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Aspects of kaolinite characterization and retention of Pb and Cd

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Abstract

This study illustrates the complimentary nature of selected techniques for characterizing kaolinite. For the particular type of kaolinte studied, scanning electron micrographs revealed the presence of crystallites and mostly larger than clay-sized particles. These findings were in agreement with the low cation exchange capacity, low specific surface area, low zero point of charge and high purity that were determined for the kaolinite. Batch equilibrium tests were conducted on kaolinite suspensions that had been adjusted to pH 4 and pH 6. These suspensions were spiked with varying concentrations of Pb (as PbCl₂) and Cd (as CdCl₂). At equilibrium, the metal uptake was greater for the pH 6 suspensions than for the pH 4 suspensions, the metal uptake was generally greater when greater concentrations of metal had been used to spike the suspensions, and there was a reduction in suspension pH that accompanied the metal uptake. A comparison of the equilibrium curves of both metal retention and suspension pH, as a function of the initial metal concentration, combined with an analysis of metal speciation, provided evidence for the adsorption of both divalent (Pb²⁺ and Cd²⁺) and monovalent (PbCl⁺ and CdCl⁺) species by the kaolinite. Cation exchange was a primary retention mechanism and the order of selectivity for the pH 4 and pH 6 suspensions of kaolinite appeared to be Pb²⁺ > H⁺>Cd²⁺. At higher pH and higher metal concentrations, there was an increase in Cd uptake relative to Pb uptake. This may have been a result of less competition between H⁺ ions and metal ions for adsorption sites, and because CdCl⁺ forms at a lower salt concentration than PbCl⁺, and so a greater proportion of monovalent Cd was adsorbed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Kaolinite; Lead; Cadmium; Adsorption; Speciation

1. Introduction

Pure kaolinite ($Al_2Si_2O_5OH_4$) is one of the more highly weathered clay minerals. It is common in tropical soils and is the second most abundant clay mineral in ocean sediments (Grim, 1968). It has a

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simple structure, is resistant to weathering, and maintains a relatively constant hydraulic conductivity when permeated with contaminants. As it is nonexpanding, it is ideal as a fine aggregate in slurry bentonite walls that are susceptible to expansion cracking under changing climatic conditions (Rumer and Ryan, 1995) and its low swelling potential and low susceptibility to desiccation also make it an ideal surface liner material. Compared to the more expansive clays such as bentonite and illite, kaolinite may be less controlled by physiochemical factors and more controlled by mechanical forces, resulting partly from

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kaolinite's larger particle size and more irregular particle arrangement (Chen et al., 2000). Large overburden pressures also improve kaolinite's resistance to chemical damage (Chen et al., 2000), although base liner materials are usually more highly retentive clays such as montmorillonite.

Typically, kaolinite has a cation exchange capacity (CEC) of 3 to 15 meq/100 g (Grim, 1968) while values quoted for the specific surface area (SSA) of kaolinite are from 10 to 20 m²/g (Yong et al., 1992) or 10 to 50 m²/g (Uehara and Gillman, 1972). One 0.72-nm-thick layer of kaolinite is composed of one silica tetrahedral sheet and one alumina octahedral sheet and the mineral is considered to be crystalline when many layers of the kaolinite are hydrogen bonded together (Bohn et al., 1985; Sposito, 1989; Yong et al., 1992).

The CEC of kaolinite is due primarily to pHdependent edge charges arising from broken bonds along the edges of the mineral (Yong et al., 1992; Bohn et al., 1985; Mitchell, 1993) and these charges increase as the diameter of the kaolinite crystals decrease (Ma and Eggleton, 1999). Exposed hydroxyl groups along the alumina faces of kaolinite may also be able to exchange H⁺ ions for some cations. The total alumina facial charges are greater when fewer kaolinite layers are bonded together. In addition, a permanently negative charge along the silica faces may result from the substitution of Al³⁺ ions for Si⁴⁺ ions within the crystal lattice (Ma and Eggleton, 1999) although this source of charge is thought to be minimal (Bohn et al., 1985).

The zero point of charge (zpc) of kaolinite, as determined by the titration method, usually occurs around pH 3. Higher values are obtained when longer equilibration times are used as the surface properties of the kaolinite are changed by the acidic test conditions (Schroth and Sposito, 1997). Similarly, kaolinite that has experienced "isoelectric weathering" tends to have a higher zpc (Parfitt, 1980).

Compacted clay soil barriers are widely used to contain wastes (Chen et al., 2000) and the adsorption of organic and inorganic contaminants by kaolinite has been widely studied. The properties of kaolinite and how they relate to processes such as the retention of pollutant metals, however, is still not completely understood. Therefore, this paper investigates further the properties and behavior of kaolinite with emphases on the retention of Pb and Cd. Both metals are wellknown environmental pollutants with Cd being the more acutely toxic of the two metals. Although the use of Pb goes back to ancient times and widespread use of Cd has only occurred during the last century, Cd contamination in soils relative to natural background levels is now more excessive than for Pb (Alloway, 1995; Davies, 1995).

2. Experimental

Hydrite Flat D kaolinite and information on its particle size distribution and SSA were obtained from the Dry Branch Kaolin (DBK) in Dry Branch, GA, US. The CEC of kaolinite was determined according to the Canadian Ministry of Agriculture calcium acetate-chloride method (Sheldrick, 1984). The zpc of kaolinite was measured following the general procedure of Van Raij and Peech (1972). Specifically, 2 g of kaolinite was mixed with 20 ml of 1.0, 0.1, 0.01 and 0.001 N solutions of NaCl and the samples were mixed for 1 h. Subsequently, 2 ml of 0.01 N NaOH or 0.1 N HCl was added every 2 min while recording the change in pH with every addition of acid or base. The SSA was estimated by the ethylene glycol monoethyl ether (EGME) method of the Ministry of Agriculture, Canada (Sheldrick, 1984). A JEOL model 6T100 scanning electron microscope (SEM) was used to take micrographs of untreated kaolinite samples. Impurities in the Flat D kaolinite were determined by an acid digestion procedure of the American Environmental Protection Agency (EPA, 1986). The organic matter content of kaolinite was determined as specified in the United States Agricultural Handbook (Richards, 1954), and the pH of a 10% aqueous slurry of the kaolinite was measured.

The retention of Pb and Cd by pH 4 and pH 6 kaolinite suspensions was obtained from batch equilibrium tests. Preliminary experiments determined that uptake of Pb and Cd by kaolinite was virtually complete in 6 h and Puls et al. (1991) concluded that Pb uptake by kaolinite reached equilibrium in 2 h. It was decided to run the batch equilibrium tests for 24 h as this duration was convenient and is most commonly used (Yong et al., 1992).

For each test, 5 g of kaolinite was combined with 50 ml of solution. Solutions of Pb (as PbCl₂) and Cd

(as CdCl₂) were prepared to give 100, 200, 500, 1000, 1500, 2000, 3000, 4000 and 5000 ppm. The Pb and Cd solutions were adjusted with HCl to approximately pH 3.6 and pH 3.9, respectively, to ensure that all the metal species were in soluble form. Distilled water (25 ml) was mixed with the kaolinite, and the suspensions were adjusted to pH 4 or pH 6 with HCl or NaOH. Then 25 ml of metal solution was added to the suspensions to give final metal concentrations ranging from 50 to 2500 ppm. The contaminated suspensions were placed on a shaker for 24 h. After measuring the equilibrium pH, the suspension was centrifuged at 6000 rpm for 5 min. The supernatant was acidified with HCl to pH 1 and the metal concentration was measured on a Perkin Elmer 3110 atomic absorption spectrometer. The difference between the initial metal concentration and the supernatant metal concentration was taken as the retained metal.

3. Characterization results

The median particle diameter for the Flat D kaolinite is 5 μ m and only 25% of the kaolinite particles are less than 2 μ m (Dry Branch Kaolin). This description is consistent with the SEM photographs of the Flat D kaolinite in Fig. 1. There are also indications in Fig. 1 that the Flat D kaolinite is crystalline. Visible in the top left corner of Fig. 1a, are plate-like, kaolinite crystals that are composed of more than 200 layers, are about 0.15- μ m thick and about 6.5 μ m in diameter. In addition, other crystals of various sizes can be seen around the center of Fig. 1b.

The Flat D kaolinite had a pH of 4.6 and therefore contained no carbonate minerals (Hesse, 1971). The organic matter content of the kaolinite was negligible (or 0.034 wt. %). Acid digestion revealed that the Fe content of the kaolinite was only 7.8 mg/kg. The earth's crust contains 26,000 mg/kg (Schacklette and Boerngen, 1984) and only three elements (O, Si and Al) are more abundant than Fe (Cotton and Wilkinson, 1988), so its scarcity in the kaolinite may indicate the kaolinite is relatively pure. The Zn, Cu, Pb and Cd contents of the kaolinite were 0.7, 0.1, 0.5, and 0.1 mg/kg, respectively, significantly less than their background concentrations (Schacklette and Boerngen, 1984) and the Pb and Cd concentrations that were used to spike the kaolinite.





Fig. 1. (a) Scanning electron micrograph of kaolinite magnified 8000 times. (b) Scanning electron micrograph of kaolinite magnified 3500 times.

Average CEC values for kaolinite are between 3 and 15 meq/100 g (Grim, 1968) whereas the pH 7 CEC of the Flat D kaolinite was 1.97 meq/100 g. The particle size is the most important factor influencing the CEC of kaolinite (Ma and Eggleton, 1999) and the low CEC here is consistent with the small proportion of claysized particles that the kaolinite contains. A low CEC is also typical of a kaolinite that is more crystalline (Ma and Eggleton, 1999) and contains fewer impurities (Greenland and Mott, 1978; McBride, 1994).

The BET-N₂ SSA for the Flat D kaolinite is 7 m^2/g (Dry Branch Kaolin) and triplicate determinations of 20.8, 19.8 and 20.8 m^2/g for the EGME SSA averaged 20.4 m^2/g . The EGME method gives higher values than



Fig. 2. Titration curves used to determine the zpc of the kaolinite. Titration solutions are 1.0 N NaCl (\blacksquare), 0.1 N NaCl (\square), 0.01 N NaCl (\blacktriangle) and 0.001 NaCl (\triangle).

the BET-N₂ method and Pennell et al. (1995) describe a kaolinite with a BET-N₂ SSA of 8.5 m²/g and an EGME SSA of 21.3 m²/g. The discrepancy in the range of literature reported values of SSA for kaolinite could be partly attributable to the use of different methods in determining the SSA. Peterson et al. (1996) report that impurities may also raise the value of the SSA although there is no reason to believe the Flat D kaolinite contains impurities to any significant extent.

The zpc of the Flat D kaolinite occurs at the intersection of the four curves in Fig. 2, or approximately at pH 2.6. The zpc of kaolinite may occur around pH 3.0 when the titration method is used and higher values are also possible (Schroth and Sposito, 1997). The low value for the zpc of the Flat D kaolinite suggests that the mineral has experienced minimal weathering (Parfitt, 1980). Above pH 2.6, the net charge on the surfaces of the Flat D kaolinite will be negative and the kaolinite will have an affinity for cations of Pb and Cd.

In summary, the characterization results are complimentary and they indicate that the Flat D kaolinite is a pure, crystalline, minimally weathered kaolinite, with 75% non-clay-sized particles, a low CEC, a low SSA, and a low zpc.

4. Pb and Cd retention results

Puls et al. (1991) determined that Pb uptake by kaolinite reached equilibrium in 2 h and preliminary

experiments using the Flat D kaolinite showed that retention of Pb and Cd by the Flat D kaolinite was complete in 6 h. The duration of the batch equilibrium tests is typically 24 h (Yong et al., 1992) and so this is the duration that was selected. The batch test results are presented in Fig. 3 and the equilibrium metal retention and suspension pH are plotted against the initial metal concentration.

All the curves of Pb and Cd retention by kaolinite at pH 4 and pH 6 (Fig. 3a and b) show that the greatest increase in metal uptake with increasing metal concentration occurs at metal concentrations of approximately 2 mmol/l or less. Across the range of higher metal concentrations, the curves of metal retention have flatter slopes.

Similarly, all the curves of change in pH (Fig. 3c and d) show that the rate of drop in pH with increasing metal concentration is most pronounced for metal concentrations of less than 2 mmol/l. The drop in pH with increasing metal concentration is less pronounced at the higher metal concentrations, and at the highest metal concentrations the slope of the curves is almost completely flat.

The speciation of Pb and Cd was calculated using the critical stability constants provided by Smith and Martell (1974) and the results suggest that cation exchange is a primary retention mechanism for the metals. At initial Pb and Cd concentrations of 2 mmol/ 1 (and for pH 4 and pH 6), 86.5% of Pb occurs as Pb^{2+} and 72% of Cd occurs as Cd^{2+} , with $PbCl^+$ and CdCl⁺ being the other species present. As the initial metal concentrations increase, the proportion of monovalent metal species increases, and the increase is greater for Cd than for Pb. At 12 mmol/l (and for pH 4 and pH 6), Pb occurs as 50.8% Pb²⁺, 47.4% PbCl⁺ and 1.8% PbCl₂ and Cd occurs as 28.4% Cd^{2+} , 65.1% $ClCl^+$ and 6.5% $CdCl_2$. The divalent cations of Pb and Cd displace two H⁺ ions (primarily from the edges of kaolinite particles) for each metal cation adsorbed while one H+ ion is exchanged for each of the monovalent metal species adsorbed. The curves in Fig. 3 show that as the initial metal concentration increases, the metal uptake over the higher range of metal concentrations continues to increase, while further change in the pH of these suspensions is minimal. These results suggest that more monovalent cations of Pb and Cd are being retained at the higher metal concentrations.



Fig. 3. (a) Pb retained by kaolinite at pH 4 (\Box) and at pH 6 (\blacksquare) as a function of the initial Pb concentration. (b) Cd retained by kaolinite at pH 4 (\Box) and at pH 6 (\blacksquare) as a function of the initial Cd concentration. (c) Equilibrium pH values for pH 4 (\Box) and at pH 6 (\blacksquare) kaolinite suspensions as a function of the initial Pb concentration. (d) Equilibrium pH values for pH 4 (\Box) and at pH 6 (\blacksquare) kaolinite suspensions as a function of the initial Cd concentration. (d) Equilibrium pH values for pH 4 (\Box) and at pH 6 (\blacksquare) kaolinite suspensions as a function of the initial Cd concentration.

Divalent metal species are generally adsorbed more readily than monovalent species (Bohn et al., 1985); however, adsorption is also proportional to the solution concentration of cations (Smedema and Rycroft, 1983). The greater proportion of monovalent species being adsorbed is due to their greater concentration.

Calculations with critical stability constants obtained from Martell and Smith (1974) indicate that the soluble hydroxy species of Pb and Cd are unimportant between pH 4 and pH 6 and this means that precipitation of Pb and Cd as a retention mechanism is also unlikely. Therefore, the variation in metal retention for the two different pH curves is due to the variation in kaolinite surface charge and not due to changes in metal speciation as influenced by the pH.

Specific adsorption of Pb and Cd by kaolinite may not occur or may be negligible. Acid dissociation of Pb and Cd does not occur below pH 7.8 (Dean, 1985; Bowden et al., 1980) and at the pH values used in these experiments the cations would be doubly protonated. Therefore, they would not be in a position to donate electrons and form a chemical bond with the kaolinite surface (Bowden et al., 1980). At high metal concentrations, some $CdCl_2$ and $PbCl_2$ will be present but only in small quantities. It is expected that the mixing of the kaolinite with these metal salts will not bring about chemical bonding of the metals with kaolinite as the formation of such complexes may interfere with metal adsorption (Yong and Sheremata, 1991).

A major difference in the way that Pb and Cd are retained is that the pH of the kaolinite suspension has little effect on Pb uptake but noticeably influences the extent of Cd uptake (Fig. 3). Gerritse and Van Driel (1984) report that soil interactions with Pb are only weakly influenced by pH, whereas soil interactions with Cd are strongly pH dependent. Puls and Bohn (1988) note that Cd is strongly attracted to the hydroxyl edge sites of kaolinite, helping to explain the increase in Cd uptake with an increase in pH. Cations of lower valence are often displaced by cations of higher valence, but the H⁺ ion sometimes behaves like a trivalent cation and this is illustrated by the lyotropic series, which shows that the relative exchanging power of selected cations on montmorillonite is $\text{Li}^+ \approx \text{Na}^+ < \text{K}^+ \approx \text{NH}_4^+ < \text{Rb}^+ < \text{Co}^+ \approx \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} \approx \text{Ba}^{2+} < \text{La}^{3+} \approx \text{H}^+ \approx \text{Al}^{3+} < \text{Th}^{4+}$ (Bohn et al., 1985). Pb also has a high exchanging capacity and is highly selected by mineral soils (Yong et al., 1992). The difference in Pb and Cd adsorption by the kaolinite may be indicating that the relative exchanging power of these cations on kaolinite is Pb^{2+}>H^+>Cd^{2+}. In other words, Pb^{2+} ions may displace H⁺ ions and become adsorbed independently of the pH, while H⁺ ions must be removed by an increase in pH before Cd can be adsorbed.

The pH 7 CEC of the Flat D kaolinite of 1.97 meq/ 100 g is equivalent to $9.85 \ \mu mol/g$ for divalent cations and 19.7 $\mu mol/g$ for monovalent cations. The zpc of kaolinite occurs at pH 2.6 and CEC values for kaolinite between pH 2.6 and pH 7 can be approximated. The pH 6 CEC of kaolinite is about 7.6 $\mu mol/g$ for divalent cations and about 15.2 $\mu mol/g$ for monovalent cations.

The CEC of the Flat D kaolinite seems to indicate the order of magnitude of metal uptake without providing a precise estimate of metal uptake. At pH 6 and for an initial Pb concentration of 2.41 mmol/l, 84% of the Pb is present as Pb^{2+} and 11.7 μ mol/g of Pb is adsorbed, or more than is predicted by the CEC. As it was already determined that Pb adsorption is not well correlated with pH, and as the CEC of kaolinite is pH dependent, the adsorbed Pb could well correspond to the CEC of the kaolinite at a higher pH. At pH 6 and for an initial Cd concentration of 22.2 mmol/l, 81% of soluble Cd species is present as CdCl⁺. Even if it is conservatively assumed that only monovalent adsorption occurs, then the maximum Cd uptake predicted by the CEC is 15.2 µmol/g, while the actual Cd uptake 21.4 µmol/g, or at least 41% greater than indicated by the CEC.

The maximum surface coverage due to the adsorption of Pb and Cd can be estimated. The approximate hydrated ionic radii of Cd^{2+} and $CdCl^+$ are 5.0 and 4.0 Å, respectively (Dean, 1985). Assuming (conservatively) that only Cd^{2+} is adsorbed, Cd uptake of 21.4 µmol/g will result in a surface coverage of 10.1 m^2/g . This is the worst-case scenario as the hydrated

radius of Pb^{2+} is 4.5 Å (Dean, 1985). As the SSA of the Flat D kaolinite may be between 7 and 20.4 m²/g, it seems very possible that monolayer surface coverage is occurring, although this cannot be stated with complete certainty.

In conclusion, the pure kaolinite used in this study has a relatively large particle size and a relatively small total surface charge. It was observed that more Pb^{2+} and Cd²⁺ ions are adsorbed by the kaolinite at low initial metal concentrations, the adsorption of PbCl⁺ and CdCl⁺ becomes increasingly important at higher metal concentrations as the abundance of these species increases, and the most important retention mechanism is cation exchange. From pH 4 to pH 6, the selectivity for kaolinite appears to be $Pb^{2+} > H^+ > Cd^{2+}$. For the pH 6 curves and at the higher initial metal concentrations, total Cd uptake becomes almost equal with the total Pb uptake and this will be at least partly because CdCl⁺ forms at a lower salt concentration than PbCl⁺ does. At higher initial metal concentrations, more metal is retained by the kaolinite, rendering the metal less mobile and less available to organisms found in soils and sediments. The formation of different metal species at higher metal concentrations may be another mechanism by which mobility and availability to organisms of metals may be potentially reduced. In this study, the CEC provides an estimate of the surface adsorption of Pb and Cd by kaolinite, but is not a precise indicator.

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