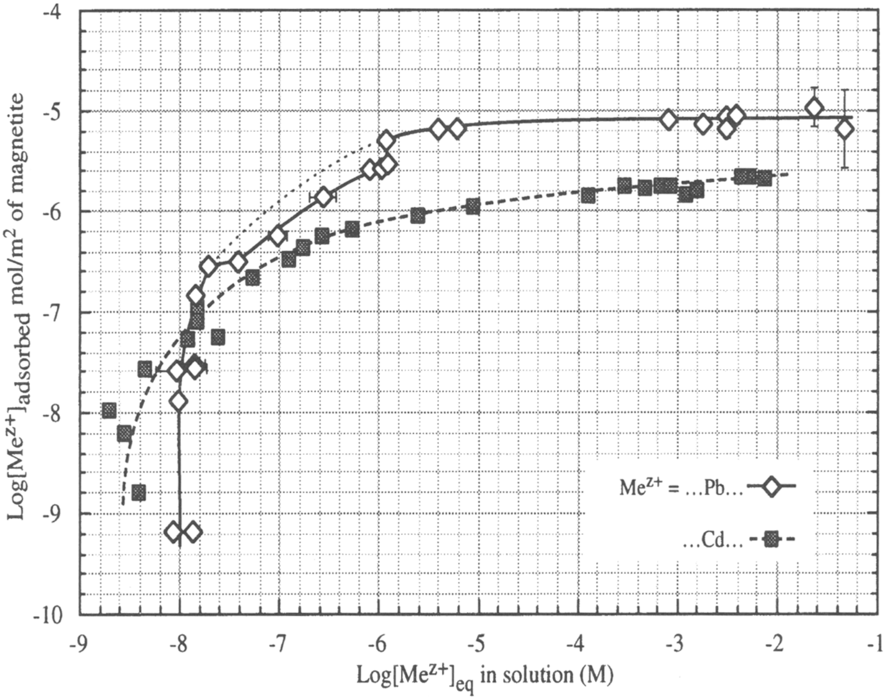

FIG. 1. Lead and cadmium isotherms.

magnetite surface can be understood using these points.

References

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