

A Comparative Study of the Adsorption of Transition Metals on Kaolinite

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Adsorption of Pb(II), Cu(II), Zn(II), Co(II), and Mn(II) to kaolinite was measured at 25°C in the presence of 5 mM KNO₃. Adsorption edges (pH 3–10; total metal concentration 100 μM) for Pb(II) and Cu(II) were sigmoid, but those for Zn(II) and Co(II), and especially Mn(II), were characterized by distinct steps after about 40% adsorption. Adsorption isotherms (concentrations up to 60 μM; fixed pH) at pH 5.50 followed the simple Langmuir equation, but those at pH 7.50 (Zn(II), Co(II), and Mn(II)) required a two-site model. More protons were released during adsorption at the higher pH. All adsorption data, and the results of potentiometric titrations of kaolinite suspensions (alone and in the presence of metals at 100 μM), can be fitted closely by a constant-capacitance surface complexation model that incorporates two bidentate surface complexes. One involves electrostatic attraction between transition metal ions and the permanent, negatively charged sites on the silanol faces of kaolinite. The other is an inner-sphere complex at the variable-charge surface hydroxyl groups situated at the crystal edges and on the aluminol faces. © 1999 Academic Press

Key Words: adsorption; kaolinite; lead; copper; zinc; cobalt; manganese; Langmuir; surface complexation modeling.

INTRODUCTION

Adsorption of metal ions onto mineral substrates is an important process in soil chemistry, hydrometallurgy, and the treatment of industrial wastes. Processes as diverse as the uptake of trace nutrients by plants and the removal of toxic heavy metals from industrial wastes often depend on adsorption to mineral systems.

Adsorption is a complex process, often involving much more than simple ion exchange on the mineral surface (1–4). Factors such as the pH, the nature and concentration of the substrate and adsorbing ion, ionic strength, and the presence of competing and complexing ions all affect the amount of metal ion that will adsorb. Even though it has been the subject of extensive study over the past 30 years, the process of adsorption is still only partially understood.

Recently, Angove *et al.* (5, 6) applied a surface complexation modeling approach to adsorption results obtained from three quite different types of experiments to test possible surface reactions

more rigorously. The ability to fit data from different types of experiments with the same model provides a measure of confidence in a reaction scheme. In this work, we have extended the range of metal ions investigated by studying five divalent transition metals (Pb, Cu, Zn, Co, and Mn) with hydrolysis behavior that ranges from quite simple (e.g., Co(II)) to rather more complex (e.g., Pb(II) and Cu(II)). Baes and Mesmer (7) suggest that the hydrolysis products include $M(OH)^+$ and $M(OH)_2$ for each of the five metals, but $Zn(OH)_3^-$, $Cu(OH)_3^-$, $Cu_2(OH)_2^{2+}$, and $Pb_3(OH)_4^{2+}$ also form in the range of metal ion concentrations and pH values studied here. Since the onset of adsorption and the formation of hydrolysis products have been linked in adsorption studies (8), one might expect that differences in metal ion hydrolysis may result in different adsorption reactions.

We studied the substrate kaolinite because of its importance both in soil systems and in industrial applications. It is a 1:1 aluminosilicate comprising a tetrahedral silica sheet bonded to an octahedral alumina sheet through the sharing of oxygen atoms between silicon and aluminum atoms in adjacent sheets. Successive 1:1 layers are held together by hydrogen bonding of adjacent silica and alumina layers. The silica face carries a small permanent negative charge due to isomorphous substitution of Si^{4+} by Al^{3+} , leaving a single negative charge for each substitution (9). Both the alumina face and the crystal edges have a pH-dependent variable charge caused by protonation and deprotonation of surface hydroxyl (SOH) groups. Hence we expect two quite different populations of metal ion adsorption sites on the kaolinite surface.

Schindler *et al.* (4) proposed that the binding of copper, cadmium, and lead on kaolinite could be described by a model that assumes two kinds of binding sites. Adsorption is via ion exchange on the first site type, whereas inner-sphere binding to ampholytic SOH groups occurs on the second population of surface sites. This view was supported by the recent comprehensive study (6) of Cd(II) and Co(II) adsorption onto kaolinite as a function of temperature.

MATERIALS AND METHODS

Kaolinite

The acid-washed kaolinite sample (Ajax Chemicals) used in this investigation was from the same batch as that used by

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