

An experimental study of lead adsorption to kaolinite surfaces in the presence and absence of organic acid

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The goal of this study is to understand lead transport in natural/near surface environments. This work is motivated by the widespread environmental impact of this metal. Lead transport is controlled in part by its relative stability in natural aqueous solutions *vs.* its tendency to adsorb on mineral surfaces. To quantify this process, the quantity of lead adsorbed on kaolinite surfaces was determined by titration of this metal onto mineral suspensions at predetermined pH.

Adsorption experiments were carried out in a water thermostated vessel, equipped with a magnetic stirring bar, under continuous N_2 flux. The pH was measured using a Shott N62 combined glass electrode and is adjusted to the pH of interest by

addition of small quantities of HNO_3 or $NaOH$. $NaNO_3$ is added to these solutions as non-complexing salt to maintain a constant ionic strength of 1×10^{-2} m during the titrations. Solution samples were taken from the vessel, filtered, acidified, and analysed using atomic absorption spectroscopy. Experiments were performed for initial solutions containing from 5×10^{-5} m to 5×10^{-3} m Pb in contact with 3.5 to 24 g/l kaolinite. Figure 1 shows an example of the results obtained from these experiments, specifically the percentage of lead adsorbed to kaolinite surfaces during a titration performed from pH 4.5–8.9 at $25^\circ C$ in a solution initially containing 2.8×10^{-4} m $Pb(NO_3)_2$ and 3.5 g/l kaolinite. Regression of these data was used to obtain

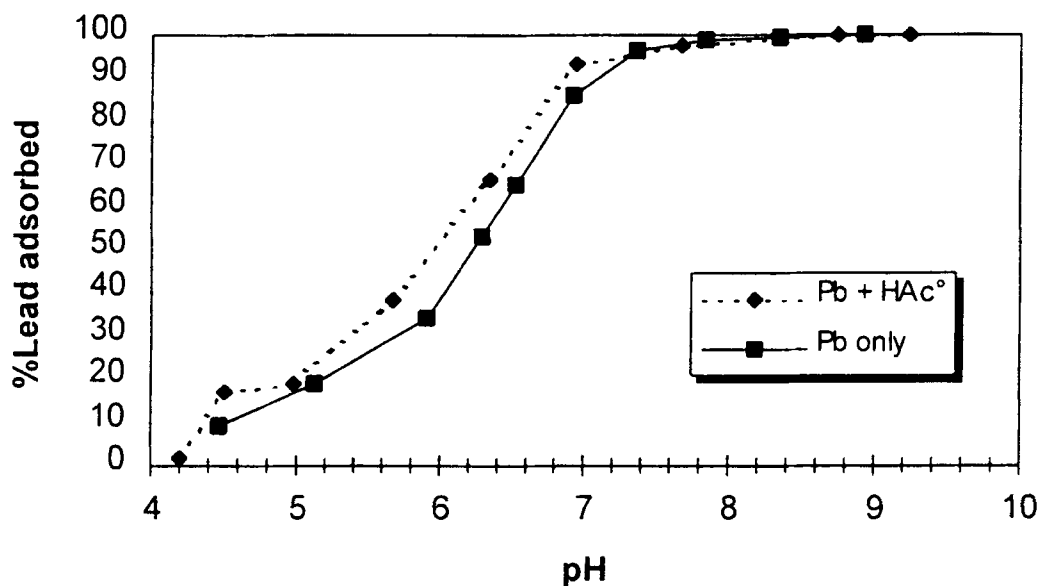


FIG. 1. Percentage of lead adsorbed from a 0.01 m ionic strength solution onto kaolinite surfaces as a function of pH. The filled squares and circles correspond to results obtained in acetic acid-free and a solution containing 7.1×10^{-2} m acetic acid, respectively. Both titrations were performed in solutions initially containing 2.8×10^{-4} m $Pb(NO_3)_2$ in the presence of 3.5 g/l kaolinite.

formation constants of lead species on the kaolinite surface.

To determine the effect of organic acids on this adsorption process, parallel titrations were performed in the presence of acetic acid. An example of the results of these titrations is also shown in Fig. 1. A significant increase in the quantity of lead adsorbed to the surface is observed compared to the acetate-free solution at $4.5 < \text{pH} < 7$. The enhancement of cation adsorption via formation of cation-organic-surface ternary complexes have been observed for Cd^{2+} and Ni^{2+} on alumina and hematite in the presence of humic acids (Davis, 1984; Davis and Bhatnagar, 1995) and for Cd^{2+} on goethite in the presence of oxalic acid (Lamy *et al.*, 1991).

The degree to which this effect is due to a change in the concentrations of aqueous lead species or to lead adsorption via acetate ternary complexes is examined by comparing: (1) measured lead concentrations on the kaolinite surface, and (2) predictions performed with adsorption constants obtained from acetate free solutions together with aqueous Pb^{2+}

activities generated from solution speciation calculations. These calculations include provision for the formation of $\text{Pb}(\text{CH}_3\text{COO})^+$ and $\text{Pb}(\text{CH}_3\text{COO})_2^0$ which were obtained from lead acetate solutions analysed by Raman spectroscopy (Fournier *et al.*, 1997). Equilibrium constants for adsorption reactions generated from these comparisons are used to assess the effect of these reactions on lead transport in natural systems. Further work is aimed at characterizing lead adsorbed surfaces using Raman and Infra-Red spectroscopies.

References

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