SORPTION AND DESORPTION OF Zn ON Ca-KAOLINITE

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Abstract. Experiments on Zn^{2+} sorption-desorption by Ca-kaolinite using a wide range of Zn^{2+} concentrations and two acid pH values allowed us to reach the following conclusions: (1) For Zn^{2+} surface coverages below the kaolinite C.E.C., Zn^{2+} was sorbed mainly via ion exchange; (2) At Zn^{2+} sorption values above the C.E.C., Zn^{2+} was sorbed with higher affinity by a mechanism stronger than ion exchange, involving a strong association of Zn ions with silicate solid phases; and (3) Use of C.E.C. values and/or Langmuir's calculated maxima would greatly underestimate Zn^{2+} sorption capacity by kaolinite, even at acid pH values.

1. Introduction

Zinc is an important heavy metal in soil-water systems since it is a micronutrient in plants and animals as well as humans. Also it can be present in toxic amounts. This possibility has increased in the last decade due to the use of sewage sludges as fertilizers, and the disposal of wastes in soils (Page, 1974; Jones and Jarvis, 1981). Kaolinite is a sorbent inorganic component present in many soils, sediments and suspended materials. Interactions of kaolinite with heavy metals are germane to the behavior of metal ions in environmental systems.

The purpose of this work was to study the sorption and desorption of Zn by kaolinite over a wide range of metal surface loading. An attempt is made to obtain information on the mechanism(s) of Zn retention at different surface coverages.

2. Materials and Methods

The mineral used in these experiments was 'Light Kaolin' supplied by BDH. This kaolin was thoroughly characterized by X-ray diffraction, infrared and C.E.C. measurements.

It was found to be a fairly pure and well crystallized kaolin, similar to Georgia kaolin according to the data given by Parker (1969). The index given by Hinckley (1963) to characterize kaolin group minerals also indicates that the mineral used in this work was a fairly well crystallyzed specimen of kaolin.

The kaolinite's C.E.C. at two pH values (3.6 and 4.7) was determined by saturating triplicate samples of 5 mL kaolinite suspension with 5 washings of 30 mL each of $0.25M-Mg(NO_3)_2$ solutions previously adjusted at pH 3.6 and 4.7 with HNO_3. Excess Mg^{2+} was washed with 5 washings of 30 mL of 2.5×10^{-4} $M-Mg(NO_3)_2$ solutions. After the last washing with the diluted $Mg(NO_3)_2$ solution the supernatant pH was measured. Four washings with 30 mL $1M-NH_4CH_3COO$ were used for displacement of exchangeable Mg^{2+}, and this cation was determined by AAS in the extracts. Excess Mg^{2+} entrapped in the interstitial solution after the last washing with diluted $Mg(NO_3)_2$

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solution, was estimated by weighting as usual, and used to calculate the C.E.C. The C.E.C. of kaolinite was 4.7 me 100 g^{-1} at pH 3.6 and 5.0 at pH 4.7.

For the sorption experiments the following procedure was followed: 40 g of kaolinite were transfer into a 250 mL centrifuge tube to which 100 mL of 0.5 M $Ca(NO_3)_2$ solution were added to make the mineral homoionic in Ca^{2+}. The suspension was shaken for 2 hr, centrifuged and the supernatant discarded, repeating the process twice to ensure a complete Ca saturation on the mineral. Then 100 mL distilled water were used to wash out the excess of $Ca(NO_3)_2$.

The volume of the suspension was finally brought up to 500 mL with distilled water. The kaolinite concentration of this suspension was determined (% W/V) and the homoionic Ca-kaolinite was used in all the sorption experiments performed in this work. Twenty five mL of this suspension (2 g/solid) were placed in 50 mL plastic centrifuge tubes and centrifuged discarding the supernatant. To each tube, by duplicate, different quantities of Zn were added, using 20 mL of $Zn(NO_3)_2$ solutions with concentrations going from 0 to 125 me of Zn L^{-1}. Metal concentrations higher than those expected in most environmentally relevant situations were employed, in an effort to cover a wide range of Zn sorption by kaolinite. Nevertheless concentration of the solutions before adding them to the mineral suspension were always such as to avoid precipitation of $Zn(OH)_2(s)$ (Sillen and Martell, 1964). These solutions were prepared with Merck (P.A.) $Zn(NO_3)_2$ reactive, and two pH series were used, one group has initial pH 3 (adjusted by adding HNO_3) and the other an initial pH of 6 adjusted with NaOH. The kaolinite + $Zn(NO_3)_2$ suspensions were shaken for 2 hr in a wrist action shaker and left resting for a 24 hr period. Previous experiments showed that after the 2 hr shaking time-24 hr rest periods, there was practically no change in Zn concentration in the equilibrium solution. Afterwards, the suspension was centrifuged at 2000 rpm for 20 min and the supernatant was separated from the solid phase. The pH of the supernatant or equilibrium solution was measured with a pH meter. Equilibrium pH values were 3.64 ± 0.13 for the lower pH isotherm and 4.75 ± 0.20 for the higher pH one. Afterwards Zn and Ca concentrations were measured by AAS using a AA-175 Varian Techtron unit.

Hydrogen sorption-desorption was estimated from Δ pH of initial vs equilibrium solutions.

Some hydrolysis should be expected due to the acid pH values used. However in a kaolinite system, due to its greater stability at acid pH (Dixon, 1977), it will be less than in the montmorillonite systems reported in the literature (Llorca and Cruz-Romero, 1977; Schramm and Kwak, 1984). Also, the use of Ca^{2+} instead of Na^+ as saturating cation goes in the same direction.

Desorption experiments were also performed as follows: the solid phase left after the separation of the supernatant, was washed once with 20 mL of distilled water to eliminate the excess of Zn left in the interstitial solution. Afterwards, an extraction with five 20 mL washings of 0.5 N KNO_3 and 2 hr shaking time, follow by centrifugation was performed. In each washing the supernatant was saved and placed in a 100 mL volumetric flask. After bringing them up to volume, the Zn in those KNO_3 extracts was measured by AAS. Following that, a similar extraction with 0.5 HNO_3 and determination of Zn in the extracts was performed.

For these kaolinite samples where the summation of Zn extracted by 0.5 N KNO_3 and 0.5 N HNO_3 was below 90%, further extraction of total Zn remaining was performed by HF + $HC10_4$ digestion following the methodology given by Pratt (1965).

Aluminium present in the exchange complex after Ca saturation was measured by AAS in the $Zn(NO_3)_2$ and KNO_3 supernatants and was very low in all cases (< 0.1 me $100\ g^{-1}$). So, the clay was essentially Ca-saturated, and behaved as such. The possible presence of some tightly held Al^{3+} (Bolland *et al.*, 1976; McBride, 1978), not displaced by K^+ and Zn^{2+}, remaining on the surfaces probably affects this behavior very slightly.

Calcium saturated kaolinite is unlikely to be found in natural acid soils. Nevertheless Ca^{2+} was used to saturate the mineral since we needed to measure the cations being exchanged by Zn^{2+} sorbed. Calcium was preferred because it is a divalent cation, so the ion exchange reaction would be homovalent. Also it was convenient to determine, and unlike Mg^{2+} is not normally found in octahedral sheets of layer silicates.

3. Results and Discussion

3.1. SORPTION ISOTHERMS

Figure 1 summarizes the results of the experiments on Zn sorption by Ca-kaolinite at two equilibrium pH values (3.64 ± 0.13 and 4. 75 ± 0.20).

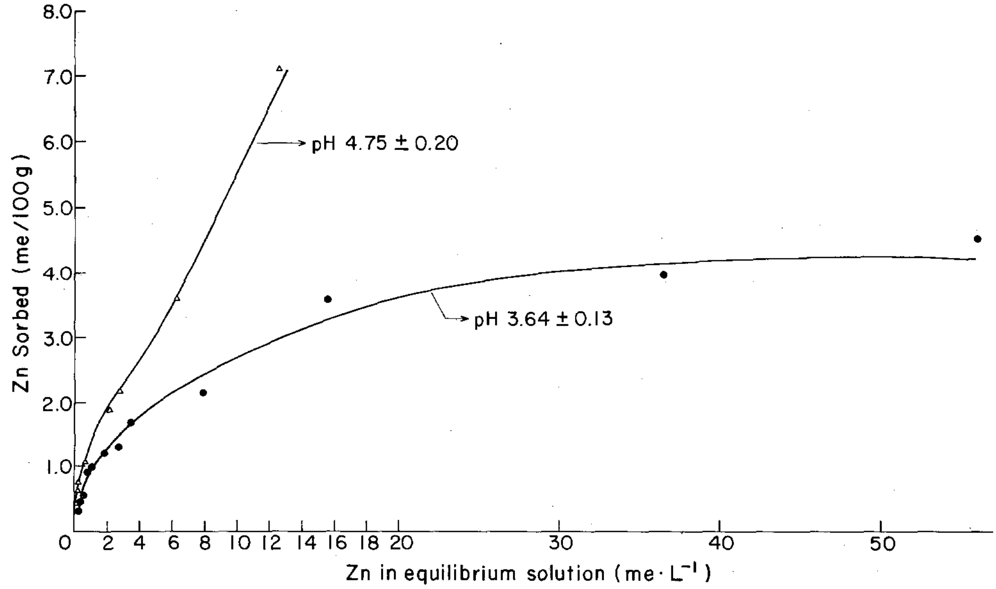

Fig. 1. Sorption isotherms of Zn on Ca-kaolinite at two pH values: (1a) Lower range of surface loading.

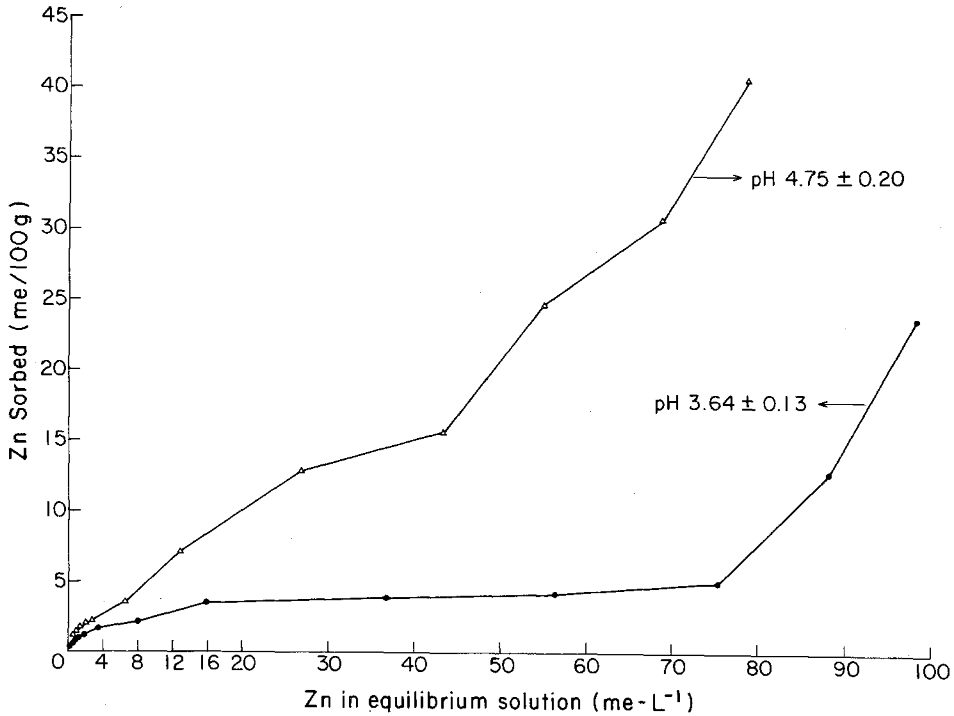

Fig. 1b. Whole range used in this work.

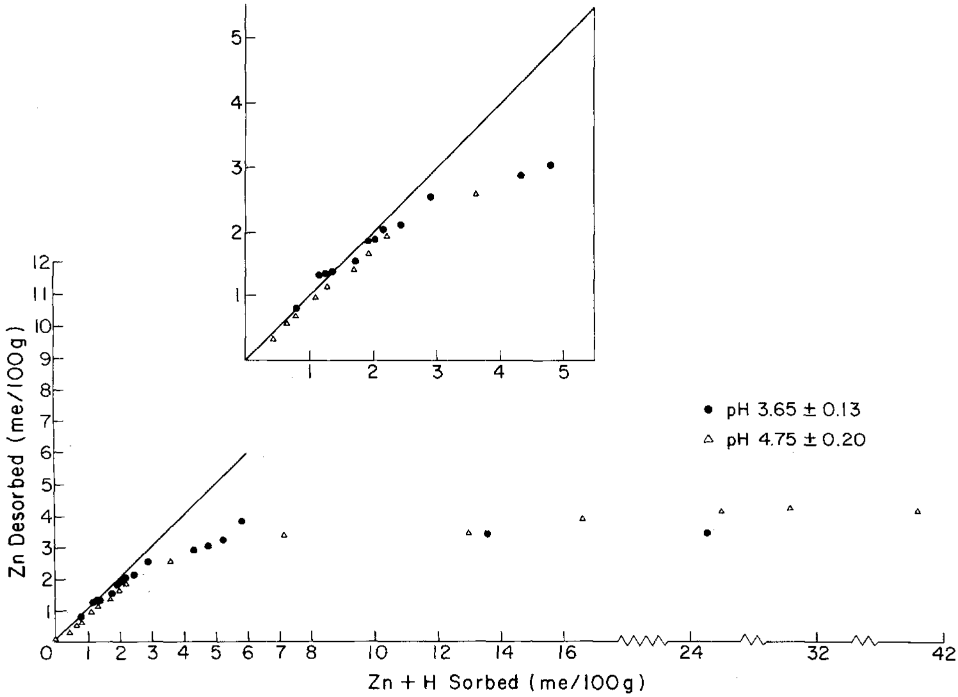

Fig. 2. Calcium desorbed from Ca-kaolinite as a function of Zn + H sorbed.

Relevant features of the sorption isotherms are the long plateau (in the low pH isotherm), corresponding to Zn amounts up to the C.E.C. At this pH (3.6 ± 0.1), sorption of Zn above the C.E.C. seems difficult, probably due to the relatively high H^+ solution activity, however at high Zn solution concentrations ($\sim$ 75 me L^{-1}) a second branch of the isotherm ends up the long plateau. For the higher pH (4.7 ± 0.2) isotherm, no long plateau is found. Also for Zn solution concentrations of 12 me L^{-1}, Zn sorbed is already above the kaolinite's C.E.C. at that pH. These features indicate a stronger interaction Zn^{2+}-kaolinite at pH 4.7, due mainly to the lower H^+ solution activity. Changes in slope (branches) in sorption isotherms are interpreted (Giles *et al.*, 1974), as evidence of a second layer of sorbed species, or another sorption mechanism occurring after saturation of exchange sites by Zn^{2+}. In both isotherms the high slope of the second branch (rapid increase in sorption with a small change in equilibrium solution concentration) could be interpreted, according to Bohn *et al.*, (1979), as indicative of a precipitation reaction.

The sorption of Zn^{2+} well above the C.E.C. even at acid pH values and in a relatively pure system like kaolinite, illustrates a limitation of using the C.E.C. (Leeper, 1972) as a parameter for estimation of metal retention capacity by kaolinite.

3.2. Zn SORPTION – Ca DESORPTION RELATIONSHIPS

Further insight in the interpretation of data comes from Figure 2, where we have a plot of me of Ca desorbed as a function of me of Zn + H sorbed. It is important to mention that H desorbed was nil at the lower pH and almost negligible on the higher pH isotherm, and H sorbed was significant only at the lower pH one. Hydrogen ion sorption was between 0.7 and 0.8 me 100 g^{-1}.

The lower part of the curve (up to 2.2 me 100 g^{-1}) has a slope of practically one, suggesting that for each me of (Zn + H) sorbed, 1 me of Ca came out to the solution phase. This indicates that an ion exchange mechanism is very likely operating on the sorption of Zn by kaolinite at these metal concentrations. At higher values of Zn sorbed, the curve deviates strongly from the straight line of slope one and it reaches a plateau at values nearby 4 me 100 g^{-1} (that is below the C.E.C. of the clay). These results would indicate that at ion surface loadings below the C.E.C., a high proportion of the Zn is being sorbed by an ion exchange mechanism, while at Zn loadings above the C.E.C. most of it is being sorbed by other mechanisms, since no Ca is being displaced from the solid phase.

3.3. LANGMUIR ANALYSIS OF DATA

The competitive form of the Langmuir isotherm (Harter and Baker, 1977; Griffin and Au, 1977; Farrah *et al.*, 1980) was employed to analyze the data. Langmuir analysis of the data applied only at surface coverages below the C.E.C. (Table I). For this range an ion exchange reaction is the predominant Zn sorption mechanism, therefore the K_{Ca}/K_{Zn} data shown in Table I should be interpreted as the relative affinity ratio of kaolinite for these two ions in an ion exchange reaction. The data indicate a preference for Ca^{2+} at the two pH values used.

TABLE I

Parameters of Langmuir competitive isotherms.

pH equilibrium	b (me 100 g^{-1})	K_{Ca}/K_{Zn}	r^a	Surface coverage included
3.64 ± 0.13	4.57	2.48	0.988[b]	up to 3.99 me 100 g^{-1}
4.75 ± 0.20	6.41	2.72	0.935[b]	up to 3.62 me 100 g^{-1}

[a] Regression coefficient of the competitive Langmuir plots.
[b] Significant at $p = 0.05$.

Experimental Zn sorption values well above the calculated Langmuir's maxima were found. These data suggests that using Langmuir analysis to calculate metal sorption capacity for kaolinite systems would greatly underestimated this parameter.

3.4. DESORPTION EXPERIMENTS

Further information on sorption mechanisms comes from desorption experiments. The desorption data are presented in Table II. The data at both pH values show that most of the Zn sorbed up to the kaolinite's C.E.C. is desorbed (extracted) by 0.5 KNO_3 (exchangeable Zn). Another interesting feature is that the amount of Zn extracted by 0.5 KNO_3 is never much higher than the C.E.C. These results indicate that at both pH values, practically all Zn sorbed up to the C.E.C. was sorbed in an exchangeable form, with very little sorbed in other forms. They are consistent with and confirm those obtained on Zn^{2+} sorption – Ca^{2+} desorption experiments. Above the C.E.C. a considerable fraction of Zn was sorbed by mechanisms stronger than normal ion

TABLE II

Data on Zn desorption by 0.5 N-KNO_3, 0.5 N-HNO_3, and HF + $HC10_4$, applied in sequence.

		Percentage of Zn desorbed		
	Zn sorbed[a]	0.5 N-KNO_3	0.5 N-HNO_3	HF + $HC10_4$
Equilibrium pH 3.64 ± 0.13	0.3 to 5.1[b]	84 to 100	0.2 to 2.1	–
	12.8	50.4	0.1	48.7
	23.9	27.0	0.1	60.3
Equilibrium pH 4.75 ± 0.20	0.4 to 2.2[c]	93.8 to 100	0.2 to 1.3	–
	3.6	89.2	0.3	–
	7.1	56.0	0.1	44.2
	13.0	34.0	0.1	63.9
	16.6	28.5	0.1	67.0
	24.9	20.6	0.1	74.9
	31.2	18.3	0.1	76.4
	41.2	14.0	0.1	80.3

[a] Units = me 100 g^{-1}
[b] Includes thirteen (13) points.
[c] Includes eight (8) points.

exchange. A third feature was that extraction with 0.5 N HNO_3 did not yield significant amounts of Zn, even in those cases where Zn sorbed was much higher than the C.E.C.

The fact that Zn retained in excess of C.E.C. was extracted only by a HF + $HC1O_4$ digestion (Table II), which disolves the silicate framework, suggests that Zn ions have been incorporated into solid phases. These are very likely silicate solid phases or very strongly associated to them.

A possible mechanism is a surface nucleated precipitation of a Zn silicate compound. Several authors (Tiller and Pickering, 1974; James and Mac-Naughton, 1977; Leggett, 1978) have reported the formation of Zn silicates at appropriated Zn concentrations and normal pressures and temperatures. In particular the surface nucleated precipitation of a 1 : 1 like Zn layer silicate, similar to those synthesized by Tiller and Pickering (1974), should be considered. The kaolinite surfaces could act as a template for the formation of this mineral, and it should be expected that this Zn layer silicate was relatively stable at acid pH values. To test these hypothesis, samples of kaolinite treated with the highest $Zn(NO_3)_2$ concentrations and aged up to 3 mo were run through X-ray diffraction analysis, but no peaks different to those characteristic of kaolinite nor a reinforcement of them was found. This could be interpreted as indicating that any hypothetical newly formed solid phase was either amorphous or very poorly crystallized.

Another mechanism probably involved is the solid state diffusion of Zn inside octahedral sheets of kaolinite, as proposed by Tiller and Hodgson (1962) for montmorillonite. Considering that we worked at acid pH values, the relatively high H ion concentration should contribute to the break down and opening of octahedral clay edge sites, which should in turn favor the extrance of Zn ions in the kaolinite lattice.

Strong Zn^{2+} sorption by $Al(OH)_x$ gels, theoretically formed on the kaolinite's surface due to acid pH, is unlikely to occur, since these gels should be very unstable on 0.5 N HNO_3, and they would bear excess positive charge.

In conclusion, it can be stated that Zn sorption up to the C.E.C. of kaolinite occurs mainly via ion exchange, while above the C.E.C. it is retained by a mechanism stronger (higher affinity) than ion exchange, probably involving a surface nucleate precipitation, and/or solid state diffusion, and clearly in strong association with silicate solid phases.

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