EFFECT ON pH OF HEAVY METALS RETENTION BY KAOLINITE

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EFFECT ON pH OF HEAVY METALS RETENTION BY KAOLINITE

By

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“If we knew what we were doing, we wouldn't call it research”
Albert Einstein

“At the end, everything is unpredictable”
Ian Malcolm

Abstract

Heavy metals are naturally present in soils but in high concentrations they can be hazardous to the environment and human health. To understand the adsorption of the metals, Batch tests were conducted to measure the adsorption of 1, 2 and 3 mM/L concentrations of cadmium, lead and zinc onto kaolinite over periods of 0.1, 1, 2, 4, 8, 12 and 24 hours and to measure the change in hydrogen ion concentration. The kaolinite was found to contain iron oxides which increased the point of zero charge of the kaolinite to pH 4.7 and the pH 7 CEC to 17.8 meq/100 g. The clay retained a maximum of 10 μM/g of lead, 8.4 μM/g of zinc and 6.0 μM/g of cadmium. Similar adsorption behaviours were found for Pb and Zn, while Cd shows a different trend. The pH of the solution highly influences the adsorption of Cd but it has little effect in the adsorption of the other two metals. Among the three metals Pb was present the slowest adsorption at 0.1 hrs. From the kaolinite reactive spaces, the aluminium hydroxyl, silicon oxide and iron oxide sites are probably involved in the release or retention of hydrogen ions. The ratio of hydrogen ions released to metal adsorbed is presented and the trend for each metal is examined with their respective equations. In addition, the desorption for the 1 mM/L concentrations of the three metals is examined. Adsorption isotherms are used to help analyze the adsorption data.

Acknowledgments

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List of Symbols

°C	degree Celsius
mmol	millimoles
µm	micromoles
g	gram
H^+	hydrogen ion
kg	kilogram
L	litre
Me^{2+}	divalent metal cation
meq	milliequivalent
N	normal
OH^-	hydroxyl ion
pH	$-\log[H^+]$
≈	almost equal
=	equals
[ ]	concentration of

List of Abbreviations

A.A.	atomic adsorption
CEC	cation exchange capacity
Cd	cadmium
Cu	copper
EDTA	Ethylene Diamine Tetra Acetate
EGME	ethylene glycol monoethyl ether
Fe	iron
La	lanthanum
Ni	nickel
Pb	lead
ppm	parts per million
pH_{pzc}	pH of point of zero charge
PZC	point of zero charge
SSA	specific surface area
Zn	zinc

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Chapter 1

Introduction

1.1 The Problem

Human beings are part of the whole environment and need to live in harmony with it. Unfortunately, with the development and industrialization of human society, that equilibrium is being disrupted, leading to the contamination and devastation of the natural resources of the earth. Heavy metals are not unfamiliar in soils since most of them are present in very low concentrations (Leeper 1978). However, elevated levels in the soils have been a concern due to the risk that these elements present to human health and agriculture.

Sources of heavy metals in soils are a result of industrial, municipal and mine waste disposals. In addition, there are other activities, such as oil spills and deposition of combustion and agricultural products that increase the metal concentration in the ground (Roberts et al. 1999, Arnfalk et al. 1996). Nevertheless, the increase of heavy metal concentration in soil yields concerns about their mobilization through the soil column and the eventual pollution of groundwater and the effect that they could have on crops (Yong 2001, Evans 1989, Arnfalk et al. 1996, Leeper 1978).

High concentrations of heavy metals are known to be potentially hazardous to human health and some of these metals do not participate in any biological activity. Therefore, it is important to determine the amount of metal that will be retained in the soil column and the amount that will be available to the food chain and humans. For this purpose, it is important to understand the adsorption mechanism, the variables that affect this process and the major transport mechanisms. (Sheidegger and Sparks 1996, Singh et al. 1998, Yong and Phadungchewit 1993, Eick and Fendorf 1998).

1.2 Background

There are several studies that report the effect of the pH on the retention of heavy metals (i.e. Farrah and Pickering 1976, Arnfalk et al. 1996, Hatton and Pickering 1980). However, most of the studies have focused their attention on how the pH level affects the adsorption of the metals at equilibrium and there is less information about metal uptake over time and the effect that the adsorption has on the pH. This information could help explain the types of interactions between clay and metal ions in solution.

The three metals that will be investigated in this research are lead (Pb), cadmium (Cd) and zinc (Zn). There are several types of clay but the clay for this study will be kaolinite, which is a mineral composed primarily of aluminium hydroxides and silicon oxides and having a chemical formula of $(OH)_8Si_4Al_4O_{10}$ (Grim 1962) and magnified particles of kaolinite often appear as hexagonal "plate like" shapes. This clay is a pH-dependant mineral and its surface charge could be affected by the change in solution pH as a result of metal adsorption. In the thesis, the term clay is used to describe all clays in general and the term kaolinite is used when only the specific clay kaolinite is being referred to.

Various authors (Evans 1989, Farrah and Pickering 1978, Yong and Phaudungchewit 1993) have established that the adsorption of heavy metals induces the deprotonization of the clay. This reaction will release hydrogen (H^+) ions to the solution, resulting in a change in the pH value of the soil solution; this phenomenon has not been studied extensively. This focus will add a new perspective in the study of heavy metal retention and it may add new information that could be useful to explain the adsorption of metals onto the soil.

The reactivity of the kaolinite is enhanced at high pH values due to the protonization of its surface. The reaction creates new reactive spaces where the cations can be held (Evans

1989, Farrah and Pickering 1978). However, this pH dependency is limited to the edge sites of the kaolinite structure and they are the main sites that contribute to the cation exchange capacity (CEC).

Depending upon the pH, the metal will present a stable species that will interact with the kaolinite and will release a certain amount of H^+ ions from the hydroxyl groups, resulting in the deprotonization of the kaolinite. The metals can be separated from the solution by adsorption, complexation or co-precipitation (Yong et al. 1992, Greenland and Hayes 1981, McBride 1994). The role of the pH in these processes is important because it could enhance or inhibit the different mechanisms as a result of the interaction in the soil-water interphase and the interaction between ions and compounds.

Even when some metals are essential to life, such as Zn, most of them are not part of the reactions that take place inside the organism of any living thing. Examples of these metals are Pb and Cd (Coles 1998). In the presence of kaolinite, both Pb and Cd increase their adsorption with the increment of the pH levels, but Cd is more easily desorbed while Pb tends to remain in the clay (Puls et al. 1991).

In the same solution, kaolinite has more affinity for Pb than for Cd, which is related also to the reversibility of the adsorption (Farrah and Pickering 1978). Due to the lack of organic matter, which enhances the adsorption of the metals, the cations will only have the opportunity to react with the kaolinite edges or with the aluminium hydroxide or silicon oxide groups leading to the deprotonization of the kaolinite. Although Zn is a vital metal for humans, animals and higher plants, the use of pesticides and herbicides has increased its concentration in the soil disrupting the equilibrium in the ecosystem (Kiekens 1990).

1.3 The Objective

Supported in the research by Coles (1998), the following research will try to establish the relationship between pH and adsorption, but unlike most of the studies, the dependent variable will be the pH of the solution rather than the concentration of metal adsorbed. In addition, this study will also provide information about the kinetics of the reactions, the adsorption reactions will be proposed for Zn, Cd and Pb and desorption data at variable times will be presented for each metal.

Due to the pH-dependency of the clay, this deprotonization should alter the adsorption conditions by lowering the pH of the solution. This reduces the negative charge on the clay surface and decreases the adsorption capacity.

The extent of change in the pH of the solution may be related to the amount of metal adsorption and therefore, both the solution concentration of metal and the solution pH will be measured to confirm this hypothesis. Also, the concentration of metals at different times of exposure will be measured to determine the kinetics of the metal retention and the movement of H^+ ions between the solid and liquid phases. An increase or decrease in the pH level means that the clay is being influenced by the metal adsorption.

The amount of hydrogen (H^+) ions released by kaolinite is enough to reflect a change in the pH of the solution. The combination of the information gathered in this study, with the information that already exists about the effect of the pH should give a better understanding of the heavy metal adsorption.

Therefore, three objectives of the research are to provide a broader explanation of the specific reactions that occur at the interphase, to study the kinetics of those reactions and to examine the effect that these reactions have on the pH of the solution. This would be accomplished through laboratory work and the findings may help to direct future studies on the adsorption and desorption of heavy metals.

The methodology used is very similar to the one used in other experiments. Hence, the results could be compared with the work of other authors. The only difference in the methodology is the concentration of heavy metals will be measured at different exposure times, not only at equilibrium. This will help to establish the kinetics of the reaction and the trend of the effect on the pH as a consequence of metal retention.

1.4 General Outline

The thesis is organized into 5 chapters. The first chapter is the introduction of the topic and a general overview of the research. The second chapter provides a summary of previous work in the area and some information linked with the research. The materials and methods are presented in chapter three. Chapter four reports and discusses the results of the characterization and batch tests. The last chapter presents the conclusions and recommendations for future research.

Raw data and other pertinent information can be found in the appendix of the thesis.

Chapter 2

Theoretical Background

2.1 Clay Characterization

Kaolinite is a 1:1 layer mineral composed of aluminium octahedral sheets stacked above silica tetrahedral sheets and this has a very stable structure formed by advanced weathering processes (Bear 1965, Van Olphen 1977). One silica tetrahedral sheet and a single alumina octahedral sheet form a common layer and these layers are repeating (Grim 1962). The silicon and the aluminium sheets share the oxygens of the silicon oxides. The hydroxyl groups are not shared but they separate the aluminums in the octahedral sheet.

The arrangement provides a solid structure to the mineral with hydrogen bonding between the aluminium hydroxide and the silicon oxides sheets between layers to form a crystal. The two exposed layers (O^{2+}, OH^-) may interact with different components in the soil (Grim 1962). A simplified model for the kaolinite crystal is shown in Figure 2.1.

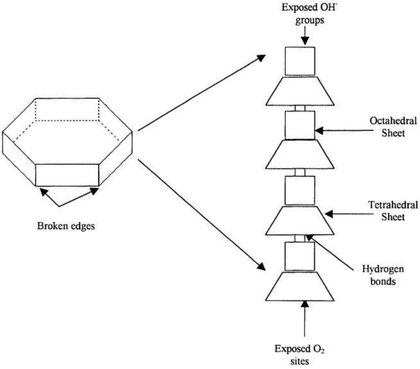

Figure 2.1 Simplified model for kaolinite crystal (Modified from Ma and Eggleton 1999).

Kaolinite particles are not easily broken down as a result of its well-packed structure. Also, this molecule does not allow water to enter between separate layers and there is no expansion in the presence of water. Soil reactivity can be quantified by determining the cation exchange capacity (CEC) of the soil. McBride (1994) defines CEC as "the quantity of cations reversibly adsorbed per unit weight of mineral and the capacity depends on the stability of the cation in the specific surface environment involved and the characteristics of the soil."

The conventional units for this property are millimoles per kilogram (mmol/kg) according to the international system of units. This property, with adsorption, plays an important role in the interaction of plants with nutrients but also with contaminants (Tan 1982).

As a result of the stability of the molecule, the isomorphous substitution, or interchange of elements of different valence within the clay lattice, is limited or non-existent (Mitchell 1993). This characteristic gives a CEC for kaolinite between the range of 3 to 15 meq/100 gm as is shown in Table 2.1. The chemical formula of this compound is the following: $(OH)_8Si_4Al_4O_{10}$ (Mitchell 1993). Figure 2.2 shows a diagrammatic sketch of the structure of kaolinite.

Table 2.1 CEC values of kaolinite reported by different authors

	pH	CEC meq/100 g
Coles (1998)	7	1.97
Ziper et al. (1988)	5	14.6
Yong and Phadungchewit (1993)	7	16
Potter and Yong (1999)	6.3 - 7	5

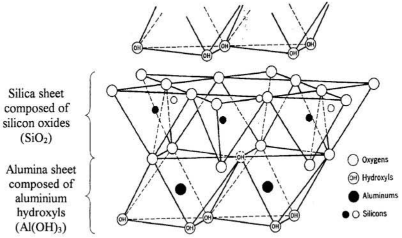

Figure 2.2 Structure of Kaolinite (©Applied Clay Mineralogy, Grim R.E. ,McGraw Hill, NY 1962 pp 11)

Mitchell (1993) proposes the following sources of CEC for the kaolinite:

- Isomorphic substitution in the silica sheet of the Si^{4+} ions by Al^{3+} ions.
- Removal of H^+ ions in hydroxyl groups.
- Unsatisfied charges at the broken edges of the kaolinite crystals.

Kaolinite is the least reactive of the clays (Suraj et al. 1998). Nevertheless, the high pH-dependency of the soil enhances or inhibits the adsorption of metals according to the pH of the environment. At low pH the surface charge will be positive therefore repelling the cations in solution and at high pH, the negative surface charge attracts the cations to the clay. The broken bonds in the structure of kaolinite are a source of CEC because they participate in the adsorption and desorption of H^+ ions as the pH changes (Mitchell 1993).

As a consequence of its well-packed structure there is no separation between the layers of the kaolinite. Hence, all the activity occurs along the surface or on the edge of the structure. The surface charge at the edges is caused by the release or adsorption of H^+ ions. Sparks (1995) suggests three sites where the adsorption could occur: on the flat oxygen-exposed surfaces of the silicon oxides, the exposed hydroxyl (OH^-) plane of the alumina sheets, and at the particle edges of the sheets. Bohn et al. (1979) identify the same sites as the ones that could participate in the adsorption.

Alumina and silica groups react under different conditions. The aluminium groups will react at low pH and the silica sheet will tend to react only at high pH levels (Bohn et al. 1979). The edges sites of kaolinite are known to be a source of variable charge, because of the unsatisfied charges present in the hydroxyl groups as a result of broken bonds. Sparks et al. (1995) suggest that the aluminium hydroxide planar sites may also be sites of variable charge. By comparison, they suggest that the silicon oxides sites are a source of "permanent" charge.

The charge of the soil is important in determining the interactions between the soil and the contaminants, and one of the properties widely used as the reference for the charge property behaviour is the point of zero charge (PZC) (Gallez et al. 1977). The PZC, also know as the isoelectric point, is the pH value where there is a transition in the clay charge from positive to negative as the pH increases. The PZC can also be the point where the total negative and positive charges balance so there is a net zero charge. This property influences the kind of soil interaction that will occur (Sposito 1984; McBride 1994) and is influenced by types of materials present in the soil. If the PZC for a pH dependent clay is known and the pH of the soil solution is known, then the surface charge can be inferred. From this information, the concentration of anions or cations attached to the clay will be known and it can be linked with the capacity to absorb contaminants (Bohn et al. 1979). The selectivity order of kaolinite is Pb>Cd>Zn according to Yong and Phadungchewit (1993).

One of the common methods for determining the PZC of kaolinite is the titration method. Tschapek et al. (1974) recommend this method because it is independent of the electrolyte concentration. Table 2.2 reports different PZC values for kaolinite and in most cases the titration method as described by Van Raij and Peech (1972) was used.

Table 2.2 PZC values of Kaolinite reported by different authors

	PZC meq/100 g
Potter and Yong (1999)	3.7
Spark et al. (1995)	4.5
Schroth and Sposito (1997)	4.0 – 7.5
Coles (1998)	2.6

The molecular composition of kaolinite suggests that the silicon oxide and aluminium hydroxides sites are the ones responsible for the PZC. As such, the titration curves for kaolinite usually present two zones of pH-dependent negative charge, the first one due to the dissociation of Al^{3+}, between pH levels of 2.8 and 7 and the second zone related to the Si sites above pH 8 (Gallez et al. 1976, Tschapek et al. 1974). However, as the experiments in this study are conducted below pH 8, only the first curve is observed.

Factors that can influence the PZC are the presence of organic matter, broken edges in the kaolinite crystal or the presence of metal oxides. In the case of kaolinite, which is a highly weathered clay, the presence of Fe oxides changes the surface charge leading to a higher PZC (Tschapek et al. 1974, Gallez et al. 1976, Van Raij and Peech 1972). It is also known that Fe oxides may coat kaolinite (Parfitt 1980). Another variable that affects the determination of the PZC is the equilibrium time used in the experiment to obtain the titration curve (Schroth and Sposito 1997).

Along with the PZC, another important characteristic of the soil is the specific surface area (SSA). The SSA of a soil sample is "the combined surface area of all the particles in the sample, as determined by some experimental technique, and expressed per unit mass of sample" (Sposito 1984). The SI units of SSA are square meter per kilogram. The numerical value of the property may vary depending on the method used. Therefore, the SSA will be a function of the method and is not an absolute value (Sposito 1984) as it was found by Gallez et al. (1974) that the surface area measured by the ethylene glycol monoethyl ether (EGME) method was greater than the SSA obtained by BET-N_2 for some selected soils.

The surface area of the clay is an approximation of the available reactive places, including the internal places between the clay layers. A lower SSA will be the result of an advanced weathering process and a higher SSA usually indicates less weathering of the clay. The principle behind the EGME method is to saturate the soil with a polar substance which will be attached to the clay and then eliminate the excess of the substance until there is a mono-layer of EGME covering the mineral (Bohn et al. 1979). Table 2.3 shows some determined values for the SSA of kaolinite obtained by different methods.

Table 2.3 SSA values of kaolinite reported by various authors

	EGME method m^2/g		BET-N_2 method m^2/g
Coles (1998)	20.4	Dry Branch Kaolin Company	7 – 21
Carter et al. (1965)	13.8	Zipet et al. (1988)	15.2
Yong and Phadungchewit (1993)	12.0	Puls et al. (1991)	25.0

The ability of the soil to interact, hold cations or react with other species to gather nutrients is an important property that will determine the quality of the soil (Bear 1965).

2.1.1 Iron Oxides

Fe is the main impurity in natural kaolinite (Balan et al. 1999). The most common Fe oxides in soils are hematite (Fe_2O_3) and goethite (FeOOH) (Bohn et al. 1979) with goethite being the most regular as a result of it greater thermodynamic stability (Schewertmann and Taylor 1977).

The reactions between the Fe oxides and compounds of the soil solution take place in the interphase. The Fe ions tend to hydrolyse forming hydroxyl compounds in the external surface as is shown in Figure 2.3. The presence of these hydroxyl groups will make the surface charge of the Fe oxides dependent of the pH of the solution. The PZC of Fe oxides is within the pH range of 7.6-8.9 and the SSA is 14-77 m^2/g (Schewertmann and Taylor 1977).

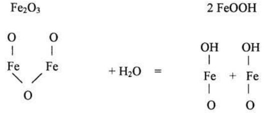

Figure 2.3 Hydrolysis of Fe oxides (Schewetmann and Taylor 1977)

Fe oxides have a CEC of 6-60 meq/100 gr. Depending on the conditions of the soil the adsorption could be cation exchange or specific adsorption. Specific adsorption involves the penetration of the ions onto the clay structure. In the case of kaolinite, cation exchange will be the dominant mechanism. The affinity of goethite for different metals is Cu>Zn>Co>Pb>Mn (Schewertmann and Taylor 1977).

2.1.2 Surface Charge

Charge development in soils occurs as a result of both isomorphic substitution and ionization of functional groups on the surface of solids that make up the soil matrix. These two mechanisms give rise to the permanent and pH dependent charge of soils (Bohn et al. 1979). In the case of kaolinite, the permanent charge is almost zero (Mitchell 1993) therefore, most of the charge is the result of the protonization of the edges as a result of the pH of the environment. This behaviour is known as pH-dependency of the clay. The pH-dependent charge is the result of the change in pH level in the soil solution and this charge is related to the gain or loss of H^+ from the functional groups of the mineral (Bohn et al. 1979, Zhou and Gunter 1992).

On the other hand if there is a small permanent charge in the soil, it is a result of isomorphic substitution. The isomorphic substitution will occur when there is the interchange of cations in the mineral structure and those cations are not equal in their valance, i.e. Mg^{2+} for Al^{3+} or Al^{3+} for Si^{4+} and O^{2-} for OH^-. These substitutions create an imbalance of charge in the molecule and negative charge development is more common in soil minerals (Bohn et al. 1979).

The buffering capacity of the soil is directly related to the CEC (Huang et al. 1995, Tan 2000) and is defined as the amount of acid or base that can be added to a system without changing the pH of the solution (Yong 2001). McBride (1994) reports the following as possible reactions that release acidity in the soil surface:

$$>\text{Fe-OH}_2]^{+1/2} = >\text{Fe-OH}]^{-1/2} + H^+$$

$$>\text{Al-OH}_2]^{+1/2} = >\text{Al-OH}]^{-1/2} + H^+$$

The first reaction will apply to the Fe oxides presented in the soil where the hydroxyl groups associated with Fe release H^+ ions. The second reaction will apply to kaolinite where aluminium sites react to release or adsorb H^+ ions. Kaolinite possesses little buffering capacity therefore, there may be a more noticeable change in pH of the solutions resulting in the release of metals adsorbed in the clay (Coles 1998). The same could be concluded for Fe oxides, as the surface charge of these compounds is pH-dependent.

As a summary of the characteristics of the kaolinite, this clay will have little if any permanent surface charge, but it could exist if there is any isomorphic substitution in the molecule. The main constituents of the clay are aluminium and silicon oxides, which are responsible for the different charge properties of the molecule (PZC, CEC). As a highly weathered soil, these values are relatively small (especially CEC) and the buffering capacity is low. The SSA is smaller than the rest of the clays because its well-packed structure does not allow internal reactive spaces. Impurities such as Fe oxides will affect these properties, as well as provide new reactive places during adsorption of ions.

2.2 Adsorption Mechanisms

The adsorption process represents one of the most relevant processes in the soil because the retention of nutrients, metals or other organic compounds depends on the interaction between the soil and the adsorbate. Sorption, in general, is the interchange of certain elements or species from one phase to another via the interphase (Yong et al. 1992, Greenland and Hayes 1981). Scheidegger and Sparks (1996) define adsorption as "the accumulation of a substance in the interphase between the solid surface and the bathing solution".

According to the characteristics of the sorption process, it can be a physical adsorption or chemical adsorption. When there is not enough information to establish what kind of process is taking place, it can be generalized by the term sorption (Greenland and Hayes 1981, Yong et al. 1992). The adsorption process is considered to be a two-dimensional process that does not include precipitation, co-precipitation or diffusion, as these are three-dimensional processes (Scheidegger and Sparks 1996). According to the interaction between interfaces, the strength of the bond could be a very weak force such as Van der

Waals forces or slightly stronger forces such as ion exchange interactions. In general the types of soil-contaminant interactions are (Yong 2001):

- **Chemical interactions, which include:**

  Ionic: attraction between the atoms as a result of different charges

  Covalent: the outside electrons are shared by two nuclei

- **Physical interactions, which include:**

  Coulombic or electrostatic: ion-ion interaction

  Van der Waals: dipole-dipole attraction as a consequence of the closeness of the molecules

  Steric: adsorption is limited by the size of the hydrated radii

The chemical interactions are not relevant in this research because the physical interactions are the dominant forces in the adsorption of metals in kaolinite (Sparks 1989) and Fe oxides (Parfitt 1980).

Physical adsorption is a process that does not require energy to take place and has its basis in the attraction of charges of different signs. Therefore, electrostatic forces rule the binding. This process depends on the diffusion of ions in the media because it requires the presence of both anions and cations in the interlayer. A smaller hydrated radii will allow the cation to attach to the surface strongly, so more molecules will be found with this characteristic in the interlayer (Greenland and Hayes 1981, Yong et al. 1992).

A consequence of physical adsorption is the exchange of cations in upper levels of the soil. Because this is not a process that requires energy, the cations held to the surface will be the ones with better spherical and charge conditions. Figure 2.4 shows an example of this phenomenon. The electrostatic forces (Coulomb's law) will attract the Pb ion to the soil and because Pb has a smaller hydrated radius, and therefore does not have the spherical impediments of the sodium (Na), there will be a switch of the ions at the interlayer without changing the charge (Yong et al. 1992).

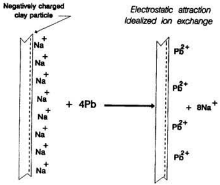

Figure 2.4 Example of physical adsorption (Reprinted with Permission © Principles of Contaminants Transport in Soils, Yong et al., Elsevier, NY, 1992 pp 150)

The adsorption is highly influenced by the pH of the solution (Puls and Bohn 1988, Farrah and Pickering 1977) and the sorption of contaminants onto the clay surfaces is likely to reduce their mobility in the soil column (Holm and Zhu 1994).

As stated before, the adsorption will depend on the interactions between the two phases therefore it will depend on the characteristics of the compounds in solution and the clay. In the case of the cations, the valence and the ionic radius will be factors that affect the retention (Puls and Bohn 1988). As for the clay, the weathering process and the functional groups will have a major impact on the retention of the metals.

Two variables that affect physical adsorption are the concentration of cations and their associated electronegativity. Assuming that there is a complete mix in the sample, Fick's law (mass transfer by diffusion, equation 2-1) will have little effect in the adsorption of the metals, as there will be no gradient in the solution concentration. The effects of the concentration will be as a result of larger amount of elements present in the solution. On the other hand, the soil will have a surface charge develop as a consequence of the pH of the soil solution. This charge will attract ions to the surface (ruled by the Coulomb's law, equation 2-2) according to the electronegativity of the elements. A compound with higher electronegativity will have a greater attraction to the clay mineral.

$$J_A = D_{AB} \frac{\partial C_A}{\partial x} \qquad \text{eqn 2-1}$$

Where J_A is the flux of the compound, D_{AB} is the diffusion coefficient, C_A is the concentration gradient and x is the distance.

$$F = K\frac{q_a q_b}{r^2} \qquad \text{eqn 2-2}$$

Where F is the force between particles, q_a and q_b are the charges of particles a and b, r is the separation between particles and K is the coulomb's constant.

According to Sparks (1989) the mass transfer phenomena and not the charge difference controls the adsorption in the interphase between liquid and solid. Sparks (1989) explains the behaviour with the Fickian and Nernst-Planck diffusion equation relating the particle size and the charge of the ions.

Adsorption isotherms are a common way to report the results of adsorption into clay (Salim et al. 1996). Langmuir and Freundlich equations are generally used to report these values, especially while using kaolinite as it has been reported that it follows those equations. The Langmuir isotherm is one of the simplest isotherms and assumes that adsorption depends on the empty spaces available for adsorption and the concentration of adsorbate (Laidler and Messier 1997). Yen (1999) describes the adsorption isotherm by stating that "the equilibrium between a surface and a solution ...[is similar to] a reversible chemical equilibrium between species." The Langmuir equation is:

$$\frac{C}{q} = \frac{1}{k_b q_m} + \frac{C}{q_m} \qquad \text{eqn. 2-3}$$

In this equation k_b is a constant related to enthalpy of adsorption, q is the moles of adsorbate adsorbed per mass of adsorbent at equilibrium, q_m is the maximum number of moles adsorbed per mass of adsorbent and C is the concentration of the adsorbate. Some of the assumptions that Langmuir made were; there is only a monolayer of adsorbate, the energy necessary for adsorption is independent of the available sites, and the bonding could be reversible (Yen 1999).

Unlike the Langmuir isotherm, the Freundlich equation assumes that the availability of sites with free energy for adsorption decreases exponentially with the increase in adsorption. The Freundlich equation is:

$$q = k_f C^{\frac{1}{n}} \qquad \text{eqn. 2-4}$$

Here q is the moles of adsorbate adsorbed per mass of adsorbent at equilibrium, C is the concentration of adsorbate and k_f and n are empirical constants. Usually the value of n is above one and saturation is not considered in the equation as the amount adsorbed increases with the concentration of adsorbate.

The desorption mechanism is as important as the adsorption mechanism, especially when dealing with soils that are already contaminated (Scheidegger and Sparks 1996). Usually, not all the metal that is adsorbed in the clay is desorbed as some reactions appear to be irreversible and this means that the adsorption and desorption isotherms should not be similar in most of the cases.

From the environmental point of view, desorption is important as it indicates the mobility of the contaminant through the soil column. A metal with weak bonds with the clay will tend to be released and migrate to contaminate groundwater. On the other hand, a strong attachment to the clay indicates the desorption process will be slow and unlikely and making the pollution of groundwater a non-issue.

2.3 Metals

Heavy metals are those compounds that have an atomic density higher than 6 g/cm^3 (Alloway 1990a). This classification includes several elements that are biologically essential, like Zn. "Trace metals" are those compounds that have a background concentration of less than 1 ppm. Many are biologically essential and all are a threat to the environment if they occur in high concentrations. Generally, high concentrations of these compounds are a consequence of anthropogenic inputs (Yong 2001). One characteristic of the trace metals is that they possess different oxidation states (Chang 1984). Therefore, the pH and the redox potential are important to establish the stable species. Nevertheless, most of the metals will have a more stable oxidation state that they will tend to have in the environment (Yong 2001). Of special concern with trace metals is their mobility through the soil column. The interest will not be only in how the metals are binding in the soil structure, but also in how these metals interact with the soil, and their possible release with time (Yong 2001).

2.3.1 Cadmium

Cd has no essential biological activity and it is highly toxic to animals and plants (Alloway 1990b). The EPA has established that Cd is hazardous at concentrations of 5 μg/l or more (Toxnet 2002). Cd is also a known carcinogenic substance and high concentrations of this element in the kidneys may cause dysfunction. The input of Cd into the soil increased with the development of the mining of Cd in the early 20th century. Besides mining other activities that increase the concentration of Cd in the environment are the use of phosphatic fertilisers and the deposition of aerosol particles from polluted air (Alloway 1990b).

Cd and Zn are two metals that are closely associated in their chemical properties. Both metals have similar ionic structures and electronegative properties. Cd is usually obtained as a by-product of the melting of sulphide minerals. The most common species found in soils are Cd^{2+}, $CdSO_4$, and $CdCl^+$ in acid soils, and Cd^{2+}, $CdCl^+$, $CdSO_4$ and $CdHCO_3^+$ in alkaline soils (Alloway 1990b). Of these species the one most likely to be adsorbed by the soil is Cd^{2+}.

The adsorption or desorption of Cd will be highly dependent on the pH of the environment and this makes it more mobile than other metals such as Pb and Zn.

2.3.2 Lead

Metals are natural components in soils but anthropogenic activities increase the concentration of Pb in soils. Unlike Cd, this metal was one of the first handled by human beings. Its contamination of soil and groundwater reservoirs is associated with mining activities and leaching in landfills (Yong 2001). The presence of Pb in plants is usually related to the deposition of the compound by air and not by uptake from soil (Leeper 1978). EPA hazardous concentration for Pb is 15 mg/l (Toxnet 2002).

Compared with the other metals, Pb has a longer residence time in the environment and tends to accumulate in soils and sediments. Also, its low rate of microbial degradation and high solubility can make it available through the food chain. Pb tends to accumulate in the soil naturally, although its mobilization is small as a consequence of the formation of stable or insoluble species. Pb will be displaced from the soil at pH between 2.5-3.0. Studies have shown that properties such as CEC, soil organic matter and soil pH are more important in the immobilization of Pb than the precipitation by carbonates and the adsorption by hydroxyl sites (Davies 1990).

Pb is more toxic to bacteria present in soils than Zn or Cd. In general, the soils polluted with Pb remain polluted due to its low mobility in soils. Although its bioavailability is low there is still a concern about the concentration of Pb in the soil as its presence in some cases possesses a risk to human health and the environment (Davies 1990).

2.3.3 Zinc

Zn is one of the metals with the highest concentration in domestic and industrial sludges. It is commonly used as a fertilizer and the plants adsorb the metal from the soil by complex adsorption of the metal with organic molecules that are thermodynamically more stable than the hydrated metal cation (Maes and Cremers 1979, Yong 2001). At around 1000 ppm, Zn is considered dangerous to humans (Leeper 1978).

Unlike Pb and Cd, Zn is an essential metal for humans, animals and plants but in high concentrations it is considered to be one of the trace metals most hazardous to the environment (Kiekens 1990) because the contamination with this metal can affect crops by retarding their growth and can affect soil and its fertility by enhancing the production of free radicals that favour oxidation (Prasad et al. 1997). The Zn species that is commonly adsorbed by plants is Zn^{2+} especially at pH levels below 7.7 while $ZnOH^-$ is more dominant above that pH.

The main sources of anthropogenic Zn are mining, agricultural activities, the use of composted materials, and also the use of fertilizers and pesticides in the soil. The acceptable use of Zn in agriculture is around 30 kg/ha over a period of 10 years (Kiekens 1990).

2.4 pH Role in Adsorption

As a result of acid rain, the pH of the soil may become more acidic (Yong and Phadungchewit 1993). This change in the soil pH affects the adsorption of contaminants, usually enhancing the mobility of the pollutants. The role of pH in the adsorption of heavy metals has been observed by several authors (i.e. Reid and McDuffie 1981, Yong and Phadungchewit 1993, Puls et al. 1991, Hatton and Pickering 1980, Farrah and Pickering 1979). In general, an increase in pH of the soil solution will lead to an increase in metal uptake.

In a pH dependent soil such as kaolinite, the change in pH will affect the surface charge. This leads to the creation of more negative sites at the edge of the molecule with an increase in the pH of the solution. This increase in negative sites, together with the decrease of competition of H^+ ions for empty negative spaces, has been identified as the main reason for the increase in the metal adsorption.

Metal speciation will also be affected by the pH. At low pH, the hydrated form of a divalent metal (M^{2+}) will be the most stable metal species and it will be released from the clay, enhancing the migration of the metal through the soil column (Reid and McDuffie 1981). Also, at low pH levels some secondary processes such as flocculation, can occur in the soil as a result of the dissolution of aluminium hydroxides that may later re-precipitate as a result of movement with the soil solution (Farrah and Pickering 1979). At high pH levels, these metals will form complexes with OH^- or CO_3^{2+}, leading to the precipitation of the metal in the soil water system and its further immobilization (Reid and McDuffie 1981).

Farrah and Pickering (1978) found that a pH level close to neutral (between 6 and 8) is ideal for the adsorption of the metals used in this study. At low pH, there will be a competition between H^+ ions and metal ions for negatively charged sites and at high pH the co-precipitation or complexation of the metals may occur.

The buffer capacity of the soil will be important to establish the effect of the pH in the soil and it will depend on the equilibrium between the H^+ ions on the clay and the ones in the solution. Studies have shown that a soil with a tolerance for change of the solution pH will retain more metals than the clays with low buffering capacity (Yong and Phadungchewit 1993). Kaolinite possesses little buffer capacity as it is considered a pH dependent soil. Hence, its capacity of retention will be limited to the negative charges created by the soil solution pH.

Iron oxides are the main impurity in kaolinites (Balan et al. 1999). Their presence affects the surface charge properties of the soils and increases properties such as SSA, CEC and PZC (Parfitt 1980). In addition, Fe oxides are pH dependent structures as shown in Figure 2.3. Therefore the buffering capacity of the kaolinite/Fe oxides structure will remain low, as it is not expected to change because both materials are pH dependable.

In summary, the main effects of pH on the adsorption behaviour will be the creation of negative charges on the surface of the kaolinite and probably precipitation of the metal in the solution at high pH. On the other hand at low pH, the effects could include the competition of H^+ ions for negative sites in the clay and the dissolution of the metal in the soil-water system. This information is summarize on Table 2.4

Table 2.4 Summary of the effect of pH on metal uptake.

pH	**Effect in uptake**
Acid (<6)	The uptake is limited due to the competition of H^+ ions for negative sites on the clay and there are less negative sites created on pH dependent clays
Neutral (6-8)	Optimal pH for metal uptake, there is little competition of H^+ ions and there is no precipitation of the metal
Basic (>8)	The uptake is enhanced by the creation of negative sites on the clay and there is less competition of H^+ ions for these sites, however, precipitation could occur

Chapter 3

Materials and Methods

3.1 Materials

The materials used for this research were kaolinite and the chloride salts of the metals Zn, Pb and Cd. A Varian spectra 50/55 spectrometer was used to determine the concentration of metal in solution. The description of the solution and the clay is presented next.

3.1.1 Kaolinite

The kaolinite used in the research is Hydrite flat D kaolinite from the Dry Branch Kaolin Company. The median particle size reported by the company is around 5.0 μm with less than 30% of the particles having a diameter of 3 μm. The particle size of this kaolinite is similar to the particle distribution in natural soils. Also, the physical size characteristics of Hydrite flat D kaolinite are similar to the ones of natural sediments (Coles 1998). The principal differences between this type of kaolinite and the others handled by the same company is its low SSA. Although the material was purchased from the same company, some of the characterization tests yielded different results from those gathered by Coles (1998).

3.1.2 Metals

The metals used in the research are $PbCl_2$, $CdCl_2$ and $ZnCl_2$. Soluble forms of these metals were prepared to expose them to the clay. The natural pH of the solution was maintained to observe the pH change during the adsorption process. However, the speciation diagrams in the literature for of each of these metals also show that the precipitation is minimal at the natural pH of the solutions (Stumm and Morgan 1981).

3.2 Characterization Tests for Kaolinite

There are four main characterization tests performed for the kaolinite: CEC, PZC, SSA and acid digestion. Unless it is indicated otherwise, the experiments were conducted at room temperature (21 °C), duplicated at least once, and following the methods described in this section.

3.2.1 Cation Exchange Capacity

For CEC, there are two methods used in the study, one with variable pH and one at constant pH. Both methods are explained in the following subsections.

3.2.1.1 CEC with variable pH

During the experiment, the pH of the solution will change due to the adsorption of the metal into the clay, therefore it is important to know how the CEC will change with the pH. The CEC was determined as a function of pH following the method reported by Hendershot et al. (1993). This method was used before by Yong and Phadungchewit (1993) with a similar type of kaolinite.

In this method the soil is saturated by adding a solution of Ca^{2+} ions and shaking the sample for around 12 hours; it is assumed that the adsorption of Ca^{2+} ions has reach equilibrium within this time. Also, the pH of each calcium solution is varied by adding different amounts of nitric acid or calcium hydroxide. Ca^{2+} ions are commonly used as the exchangeable cation due to the affinity of the clay for calcium as compared to other divalent or monovalent cations (Coles 1998).

After the saturation of the soil, the Ca^{2+} ions are released by adding potassium chloride to the clay to exchange the calcium trapped in the soil. The amount released is considered to be the capacity of the soil to attach cations. A small amount of lanthanum solution is added to each sample before analyzing the calcium concentration in solution by atomic adsorption (A.A.) spectrometry. This prevents interference in the reading of the concentration. Since kaolinite is a pH dependent soil, the CEC is expected to increase with the rise in pH (Zhao et al. 1997).

3.2.1.2 CEC at constant pH

In order to confirm the values obtained by the method with variable pH, the CEC was determined at a constant pH with the method proposed by Jackson (1958) and reported by Sheldrick (1984) in the agricultural manual of soil testing. Again the method is based on the saturation of the clay by Ca^{2+} ions but in this case, calcium acetate/calcium chloride is used as the saturated solution.

The pH of the kaolinite solution with calcium acetate is adjusted by adding small quantities of calcium hydroxyl or hydrochloric acid as needed. After adjusting the pH to neutral, the solution is shaken overnight. After the saturation of the soil, the Ca^{2+} ions are extracted from the soil with sodium chloride and the solution is washed three times with distilled water. Again, the concentration of Ca^{2+} extracted is measured by A.A. spectrometry and a La solution is added to avoid interference in the reading.

3.2.2 Point of Zero Charge Determination

The method used to determine PZC was the one proposed by Van Raij and Peech (1972). This method consists of determining the potentiometric titration curves of the clay which is the determination of the surface charge at different ionic strengths of electrolyte. The titration method has also been used before by Tschapek et al. (1974), Benyahya and Garnier (1999) and Gallez et al. (1976) among others.

The procedure of PZC determination is reported by Van Raij and Peech (1972). Samples of 2 g kaolinite were placed in a 20 ml solution of NaCl solution (concentrations of 1.0, 0.1, 0.01 and 0.001 M; each concentration in duplicate to be used for the acidic and alkaline parts of the titration curves) and then agitated for one hour to equilibrate the solution. After equilibrium, an alkaline solution (NaOH 0.01 M) was added to half samples and an acid solution (HCl 0.1 M) to the rest of the beakers.

Coles (1998) found that the addition of diluted acid (0.01 M as proposed by Van Raij and Peech) was not enough to detect a significant change in the pH of the solution and therefore convergence of the curves was slow. For this reason a more concentrated acid was used. The addition of acid or alkaline solution was made every two minutes with 2 ml in every dose; the pH was reported after each addition. The PZC is determined by observing the point or pH where the curves intersect.

3.2.3 Specific Surface Area

The SSA of the kaolinite was determined by the method used by Jackson (1956) reported by Sheldrick (1984) in the analytical methods manual. This method is based on the assumption that the clay will absorb a monomolecular layer of a polar liquid (Ethylene Glycol Monoethyl Ether EGME). The reason for using this polar substance rather than another adsorbate is the quick evaporation of any amount of EGME (Carter 1993).

The value of the SSA will depend on the method used and in the composition of the mineral (Sposito 1984). Various authors (Bohn et al. 1979, Sheldrick 1984, Carter et al. 1965) suggest that there could be a difference of 40% or more depending on the method used to estimate this property. The other method used commonly is BET-N_2 but as it requires more sophisticated equipment the EGME method was preferred. Differences between the EGME and BET-N_2 methods for some soils could be in orders of magnitude, although in the case of the kaolinite, the difference is not usually that significant. After saturating the soil with the polar substance and drying the excess of chemical, the SSA is obtained by dividing the EGME adsorbed by the original weight of the sample and then multipling by the packing area of the EGME that has being estimated to be 2.86×10^{-4} g/cm^2.

The surface area of clays not only includes the external surface area, which is available to react with or to be in contact with the solution, but also the internal surfaces of the clay.

However, well-packed clays such as kaolinite do not have any internal surface and will yield a lower SSA value than other clays. Also, this test is a method to reaffirm the particle size of the clay since a high particle size will have a low SSA and vice versa.

3.2.4 Acid Digestion

The acid digestion test is used to determine any impurities that the kaolinite might have. The method used in the research is the method suggested by US EPA entitled "Acid digestion of sediments, sludges and soils" (American Chemical Society 1986). The main purpose of the method is to dissolve the clay using concentrated acids. Oxygen peroxide is also used to enhance the oxidation of some compounds. The acids that were used in the experiment were hydrochloric acid and nitric acid. The test indicates that the acid must be heated without boiling and water baths are recommended to control the rise of temperature.

The test was conducted in duplicate and the samples were not moved from the original beaker to avoid losses in the process. After the dissolution of the clay in the acids, the mix is diluted in water and then the concentration of metals such as Fe, Pb, Cd and Zn are measured in the A.A. spectrometer.

3.3 pH stabilization test

The equilibrium time for adsorption of metals onto clay is 24 hours (Yong et al. 1992). Since the dependent variable in this research is not adsorption but pH level, the pH equilibrium time was checked for the highest concentration of metals used in the study.

Two grams of kaolinite were placed in each beaker and then 20 ml of metal solution was added. These amounts maintain the 1:10 relationship between clay and solution that is suggested by Yong et al. (1992). The samples were agitated and the pH level was measured for each metal solution during the 24 hours at times of 1, 2, 4, 8, 12 and 24 hours. The pH was considered stable if the change was not greater than ±0.1. However, as the results for Cd did not appear to stabilize for 24 hours, as there was a drop in the pH of the solution between 12 and 24 hours, and additional stabilization test was run until 48 hours for this metal only.

3.4 Batch Equilibrium Test

The adsorption of the metals onto the clay was studied using batch equilibrium tests. This method has been used by several authors (Yong et al. 1992, Haas and Horowitz 1985, Farrah and Pickering 1976) in the past to study the same phenomena, but unlike those studies, samples will be taken at different times before 24 hours and at 24 hours. The clay/solution ratio used was 1:10 as suggested by Yong et al. (1992) and there were 3 different concentrations used for each metal (1 mM/L, 2 mM/L, 3 mM/L). For each concentration, the clay was put in contact with a soluble form of the metal and agitated to enhance the contact of all the kaolinite with the solution.

The shaking times for the batch tests were 0.1, 1, 2, 4, 8, 12, 24 hours. Each sample was shaken separately; in other words, one sample was shaken for one hour and a different sample for two hours and so on. The different phases were separated by centrifuging at 5000 rpm for 10 min.

After the separation the pH level was measured in the supernatant and then, the metal concentration was measured using the A.A. spectrometer. The concentration adsorbed by the clay is considered to be the difference between the initial and final concentrations in the solution.

Figure 3.1 shows a schematic diagram of batch equilibrium tests. One liter of each concentration (i.e. 1 mM/L, 2 mM/L and 3 mM/L) of metal solution was made and the concentration of those solutions was checked in the A.A. spectrometer.

The adsorbed metal is reported in μm of metals per grams of kaolinite. Reported with each sample is the weight of kaolinite used and it is accurate to ±0.001 grams. The whole test was done in centrifuge tubes to avoid loss of clay during the transfer from one beaker to another. In order to avoid experimental error, the supernatant should be sufficient so that no clay is transferred during decantation.

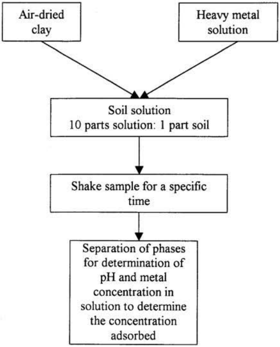

Figure 3.1 Batch test diagram (Modified from Yong et al. 1992)

3.5 Desorption Test

The methodology for the desorption tests is similar to the one used by Farrah and Pickering (1978), in that the solution used to extract the metal was ethylene diamine tetra acetate (EDTA). The clay was saturated with the heavy metal and then the metal was extracted with different solvents. For the first part, the method proposed by Yong et al. (1992) for the batch equilibrium tests was followed using a 10:1 ratio of metal solution:clay and the metal clay suspension was mixed for 24 hours. The solid and liquid phases were separated by centrifugation (5000 rpm for 10 min) and the concentration of heavy metal was measured in the first supernatant.

The next step was to add the EDTA solution and shake the samples for different exposure durations (1, 2, 4, 8, 12, 24 hours). The concentration of heavy metal was measured at each time and the results were compared with the adsorption data. For this part of the research only a concentration of 1 mM/L of heavy metals was used.

Chapter 4

Characterization and Batch Test Results

4.1 Foreword

The results of characterization and batch tests are presented in this chapter. Following the methods explained in chapter 3, the adsorption and desorption tests were run in duplicate. The raw data of the adsorption and desorption tests are presented in appendix A.

In the case of the characterization tests, the CEC test was done by two different methods (variable pH and constant pH) and both tests yielded similar results for the same pH. The values obtained in all of the characterization tests are compared with values reported in similar studies with the similarities and discrepancies among these values being discussed. Also, the results of the acid digestion test are presented first because they influence the results of SSA, CEC and PZC.

4.2 pH Stabilization Results

The adsorption of heavy metals reaches stabilization after 24 hours (Yong et al. 1992, Farrah and Pickering 1977). Nevertheless, this test was performed to ensure that the pH of the solution would also reach equilibrium during the time that the adsorption occurs. The results are presented in Table 4.1 and in Figure 4.1 for the three metal concentrations of 3 mM/L.

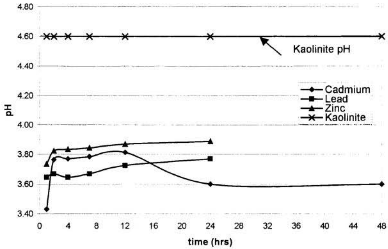

Figure 4.1 Stabilization of solution pH as a function of metal type and time

Table 4.1 Raw data for pH stabilization graph (Figure 4.1)

Time (hrs)	**pH levels**		
	Zn	**Cd**	**Pb**
1	3.7	3.4	3.7
2	3.8	3.8	3.7
4	3.8	3.8	3.7
8	3.9	3.8	3.7
12	3.9	3.8	3.7
24	3.9	3.6	3.8
48	---	3.6	---

The final pHs of the solutions are between pH 3.6 and 3.9, which is below pH 4.6 of the kaolinite and well below the natural pH of the metal solutions, as indicated in Table 4.2. These results indicate that there is an interrelation between the clay and the metal solution and the release of H^+ ions. Between 12 and 24 hours of exposure, the change in the pH of the solution due to the adsorption of heavy metals is minimal for Pb and Zn and the adsorption tests could reach equilibrium at 24 hours. For Cd there is a sudden drop in pH between 12 and 24 hours of exposure, but the pH does not change further between 24 and 48 hours. The drop in pH between 12 and 24 hours is indicating a release of H^+ ions from the clay. The change in the pH is evident during the first two hours, where there is a difference of 0.4 between the pH of the first hour and the second hour.

Table 4.2 Natural pH of the metal solutions

Metal	**pH level**		
	Solution 1 mM/L	**Solution 2 mM/L**	**Solution 3 mM/L**
Cd	7.2	7.0	6.9
Zn	6.2	6.1	6.0
Pb	5.5	5.6	5.6

4.3 Acid Digestion Results

The results for the acid digestion test are presented in Table 4.3. These values are compared with the values obtained by Coles (1998) since the kaolinite used is similar in both studies. The concentration of all of the metals is higher in the kaolinite used in this study compared with the study of Coles (1998). This suggests a contamination of the kaolinite, with Fe, probably as oxides (Potter and Yong 1999). The concentrations of the Pb, Cd and Zn are low enough that they do not influence the results in the adsorption and desorption experiments, even through these values are higher than the values in the study of Coles (1998).

Table 4.3 Amount of metals present in kaolinite

Metals (mg./kg)	This study Flat D kaolinite	Coles (1998) Flat D kaolinite
Fe	1247	7.8
Pb	14.9	0.5
Cd	10	0.1
Zn	70	0.7

4.4 PZC Results

The results of the PZC test are presented in Figures 4.2a, 4.2b and 4.2c and Table 4.4. Figure 4.2a presents the titration curves obtained in this study over the full range of pH. Figure 4.2b and 4.2c show the blown up sections b and c respectively that are identified in Figure 4.2a.Table 4.4 compares these results to the pH of the PZC (pH_{pzc}) obtained by other authors.

Table 4.4 Values of pH_{pzc} for kaolinite from others authors and this study

	This Study meq/100 g	Others authors meq/100 g
PZC of Kaolinite	4.7	3.7[1] 4.5[2] 4.0 – 7.5[3] 2.6[4]

[1] from Potter and Yong (1999)
[2] from Spark et al. (1995)
[3] from Schroth and Sposito (1997)
[4] from Coles (1998)

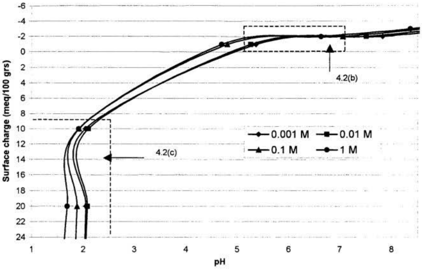

Figure 4.2a Titration curves for determination of PZC of kaolinite

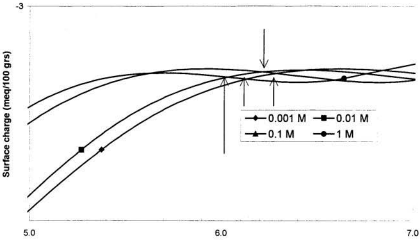

Figure 4.2b Titration curves for kaolinite between pH 5 and pH 7, showing the pHs where the lines cross

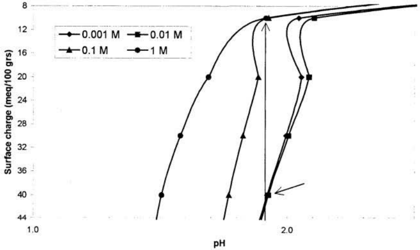

Figure 4.2c Titration curves for kaolinite between pH 1.0 and pH 2.5, showing the pHs where the lines cross

According to the method proposed by Van Raij and Peech (1972) the curves should intersect each other near the same point on the graph, but in this experiment, the curves intersected at the following pH values: 1.9, 1.9, 6.0, 6.1, 6.1 and 6.3. Therefore the average of the pH values is taken as the PZC and it is 4.7.

The pH_{pzc} of 5.9 to 6.3 is close to the pH_{zpc} of the aluminium hydroxyl groups and edge surface groups (Suraj et al. 1998). The adsorption experiments begin at pH levels slightly above the PZC. However, the solution pH drops below the PZC during the course of the experiment. Hence, the soil will have a positive charge that will inhibit further uptake of the metal. If the electrostatic attraction is the dominant force then there should not be any additional metal retention below the PZC as both, clay and cations, have the same charge (Potter and Yong 1999). However, adsorption data are still showing retention of metal and this could indicate that at the conditions of the study the Fe oxides sites yield a positive charge but the kaolinite yields a negative charge as its PZC is usually below pH 4.7.

The value of pH_{pzc} obtained in this study is similar to values obtained by other authors as is shown in Table 4.4. However, Coles (1998) used a similar type of kaolinite to the one used in the study and obtained a lower pH_{pzc} than the one obtained here (pH_{pzc} of 2.6 compared with 4.7). Tschapek et al. (1974) suggest that the presence of Fe_2O_3 could increase the value of pH_{pzc}. Since kaolinite is a mixture of aluminium hydroxides and silica oxides and the acid digestion test shows that there is a high concentration of Fe impurities, the value of 4.7 for pH_{pzc} is reasonable. Schroth and Sposito (1997) suggest that the equilibration time during the determination of the pH_{pzc} can increase the value of this property.

4.5 SSA Results

The value of SSA obtained in this study along with other values obtained by other authors using the EGME or the BET-N_2 methods are presented in Table 4.5. Gallez et al. (1976) reported that the EGME-surface area is much greater than BET-N_2 surface area for most soils due to loss of sample during the latter method. However, both methods give comparable results for kaolinite as illustrated in Table 4.5.

Table 4.5 Values of SSA for kaolinite

	This Study EGME method m^2/g	Others authors EGME method m^2/g	Other authors BET-N_2 method m^2/g
Kaolinite	16.41	20.4[1]	7 – 21[4]
		13.8[2]	15.2[5]
		12.0[3]	25.0[6]

[1] from Coles (1998)
[2] from Carter et al. (1965)
[3] from Yong and Phadungchewit (1993)
[4] from Dry Branch Kaolin Company
[5] from Ziper et al. (1988)
[6] from Puls et al. (1991)

Potter and Yong (1999) propose that the SSA would increase with the presence of Fe compounds in the clay. The results presented for the acid digestion test show that the clay contains a high concentration of Fe. The results of the SSA test are within the range of 10 to 20 m^2/g established for kaolinite (Bohn et al. 1979), although the Fe compounds present, may also be influencing the SSA. Nevertheless, the value of the SSA will strongly depend on the method used (Sposito 1984).

The SSA will determine the spaces available for the metal to react with the clay, but a large area does not necessarily represent more reactive spaces. In the case of kaolinite, for example, most of the reactive spaces are on the edges of the clay and not inside the clay (Sparks et al. 1995; Potter and Yong 1999; Reid and McDuffie 1981). Besides, due to the compact structure of the clay, the SSA calculated for kaolinite does not usually involve many intermolecular spaces.

4.6 CEC Results

The results gathered for the two CEC methods of variable and constant pH along with values reported in the literature are shown in Table 4.6. The pH of the solution influences the adsorption of heavy metals onto clay and the method proposed by Hendershot (1993) shows how the CEC varies with the change of pH.

Since the results obtained by this method were a little higher than expected (Bohn et al. (1979) proposed a value within 1-10 meq/100 g), the method proposed by Sheldrick (1984) was used to verify the results. The difference with this method is that the pH level is maintained at 7.

As can be seen in the table, the value obtained by the pH at 7 is between the values of pH at 6 and 8.41 from Hendershot's method, confirming that the clay is most likely polluted with a material that increases the CEC of the soil.

Table 4.6 Values of CEC of kaolinite

	This study		Other authors	
	pH	CEC[1] meq/100 g	pH	CEC meq/100 g
Kaolinite	3.8	16.63	5	14.6[4]
	4.0	16.56		
	4.1	16.92	6.3-7	5[6]
	4.2	16.59		
	4.4	16.37	7	1.97[3]
	4.8	16.90		
	5.3	16.76	7	16[5]
	6.0	17.18		
	7.0	*17.76*[2]		
	8.4	18.41		

[1] Values obtained using method of Hendershot (1993) except at pH 7
[2] Value obtained using method of Sheldrick (1984)
[3] from Coles (1998)
[4] from Ziper et al. (1988)
[5] from Yong and Phadungchewit (1993)
[6] from Potter and Yong (1999)

The kaolinite is a pH-dependent soil, meaning that the soil will be charged according to the pH of the environment (Bohn et al. 1979; Mitchell 1993). Therefore, the tendency of the values is as expected, with a lower CEC at lower pH. The high values of CEC reported are probably a consequence of the presence of Fe oxides in the clay.

4.7 Batch Test Results

4.7.1 Adsorption

The adsorption results are divided in two parts; the first part is the change in H^+ ions in solution, which is presented in Figures 4.3a to 4.3c and Table 4.7. The second part is the adsorption of the metal onto the clay and these values are reported in Figures 4.4a to 4.4c and Table 4.8.

For the adsorption results, there are several behaviours that are worth analyzing. Although the CEC of the soil is higher than usual for kaolinite, the adsorption results do not reflect the high reactivity of the soil. The highest concentration of metals adsorbed occurs when the clay is in contact with the highest concentration of the metals occupying only 12%, 9.6% and 7.2% of the CEC for Pb, Zn and Cd respectively.

The stabilization of the adsorption is reached after 12 hours for Zn, and after 8 hours for Pb. In the case of Cd, there is stability after 1 hour as also found by Taylor and Theng (1995), but between hours 12 and 24 there is a considerable drop in the metal adsorbed. This could be related to the increase in H^+ ions in solution (or the drop in the pH of the solution). In the case of Zn, the adsorption is close to being stabilized after hour one, but there is a small declination at hours 2 and 4 for the concentration of 1 mM/L and 3 mM/L.

For the three metals, Pb shows the highest retention onto kaolinite and Cd shows the highest mobility in the clay. The most significant changes in pH are obtained in the first minutes of adsorption when there is a drop from the pH of the kaolinite (or pH 4.6) to between pH 3.9 and 3.6 as will be seen later in Table 4.11 on page 66. This indicates that the adsorption process is fast.

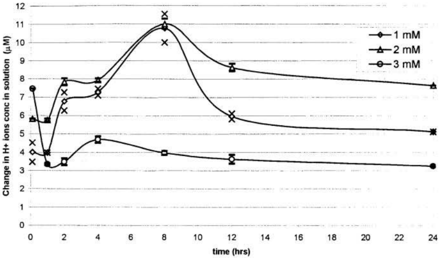

Figure 4.3a Change in hydrogen ion concentration during Pb adsorption as a function of time and Pb concentration (x and – represent the experimental values)

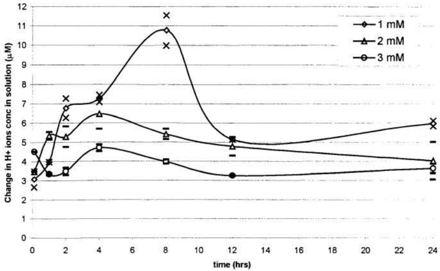

Figure 4.3b Change in hydrogen ion concentration during Zn adsorption as a function of time and Zn concentration (x and – represent the experimental values)

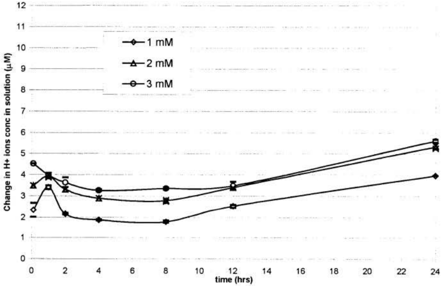

Figure 4.3c Change in hydrogen ion concentration during Cd adsorption as a function of time and Cd Concentration (– represent the experimental values)

Table 4.7 Data used for the figures 4.3a to 4.3c

		Difference in H^+ concentration (μM)						
Metal/time(hrs)		**0.1**	**1**	**2**	**4**	**8**	**12**	**24**
Cd	**1 mM**	2.3	3.9	2.7	2.4	2.3	3.0	4.5
	2 mM	3.5	4.4	3.8	3.4	3.3	3.9	5.8
	3 mM	4.5	4.5	4.1	3.8	3.9	4.0	6.1
Zn	**1 mM**	3.1	4.5	7.3	7.8	11.3	5.6	6.5
	2 mM	3.5	5.8	5.8	7.0	5.9	5.3	4.5
	3 mM	4.5	3.8	4.0	5.2	4.5	3.7	4.1
Pb	**1 mM**	4.0	4.4	7.2	7.7	11.2	6.4	5.6
	2 mM	5.8	6.2	8.3	8.4	11.5	9.1	8.1
	3 mM	7.5	3.8	3.9	5.2	4.4	4.1	3.7

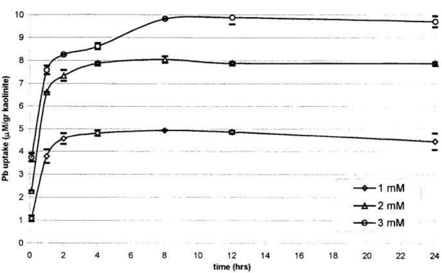

Figure 4.4a Sorption of Pb by kaolinite as a function of time and Pb concentration (– represent the experimental values)

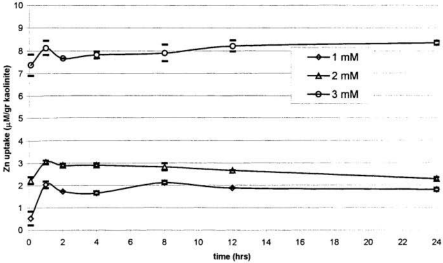

Figure 4.4b Sorption of Zn by kaolinite as a function of time and Zn concentration (– represent the experimental values)

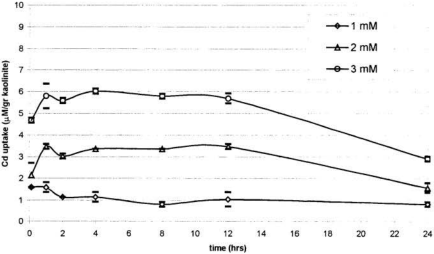

Figure 4.4c Sorption of Cd by kaolinite as a function of time and Cd concentration (– represent the experimental values)

Table 4.8 Data used for the figures 4.4a to 4.4c

		Metal uptake (μM/gr kaolinite)						
Metal/time (hrs)		**0.1**	**1**	**2**	**4**	**8**	**12**	**24**
Cd	**1 mM**	1.6	1.6	1.2	1.2	0.8	1.0	0.8
	2 mM	3.5	3.5	3.0	3.4	3.4	3.5	1.6
	3 mM	4.7	5.8	5.6	6.0	5.8	5.7	2.9
Zn	**1 mM**	0.5	2.0	1.7	1.7	2.1	1.9	1.8
	2 mM	2.2	3.1	2.9	2.9	2.8	2.7	2.3
	3 mM	7.4	8.1	7.7	7.8	7.9	8.2	8.4
Pb	**1 mM**	1.1	3.8	4.6	4.8	4.9	4.9	4.4
	2 mM	2.3	6.6	7.3	7.9	8.1	7.9	7.9
	3 mM	3.7	7.6	8.3	8.6	9.8	9.9	9.7

The graphs present the change in the H^+ ions concentration. The initial pH of the kaolinite metal suspension was established to be the pH of the kaolinite (pH=4.6). Regardless of the fact that all the metal solutions have different natural pH levels as can be seen in Table 4.2, the concentration of the metal solution is extremely low in comparison with the amount of kaolinite present in solution. Hence, kaolinite was in excess during the experiments and the pH of the kaolinite solution will be dominant over the natural pH of the metal solutions. Also, the difference in μM of H^+ ions present between the pH levels of the metal solutions and the pH of kaolinite is negligible as explained by the following equation:

$$pH= -\log[H^+] \qquad \text{eqn. 4-1}$$

The pH increases logarithmically with a $[H^+]$ increase as the equation demonstrates.

The pH level and the concentration of chlorides have an effect on the speciation of the metals in solution. The type of species that are stable under the experimental conditions are important to determine the relation between the metal adsorbed and H^+ ions released.

Table 4.9 shows the percentage of the most significant species under the experimental conditions, using the method reported by Hahne and Kroontje (1973) and using the stability constants reported by Smith and Martell (1995) at zero normality. The most stable species for Cd, Pb and Zn is M^{2+} (i.e. Pb^{2+}, Cd^{2+} or Zn^{2+}), which is expected given the conditions of the experiment. For Cd and Pb, the MCl^{+} species make up a considerable percentage and would have an influence on the release of H^{+} ions during the adsorption. Zn does not make up a significant percentage of this species and it could be assumed that most of the metal adsorbed is in the form of Zn^{2+}. Finally, the metal presence in the form of MCl_2 is insignificant for the three metals.

Table 4.9 Speciation of the metals under the experimental conditions

Species **M=metal**	**Metals**								
	Cd			**Pb**			**Zn**		
	1 mM/L	2 mM/L	3 mM/L	1 mM/L	2 mM/L	3 mM/L	1 mM/L	2 mM/L	3 mM/L
% M^{2+}	84	72	63	93	86	81	99	99	98
% MCl^{+}	16	28	36	7	14	19	1	1	2
% MCl_2	≈0	≈0	1	≈0	≈0	≈0	≈0	≈0	≈0

The relationship between the adsorption of metals and the release of H^{+} ions seems not to follow a completely consistent pattern, especially for Zn and Pb; these same results were found by Farrah et al. (1980). Nevertheless, during certain times there are some similarities in the types of reactions observed and there does seem to be an implied relationship between the process of metal adsorption and change in the H^{+} ion concentration as shown in Table 4.10 and Figures 4.5 to 4.7. However, the fact that there is no linear relationship between the release of H^{+} ions and metal adsorbed does not mean that the pH of the solution will not affect the retention of the metal. The ratio of H^{+} ions released to metals cations adsorbed is obtained by dividing the amount of H^+ desorbed and the amount of metal adsorbed using the values presented in Table 4.7 and 4.8.

If the changes in pH are merely a consequence of the adsorption process, then the ratio should be always be between 1 and 2 since the two species that the clay would adsorb are M^{2+} and MCl^+. However, the data shows some ratios higher than two in 1 mM/L and 2 mM/L Cd solutions, 1 mM/L and 2 mM/L Zn solutions and the 3 mM/L Pb solutions (data in Table 4.8) and ratios lower than one in the 3 mM/L of Cd solution, 3 mM/L of Zn solution and 2 mM/L and 3 mM/L of Pb solution (data in Table 4.8). This indicates that there are other processes occurring during the adsorption of the metals that increase and decrease the pH of the solution.

Table 4.10 Ratio of the H^+ ions released to the metal cations adsorbed

	1 mM/L			2 mM/L			3 mM/L		
Time hrs	**Zn**	**Pb**	**Cd**	**Zn**	**Pb**	**Cd**	**Zn**	**Pb**	**Cd**
0.1	6.2	3.6	1.4	1.6	2.5	1.6	0.6	2.0	1.0
1	2.0	1.1	2.1	1.7	0.9	1.1	0.4	0.4	0.7
2	4.0	1.5	1.8	1.8	1.1	1.1	0.5	0.4	0.6
4	4.3	1.5	1.6	2.2	1.0	0.9	0.6	0.5	0.6
8	5.1	2.2	2.3	1.9	1.4	0.8	0.5	0.4	0.6
12	2.7	1.2	2.5	1.8	1.1	1.0	0.4	0.4	0.6
24	3.3	1.2	5.0	1.7	1.0	3.3	0.4	0.3	1.9

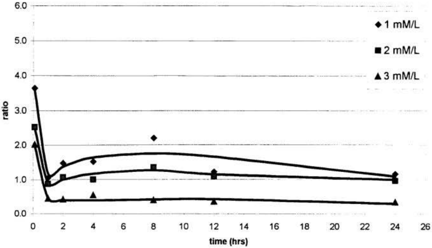

Figure 4.5 Relationship between ratio of H^+ ions desorbed over Pb ions adsorbed as a function of time

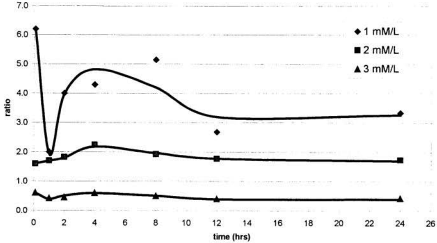

Figure 4.6 Relationship between ratio of H^+ ions desorbed over Zn ions adsorbed as a function of time

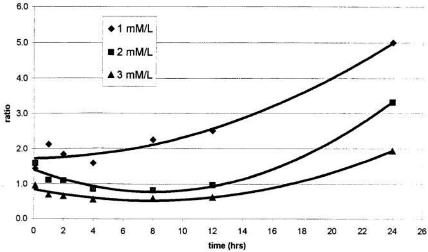

Figure 4.7 Relationship between ratio of H^+ ions desorbed over Cd ions adsorbed as a function of time

There is a relationship between the ratio and the time for the three metals that can be represented by a polynomial equation for all the solutions of Cd, for the 1 mM/L solution of Zn and 3 mM/L solution of Pb, and by a logarithmic equation for the other Pb and Zn solutions (trend line represented by the dark line in Figures 4.5 to 4.7). In the case of Cd, the polynomial equations of second order calculated using excel are in agreement for the data up to 24 hours. The equations for each Cd solution are:

$$r = 0.0055t^2 + 0.0033t + 1.73 \quad \text{eqn 4-1}$$

$$r = 0.0099t^2 + 0.159t + 1.4121 \quad \text{eqn 4-2}$$

$$r = 0.0054t^2 + 0.0083t + 0.8432 \quad \text{eqn 4-3}$$

Where r is the ratio and t is time in hours. The trends of these equations are in good agreement with the trend of the Cd adsorption found in this research and can be used to predict the amount of metal adsorbed onto kaolinite at any given time. The only condition will be to use the same kaolinite used in this study.

The curves for Pb are also in good agreement with the results gathered, and can predict the ratio values with time to some extent of accuracy until 24 hours. The equations are as follows:

$$r = 1.1776 + 0.1518\ln(t) + 0.2788(\ln t)^2 - 0.1054(\ln t)^3 \qquad \text{eqn 4-4}$$

$$r = 0.7246 + 0.1226t - 0.0169t^2 \ln t + 0.0099t^{2.5} + \frac{0.0557}{t^{1.5}} \qquad \text{eqn 4-5}$$

$$r = 0.2718 + 0.02347t - 0.0009t^2 + \frac{0.1721}{t} \qquad \text{eqn 4-6}$$

Where r is the ration and t is time in hours. As expected between 12 and 24 hours, there is stabilization between the ratio and time, which indicates an equilibrium in the adsorption. Finally, the equations for Zn are:

$$r = 11.7196 - 0.5525t + 0.0004t^3 - \frac{9.4773}{t^{0.5}} + \frac{0.245061}{t^2} \qquad \text{eqn 4-7}$$

$$r = \frac{1.6993 - 1.821\ln t + 0.5380(\ln t)^2}{1 - 1.1233\ln t + 0.3453(\ln t)^2 - 0.0039(\ln t)^3} \qquad \text{eqn 4-8}$$

$$r = 1.9760 - 1.6056t + 0.0271t^2 - 0.0003t^3 + 1.6677t^{0.5} \ln t \quad \text{eqn 4-9}$$

Where r is the ratio and t is time in hours. The complexity of the Pb and Zn equations could be due to the fact that more variables are affecting the retention of these two metals, than occurs for Cd. These variables could be the pH of the solution, the concentration of the metal and the amounts of kaolinite and the Fe oxides that are participating in the sorption process. For Pb and Zn, the ratio of metal uptake with time can be predicted using these curves, including for those times where is a sudden drop in the pH of the solution.

In the case of Cd, the second order polynomial equations are in good agreement with the experimental data. This could be as a result of fewer factors being involved in the relationship between ratio and time. In this case, the pH of the solution will be an important factor affecting the adsorption with the concentration of the metal solution playing a minor role.

For the three metals, the biggest ratio is present in the 1 mM/L solution and the lowest ratio is present in the 3 mM/L solution (Table 4.10). This behaviour is explained in part by the speciation of the metals; the higher the concentration, the higher the presence of MCl^+ species which in theory, would only release one H^+ ion at the time the metal is adsorbed. Comparing the three metals, Zn presents the largest ratios for the 1 mM/L and 2 mM/L solutions while Cd shows the largest ratios for 3 mM/L solution. Zn is expected to release the highest concentration of H^+ as almost all of the metal is present in Zn^{2+} form. On average, Pb has the smallest ratios for the three concentrations but the presence of MCl^+ is higher for Cd than for Pb. Hence, the adsorption of Pb is either taking place in sites that do not release H^+ ions or the H^+ ions are being adsorbed in other sites after the retention of Pb.

The kaolinite has a higher affinity for Pb than for Cd and Zn. This same behaviour was reported by Li and Wu (1999) and Yong and Phadungchewit (1993). Also, Yong and Phadungchewit (1993) suggest that Zn has a higher retention than Cd at low pH levels. This trend is also obtained in this study as Zn shows a higher adsorption onto the clay than Cd for the concentrations of 1 mM/L and 3 mM/L. For the 2 mM/L solutions of each metal, the difference in the adsorption is minimal until 12 hours.

The difference in the adsorption between Zn and Cd could be due to the fact that Cd could be limited by the electrostatic forces. The low pH of the solution yields a positive charge in the soil that reduces the attraction of cations. This could be inhibiting the reaction of Cd with the clay, especially with the Fe oxides that are electrostaticly more active than the other sites of the clay.

The adsorption behaviour through time is different for each metal; however, there are some similarities between the adsorption of Zn and Pb as both metals reach a saturation stage in the clay (Figures 4.4a and 4.4b). Also, Zn and Pb present a peak in release of H^+

ions at 8 hours for the 1 mM/L solutions and the H^+ ion release is similar for 1 mM/L and 3 mM/L solutions (Figures 4.3a and 4.3b). This similarity could indicate that both metals are attached at similar sites on the kaolinite, while Cd is attached at other available sites. Cd also has a constant metal uptake until between 12 and 24 hours when there is a drop in the pH and a release of Cd to the solution. Suraj et al. (1997) report that Cd adsorption decreases with time and this is in agreement with the results obtained in this research. A reason for this behaviour could be that after the metal is attached to the clay there are physical interactions, such as mixing, that could be strong enough to break the electrostatic bonding between the clay and the metal.

Kaolinite releases the least amount of H^+ ions in the presence of the 3 mM concentrations of Pb and Zn (Figures 4.3a and 4.3b) while Cd releases the most H^+ ions in the presence of 3 mM concentrations of Cd (Figure 4.3c). This difference in the release of H^+ ions and the fact that there is no direct linear relationship between adsorption of the metals and release of H^+ ions, as shown in Figures 4.5, 4.6 and 4.7, could indicate the presence of a secondary reaction during the adsorption process.

Some of those secondary reactions could be the interaction of the metals with the Fe oxides and silicon oxides present in the solution, as several authors (Reid and McDuffie 1981, Gerritse and Van driel 1984, Chaun et al. 1995) suggest. The percentage of Fe oxides present in the kaolinite is 0.125 %, which is equivalent to 2.5 mg of Fe oxide in a 2 g sample as used for the batch tests. Regardless of the low amount of Fe, the CEC clearly increases indicating that this amount will be enough to interact with the H^+ ions and the metals, changing the shape of the curves in Figures 4.3 and 4.4.

It is established that the type of kaolinite metal interactions that are important during the adsorption of Pb and Zn are different from those involving Cd.

The adsorption of Pb is similar to the behaviour observed by Scheidegger and Sparks (1996) in their study of the adsorption of Ni onto pyrophyllite. The tendency in the adsorption of Pb is that there is an increment in the adsorption during the first 4 to 8 hours then the saturation or stabilization point is reached. However, the release of H^+ ions does not follow the same trend as the adsorption. Figure 4.3a shows one peak at 8 hours for the 1 mM/L and 2 mM/L solutions and a peak at 4 hours for the 3 mM/L solution. These peaks mean a drop in the pH of the solution but as shown in Figure 4.4a, this change in the pH does not affect the adsorption of the metal.

The ratios between H^+ ions released and Pb adsorbed are usually lower than 2 except at 0.1 hours where the ratio is 2 as shown in Table 4.10. With the 3 mM/L solution, the ratio is lower than one indicating that during the adsorption of Pb, the H^+ ions are being adsorbed by the clay. Potter and Yong (1999) suggest Fe oxides are probable sites for Pb to react but the metal could also react with aluminium or silicon sites releasing H^+ that are later re-adsorbed by kaolinite or the Fe oxides sites. These reactions are explained later in section 4.7.3

Table 4.11 Initial and final pH of the metal solutions

	Final pH of the solutions								
	Zn			**Cd**			**Pb**		
	1 mM/L	2 mM/L	3 mM/L	1 mM/L	2 mM/L	3 mM/L	1 mM/L	2 mM/L	3 mM/L
Time (hrs)	**pHo* 4.6**	**pHo 4.6**	**pHo 4.6**	**pHo 4.6**	**pHo 4.6**	**pHo 4.6**	**pHo 4.6**	**pHo 4.6**	**pHo 4.6**
0.1	3.8	3.7	3.6	3.9	3.7	3.6	3.7	3.5	3.4
1	3.6	3.6	3.7	3.7	3.7	3.7	3.7	3.5	3.7
2	3.4	3.6	3.7	3.8	3.7	3.7	3.5	3.4	3.7
4	3.4	3.5	3.6	3.9	3.8	3.7	3.4	3.4	3.6
8	3.2	3.5	3.7	3.9	3.8	3.7	3.3	3.3	3.7
12	3.5	3.6	3.7	3.8	3.7	3.7	3.5	3.4	3.7
24	3.5	3.7	3.7	3.6	3.5	3.5	3.6	3.4	3.7

*pHo is the initial pH of the kaolinite. This is the pH that is considered as the initial pH to calculate the change in H^+ ions.

The data in Table 4.9 show that Pb^{2+} and $PbCl^+$ are the dominant species during the adsorption of Pb. For the 1 mM/L solution, the ratio of H^+ ions released and Pb adsorbed is higher than 2 at 8 hours. The pH level at this point (pH=3.3) is the lowest among the 1 mM/L solution (data presented in Table 4.11).

This could mean that after 8 hours, the dissolution of $Al(OH)_3$ reachs its peak decreasing the pH of the solution (the dissolution of aluminium hydroxide from the kaolinite begins around pH 4.4). This could explain the drop in the pH after 8 hours of exposure and a similar explanation could be made for the peak in the 2 mM/L solution despite the fact that the ratio in this case is higher than 2 only at 0.1 hours. The 3 mM/L is different (Figure 4.3a). There is a peak in the release of H^+ ions at 4 hours and the moles of H^+ ions released are lower than the moles of Pb adsorbed at all the times except for 0.1

hours. The Pb species with the lowest valence is $PbCl^+$ and therefore having a ratio below one indicates that the H^+ ions are being adsorbed onto the clay or they are reacting with another compound in the solution. Therefore, there is a possibility that the H^+ ions could be reacting with the Fe to form Fe hydroxyls or that the metal is reacting directly with the Fe oxides (Potter and Yong 1999).

The drop in the pH level during the adsorption of Pb has little effect on the trend of the adsorption. The low adsorption at 0.1 hours is an indication that the adsorption of Pb is slightly slower than the adsorption of the other metals and the pH of the solution has marginal interference during the process. Only for the 3 mM/L concentration there is a slight drop in the adsorption at the fourth hour that coincides with the drop in the pH level, but it is also noticeable that during the adsorption of the higher Pb concentration there is no significant change in the pH of the solution (Table 4.11). Since the drops in the pH are generally not reflected in the adsorption, there could be a lack of competition of the H^+ ions with Pb for the negative spaces in the clay. This lack of competition could be as a result of the higher electronegativity of the Pb (compared to H^+ ions), enhancing the attraction of the metal to the clay and therefore the reaction is by cation exchange (Cotton and Wilkinson 1998). There is also the fact that the clay shows a large affinity for Pb (Yong and Phadungchewit 1993), possibly due to the presence of specific sites for adsorption.

The release of H^+ ions with the Zn solution is similar to that observed with the Pb solution. Both metals, Zn and Pb, show a decrement in the pH of the lowest metal concentration during the first eight hours of exposure (Table 4.11). Nevertheless, the adsorption of Zn seems not to be affected by these changes, as the concentration of metal in the clay remains almost constant during the 24 hours (Figure 4.4b). The maximum concentration of Zn adsorbed is observed during the first hour of exposure with the clay and the minimum is observed during the first minutes of exposure (Table 4.8).

The maximum amount of Zn adsorbed coincides with the lower concentration of H^+ ions in the solution. A competition of H^+ ions for the negative spaces in the clay cannot be established as the pH level drops after the first hour and the metal adsorbed does not change more than 0.5 μM/ gr. Like the Pb, the higher concentration of Zn solution yields the lower release of H^+ ions or the low concentration of H^+ ions in solution.

This coincides with the fact that the pH level of the 3 mM/L is the highest for the three solutions indicating that for the 1 mM/L and 2 mM/L solution the increment in the dissolution of aluminium hydroxyls is possible. The Fe oxides present in the kaolinite could participate in the adsorption of H^+ ions that are released during the first 8 hours.

The H^+ ions seem not to interfere in the adsorption of Zn; probably because the sites where the metal is adsorbed are different than the sites where the H^+ ions are adsorbed.

At the pH levels present in the solution the stable species will be Zn^{2+} (Farrah and Pickering 1976).

The trend of Cd is different than the other two metals, as the pH level in the solution increases until 12 hours (Table 4.11) and then drops for the final 12 hours. At the same time, the metal adsorbed remains almost constant until the end where there is a steady drop in the concentration adsorbed by the clay. This indicates that the clay has a higher affinity for H^+ ions than for Cd. Alloway (1990b) reports that Cd and Zn behave similarly during the adsorption process and that the affinity between the two metals for kaolinite is hard to differentiate.

The two metals present some similarities during the first 12 hours of the adsorption, as the concentration adsorbed remains somewhat constant for that time. Also, in both cases there is a small decrement in the adsorption at the second hour of the exposure time. In the case of the Zn, this drop in the adsorption could be related with the increase of the H^+ ions in the solution, but the same could not be concluded for Cd as the pH increases during that time.

The maximum pH of the solution is reached between 2 and 12 hours (Table 4.11 page 66) and this does not affect the adsorption of the Cd, as there is no significant change in the adsorption curve between these times (Figures 4.3c and 4.4c and Table 4.11). Between the 12th and 24th hours there is a significant drop in the pH in the solution and in the adsorption of metal (Figures 4.3c and 4.4c). The drop in pH may be causing less Cd to be retained.

Another difference, with respect to Pb and Zn, is the fact that the highest concentration of Cd results in the lowest pH. This suggests that the interactions of Cd with kaolinite are somewhat different that those involving Pb and Zn. The lowest equilibrium pH values occur for the 1 mM/L of Zn solution and the 2 mM/L of Pb solution (data in Table 4.11).

The dominant Cd species is Cd^{2+} and the release of H^+ ions is expected in the solution. However, the data show a maximum in the pH of the solution between 2 and 12 hours of Cd adsorption. These pH values could be as a result of Cd and H^+ ions retention by Fe oxides and kaolinite at the same time. Between 12 and 24 hours of exposure, Cd does not reach a constant metal uptake, as there is a drop in the concentration adsorbed between these times. This trend agrees with the observations made by Suraj et al. (1997).

This means that the adsorption of Cd is more efficient at 12 hours instead of at 24 hours. Possibly over-saturation of the kaolinite with Cd^{2+} and H^+ ions up to 12 hours occurred, and therefore some of these cations were released later.

4.7.1.1 Adsorption Isotherms

Adsorption isotherms are an approach commonly used to report the results of heavy metal adsorption onto clay. In some studies (Farrah and Pickering 1979) Langmuir isotherms have been used where the adsorption behaviour has been compared in terms of the slopes of results. In this study the data is limited, however, the measurement of the adsorption at different times of exposure yields different isotherms, giving some extra information on the adsorption process. Since the initial amount of metal is required, each concentration is multiplied by the 20 mL used in each sample. The Langmuir isotherm can be presented in different ways.

Ziper et al. (1988) plotted total Cd against Cd adsorption; Laidler and Meiser (1997) suggest the plot of total space available for the adsorption against the initial concentration of heavy metal. CEC is considered to be a measure of the reactive spaces available in the clay to retain metals but as the kaolinite used in this study is contaminated, it is uncertain that all the sites are available for the adsorption. Therefore, the adsorption isotherms were plotted following the method of Ziper et al. (1988).

Figures 4.8a to 4.8c show the isotherms for the three metals studied at different exposure times.

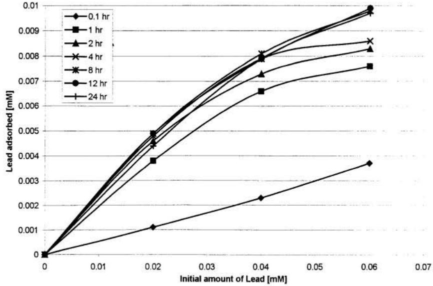

Figure 4.8a Isotherm Adsorption of Pb onto Kaolinite

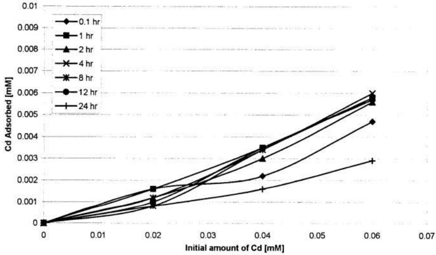

Figure 4.8b Isotherm Adsorption of Cd onto Kaolinite

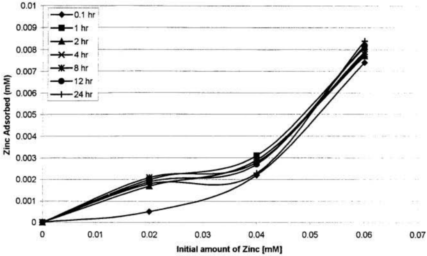

Figure 4.8c Isotherm Adsorption of Zn onto Kaolinite

In this type of graph, the adsorption is expected to follow one of three behaviours, as shown in Figure 4.9 and as described below:

(1) At a low metal concentration, the relation will be linear $Me_a=K[Me_o]$

(2) At an intermediate metal concentration the relation will be $Me_a = 1 + \frac{k[Me_o]}{1+k[Me_o]}$

(3) At saturation the relation will be close to $Me_a = \frac{k[Me_o]}{1+k[Me_o]}$

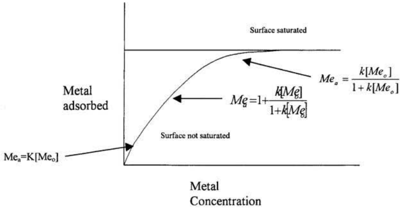

Figure 4.9 Representation of the Langmuir Isotherm (Modified from Laidler and Meiser 1997)

Figure 4.8a shows the adsorption isotherm for Pb. The trend of the data gives the idea that the metal may be reaching the saturation stage with the 3 mM/L solution. Nevertheless, the exposure time seems to be an important variable, as the data can be classified in two major groups. The first group is composed of the samples that were exposed for 1, 2 and 4 hours. In this group, the saturation stage is almost reached as the graphs start to be asymptotic; the second group (8, 12 and 24 hours) does not show this trend. This suggests that between the fourth and eighth hour there are certain reactions in the clay that open new reactive spaces, allowing higher metal retention. The isotherm for 0.1 hours is clearly below those two groups already identified. This isotherm shows that the adsorption of Pb is relatively slow as in the first 6 minutes of exposure the stage of the isotherm is still in the transition stage and the amount of Pb adsorbed is between a half or a third of the amount adsorbed between 1 and 24 hours. This suggests that the adsorption of Pb is slow in comparison to the adsorption of Zn and Cd.

The presence of secondary reactions in the clay interphase, besides the deprotonation of the clay, is supported by the adsorption isotherms. These reactions could be the reason for the change of pH in the solution at 8 hours (Figure 4.3a and Table 4.11) and explain why the adsorption of Pb is not affected by this change.

Unlike Pb, the data for Cd shows that this metal is still at the first stage of the adsorption, as most plots are almost straight lines with similar slopes except for the points at 0.1 and 24 hours. The highest slope is reached at the time of 4 hours, which also coincides with the highest pH in the solution. Ziper et al. (1988) suggest that the ion exchange process rules the adsorption of Cd. Therefore, the presence of less H^+ ions favours the adsorption of Cd, which results in an isotherm with a steeper slope in Figure 4.8b. Following the behaviour of low amounts of metal adsorbed, the slope of the adsorption isotherm represents the ratio between k_a and k_d, which are the velocity constants of adsorption and desorption respectively. Having a k lower than unity means that the desorption velocity is higher that the adsorption velocity. Therefore, the reactions that happen in the interphase show that the release of the metal from the clay is favoured. k_d is almost 10 times higher than k_a. This explains the low amounts of metal adsorbed and also indicates that 24 hours is not the ideal time to retain Cd as for this time k_d is around 20 times higher than k_a.

The change in the adsorption isotherm at 24 hours coincides with the decrease in pH of the solution (Table 4.11 and Figure 4.4c). This difference between the first 12 hours of adsorption and 24 hours could indicate that after 12 hours, there are certain reactions that inhibit the adsorption of Cd. The drop in pH between 12 and 24 hours indicates the deprotonization of the clay and this enhances the competition of H^+ ions for empty negative spaces in the clay that results in lower retention of Cd. It is believed that the drop in pH is causing the reduced Cd uptake by the kaolinite. If the pH had remained constant this reduction would not have been expected. At the exposure time of 0.1 hours, the pH is not as low as for 24 hours but as can be seen in Figure 4.8b the adsorption is not as high as for the other times. This behaviour indicates that despite the fact that the adsorption phenomena is a relatively fast phenomena, the clay adsorbs higher amounts of Cd between 1 and 12 hours.

From the adsorption isotherm data it is concluded that 24 hours is not the time of maximum adsorption of Cd due to the appearance of secondary reactions inhibiting the process. This is probably caused by the decrease in pH.

The isotherm for Zn does not follow the trend expected, as it does not fit any of the 3 stages explained earlier. A trend similar to Cd might be expected because the two metals posses similar characteristics. Nevertheless, the adsorption appears to stabilize between the 1 mM/L solution and 2 mM/L solution but then there is an increase in the amount of Zn adsorbed when kaolinite is in contact with the higher metal concentration. The changes in the pH are not being reflected in the adsorption isotherms, as the drops in the pH do not impact the shape of the curve. This indicates the presence of secondary reactions involving the adsorption or release of H^+ ions. Like the other metals, the isotherm for 0.1 hours yields the lowest amount of metal adsorbed probably as a result of the exposure time.

4.7.2 Desorption

The desorption test results are presented in Table 4.12. Desorption was performed on the 1 mM/L solution of each of the three metals. The amount of metal adsorbed prior to exposing the clay to the EDTA solution is similar to the amount of metal adsorbed in other adsorption experiments. In other words, for the desorption tests, separate adsorption tests were conducted. The desorption data yields unexpected results for Cd and Zn as the concentrations of metal desorbed are higher than the concentrations of metal initially adsorbed. Only Pb yields coherent results with a desorption between 70-100% depending on the exposure time.

Table 4.12 Desorption results for the three metals for 1 mM/L concentration.

	Metals								
Time of desorption	Cd			Pb			Zn		
	A	D	% d	A	D	% d	A	D	% d
1	0.7	4.8	670	5.7	5.8	101	1.5	4.8	317
2	0.6	4.5	755	5.6	5.6	100	1.7	4.5	262
4	0.7	4.4	622	5.6	5.1	91	1.7	4.8	288
8	0.8	4.4	525	8.2	5.9	72	1.8	4.7	256
12	0.9	4.4	474	5.8	5.5	95	1.8	4.8	288
24	0.8	4.4	538	5.9	5.8	98	1.7	4.8	288

A= adsorption (µm/g kaolinite) D= desorption (µm/g kaolinite) % d= percentage desorbed

The high desorption of Pb is in agreement with the results found by Farrah and Pickering (1978) and Hong and Pintauro (1996) where Pb is desorbed from kaolin at around 90% of the total amount of metal adsorbed initially. EDTA is a chelator that is widely used in the desorption of metals and it possesses a large affinity for Pb (Hong and Pintauro 1996) and in general for most metals in solution. The desorption mechanism seems to be effective in the first 2 hours, declines in the next 6 hours to only 70% of the total possible desorption, and then increases to 100% again at 12 and 24 hours. The quickness of the reactions also indicates that the metals, at least Pb, are attached on the outside surfaces of the clay as the chelant has accessibility to them.

An affinity of EDTA for the different metals cannot be established as tests with Zn and Cd yield results that are not in agreement with the mass balance. As can be seen in table 4.12, the percentages of Cd and Zn released are higher than 100%. The results of the acid digestion tests show that the amount of these metals present in the clay are not high enough to give these percentages. The pollution of the sample during the runs was not an option because the tubes were compatible with the samples used, and also the experimental procedure was careful enough to avoid that problem.

It may be that the reason for the results obtained is the interference of Fe oxides in the reading of the concentrations of Cd and Zn (Alberga et al. 1994). The results of the acid digestion test show that the clay has a high amount of Fe, supporting the supposition of interference. Both Cd and Zn overlap the spectrum signal of Fe on the A.A. spectrometer and this overlap usually produces readings of higher concentrations than are actually in solution (Zhang et al. 1997). In the case of Zn the concentration could increase readings by up to 2.3 mM/L (Alberga et al. 1994). Since the concentrations handled are small, an interference of this magnitude could result in desorption data being much higher than 100%.

The concentrations of EDTA used during desorption are much greater than the amounts of metal adsorbed, therefore, the EDTA could react with the Fe that is in the clay, making it soluble, with the possibility of its being in the supernatant along with the desorbed metal. In this way, the only readings affected are the ones taken while the samples are exposed to the EDTA solution and the adsorption data would not be affected.

4.7.3 Proposed Reactions

The data obtained in the study gives some information about the reactions that are taking place in the interphase between the clay and the solution. In the literature, there is little information about the specific reactions during adsorption. However, the information gathered in the study is sufficient to propose some reactions between the metal solution and the clay. The adsorption is taking place in a closed system hence; there is a limitation of compounds that could react with the metal in solution. These compounds are likely to be the reactive spaces of the kaolinite, which have been identified by Suraj et al. (1997) and Sparks et al. (1995), and the iron oxides present in the clay as an impurity. The reactions could not be confirmed by thermodynamic equilibrium due to the lack of data available, especially for the products of the reactions. However, as a result of the closed system, there is a good opportunity that the reactions proposed in this section or a similar reaction, take place during the adsorption of the metals.

The reactions involve the exchange of H^+ ions for different metal cations and the electrostatic attraction of metal cations for negative sites on the kaolinite. The available reactive spaces for kaolinite are the broken edges of the kaolinite structure, the exposed hydroxyl groups, the exposed oxygen groups and finally the silicon oxide groups (Suraj et al. 1997, Sparks et al. 1995). From these sites, the most important during the metal adsorption are the kaolinite broken edges due to the unsatisfied charge in the clay structure; these sites are shown in Figure 2.1. Following in importance are the exposed hydroxyl groups and the exposed oxygen groups, which participate in the adsorption mainly as a consequence of the oxygen high electronegativity creating a negative charge around oxygen that attract cations; these sites are shown in Figure 2.2. Finally, the silicon oxides sites could also participate in the adsorption of metals. However, their importance in the adsorption depends on the dissolution of aluminium hydroxides at around pH 4.4; these sites are shown in Figure 4.10.

Under the experimental conditions of the solutions, precipitation is not likely a predominant retention mechanism (Potter and Yong 1999, Farrah and Pickering 1976, Farrah and Pickering 1979, Schultness and Huang 1990). In agreement with the results reported by Farrah and Pickering (1979), the ratio of H^+ ions released does not correspond exactly with the amount of metal adsorbed. This has been discussed earlier in the chapter yielding a conclusion that there are secondary reactions besides cation exchange between the metals and hydroxyl groups.

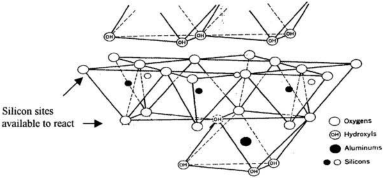

Figure 4.10 Example of the structure of kaolinite with $Al(OH)_3$ dissolved (Modified from Grim 1962)

Since the sample is polluted with Fe oxides, these sites will also play a role in the adsorption of the metal. Potter and Yong (1999) reported a larger affinity of metals for Fe oxides than for kaolinite. Of the elements of which the clay is composed, the aluminum hydroxide sites are favoured for adsorption but some dissolution of these sites could occur at pH levels below 4.4 (Schultness and Huang 1990).

In general the adsorption reactions for the Pb, Cd and Zn involve similar reactions in the interphase. However, each metal interacts differently with the clay yielding different proportions for each reaction that results in the difference in the amount of metal adsorbed. The general form of the reactions is presented in Figure 4.11.

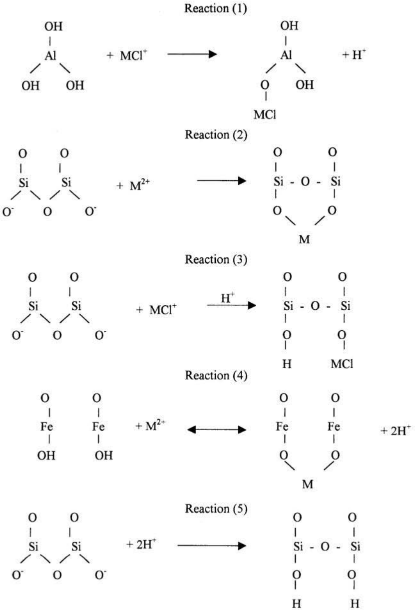

Figure 4.11 Proposed reactions between metals and kaolinite

In the case of Pb, the pH data shows that the adsorption could be happening at both, the Fe oxide sites and some of the $Al(OH)_3$ sites, for the 1 mM/L, 2 mM/L and 3 mM/L solutions (reactions 1 and 4 in Figure 4.11). At the experimental conditions, the dissolution of aluminum hydroxide sites will be limited (dissolution of $Al(OH)_3$ begins at pH=4.4) and the metal will interact with these sites and the exposed silica sites (Schultness and Huang 1990).

The release of H^+ ions from reactions (1) and (4) will reach a maximum at the eighth hour for Pb and the decrement in H^+ ions concentration will be due to reactions with silica sites present in the clay (reaction 3). Another option for the adsorption of Pb is reaction (2), which is the interaction with the silicon oxides sites exposed by the dissolution of aluminium hydroxides. Among the three Pb concentrations, the reactions that are the most important could vary.

The case of Cd is different than the other two metals. Since the pH of the solution reaches a maximum between 2 and 12 hours of exposure, this is an indication that the H^+ ions are being adsorbed at the broken edges of the clay or by the Fe oxides (the adsorption of H^+ ions onto Fe oxides is represented in Figure 2.3). Since the Fe oxides increases the CEC of the kaolinite and reactions with Cd are ruled by electrostatics forces (Ziper et al. 1988), it can probably be concluded that Fe oxides will play an important role in the adsorption of Cd (Reaction 4 in Figure 4.10) despite Cd preference for Al-OH sites (Puls and Bohn 1988). The increases in the pH of the Cd solution could also be explained by the presence of reaction (5).

Finally, the Zn shows a similar trend to that of the Pb, but the pH of the solution is slightly higher for this metal. For the 1 mM/L solution, the dominant species of Zn will be Zn^{2+} (Farrah and Pickering 1976) and since this metal can penetrate through the pore-spaces and has a large affinity for Al sites (Suraj et al. 1997, Schultness and Huang 1990) the reaction is likely to happen at the aluminium hydroxyl sites yielding a release of H^+ ions to the solution (reaction 1 in Figure 4.10). The peak in release of H^+ ions is obviously at the 8th hour, decreasing after that. The decrement of the H^+ ions in the solution could be a consequence of their reacting with exposed silicon sites (reaction 2).

For the other two Zn concentrations, the pH is higher. These conditions will favour the adsorption on aluminium hydroxyl sites. However, The pH of the solution remains somewhat constant. The adsorption is releasing H^+ ions (reactions 1 and 4) but there are empty negative spaces available for the H^+ ions to be readsorbed (reaction 2), therefore the pH in the solution will not be changed during time.

After reviewing the behaviour of the three metals, some conclusions can be established: (1) For Pb and Zn, the pH change in the solution is too insignificant to interfere with the adsorption, (2) For Pb and Zn, the adsorption happens in specific sites for the metals, therefore there is little competitions with H^+ ions (3) the adsorption of Cd is more influenced by the change in the pH compared to Pb and Zn (4) the presence of Fe oxides affects the pH in the solution, probably creating specific sites for the H^+ ions to react and be adsorbed in the clay (5) the affinity for this clay could be established as $Pb^{2+}>Zn^{2+}>H^+>Cd^{2+}$ (6) the adsorption of Cd and Zn occurs quickly in comparison with the adsorption of Pb.

Chapter 5

Conclusions and Recommendations

5.1 Foreword

This final chapter presents a review of the results and analysis gathered in the study. From the analysis made in chapter four, it can be concluded that the results are in agreement with similar adsorption studies. The suggestions for future research are also given at the end of the chapter.

5.2 Conclusions

The adsorption of Cd, Zn and Pb were studied over different exposures of time. The results gathered in the study present further information about the interactions in the interphase between the metal solution and the clay.

The acid digestion test on the clay shows that the concentration of Fe in the kaolinite is higher than would normally be expected. This suggests the presence of Fe oxides which adds more variables to the problem. The Fe oxides probably caused the increment in the CEC, the PZC and possibly the SSA of the soil. They also, provide the clay with another possible site for interactions with the metal during the adsorption process. Despite the indications that there could be an increase in the amount of metal adsorbed with these changes, the adsorption was not extremely high and the percentage of the CEC used was relatively low. Also, the excess Fe does not change the affinity sequence for kaolinite as Pb yields higher amounts of metal adsorbed, with Zn and Cd following in that order.

One of the objectives of the research was to observe the relationship between the H^+ ions released and the metal adsorbed in the clay. From the results obtained in this study, there is no linear relationship between these two variables as the kinetics of the adsorption of metals and desorption of H^+ ions is different among the experimental time. Hence, the interactions will depend on the time of exposure and the type of metal used. However, the ratio of H^+ ions released and metal adsorbed yields a polynomial and logarithmical trend that seems to fit the metal behaviour for the 24 hours for the three metals. The complexity of the Zn and Pb curves could be that the adsorption of these metals depends on more variables than Cd. Those variables could be the amount of Fe oxides that participate in the reaction, the amount of kaolinite, the pH of the solution, and the metal used. The ratio of H^+ ions released to metal ions adsorbed is also affected by the presence of Fe oxides because they provide the H^+ ions with another site for interactions and the possibility of their re-adsorption onto the clay.

The pH level in the solution undergoes significant changes during the adsorption of the metals. Nevertheless, in the case of Zn and Cd, between 0 and 12 hours these two variables seem not to be related as the concentration of metal retained remains approximately constant while the pH in the solution changes. Hence, the change in the pH of the solutions during the first 12 hours seems to be independent of the adsorption. Also, the stabilization of the adsorption of Zn and Cd until twelve hours shows that the changes in the pH levels do not affect the adsorption process and therefore, it seems possible that the H^+ ions are being adsorbed at different sites than the metals. With Pb adsorption there is also a significant change in the pH level during the first hours that does not affect the adsorption of the metal. The difference with Zn is that when adsorption equilibrium is reached, the H^+ ions released seems to yield equilibrium too.

The time of exposure is a variable that is overlooked in many studies but as the data shows, the timing is important in determining the amount of metal adsorbed. There are instances with each of the three metals where a greater amount of metal adsorbed occurs other that at a time of 24 hours (which is considered the equilibrium time). Also, the data shows that Cd and Zn are adsorbed quicker that Pb (Table 4.8, time 0.1 hours) but after an hour Pb adsorption increases. Only Pb shows a small difference between the value at equilibrium and the highest amount adsorbed. In the case of Cd, the difference is notorious between the first 12 hours, where there is temporary equilibrium in the adsorption, and 24 hours. The adsorption of Zn remains reasonably constant thought the exposure time. Nevertheless, the first hour of exposure reports a higher adsorption of Zn and the trend shows that the adsorption concentration reduces with time. With this information, it can be concluded that 24 hours is not the time when there the highest adsorption of the metals, and depending on the purpose of the study this must be considered along with the other variables such as pH, type of clay and metal used.

The trends obtained in the adsorption isotherms are anticipated in the case of Pb and Cd. In the case of Pb, this metal is reaching the equilibrium with the solution of 3 mM/L and possesses two types of reactions for different exposure times. This explains the presence of two different slopes in the adsorption isotherms. Cd is still in the transitory stage and the presence of higher concentrations of Cd in solution should yield higher amounts of metal adsorbed. Unlike the other two metals, the trend of Zn does not show if the adsorption is at the equilibrium or the transitory stage. The collection of more data will provide an answer as this study only used three different concentrations of the metal solution. Nevertheless, it is important to notice that the three different concentrations of Zn have the same trend along all the exposure times.

The desorption study could not be completed as a consequence of interference of Fe during the A.A. spectrometry measurements. Nevertheless, some insight was obtained about the efficiency of EDTA as an extracting agent. For desorption, the exposure times were not that conclusive as the metal desorbed remains constant during the first hours of exposure with only a drop at the eighth hour. Hence, for the treatment of polluted kaolinite it will only take one or two hours to detach more than 90% of the metal adsorbed if the metal is Pb. In future studies, the presence of Fe must be carefully monitored to avoid problems with the A.A. spectrometry readings, especially if the metals used are Cd and Zn.

The specific reactions proposed at the end of chapter four are based on the information available in the literature and the information gathered in this study, however, this reactions were not validated by any analytical method. Nevertheless, the reactions are likely to happen, as there is a limited amount of compounds present in solution. From the results obtained, it can be concluded that Fe oxides play an important role during the adsorption process for the three metals by either reacting directly with the metal or adsorbing H^+ ions present in the solution. As a consequence of the contamination of the kaolinite, the amount of Fe oxide sites present in the clay are higher than usual, therefore, there is the possibility that not only are the metals reacting with these sites but the H^+ ions present in the solution are also reacting there.

The low pH levels present during the adsorption process do not seem to prevent the adsorption of the metals .The changes in the pH levels as a result of the adsorption also do not seems to prevent adsorption except for Cd after twelve hours.

The information gathered in this research will be helpful in the soil remediation process. EDTA is commonly used to extract metals and its efficiency is a function of pH (i.e. low pH levels yield low desorption), hence, the change in pH as a consequence of the adsorption could affect the extraction of the metals from the soil. Also, by examining the results of the research, it is clear that pH is changing over time. Models that try to characterize soils need to take this into account to represent the phenomenon accurately. Presently, many models assume a constant pH during adsorption. For the three metals, maximum uptake occurs between 4 and 12 hours suggesting that remediation processes could be more efficient with the knowledge of the kinetics of the metal adsorption and H^+ ions desorption.

More extensive research should be done in this area to expand the information gathered in this study. Nevertheless, the fact that there are specific reactions in the interphase that have been proposed could reduce the uncertainty and could help to manipulate the adsorption behavior in benefit of human activities.

5.3 Recommendations

The use of unpolluted clay is highly recommended for the study of the reactions between the clay and the metal solution. The reason for this is that the pollutants add more variables to the study, which affects the trends in the adsorption and increase the reactions that need to be followed.

In the case of Cd and Zn, it will be worth following the adsorption of these metals in the range of minutes instead of hours to observe how the adsorption and the pH levels are changing during that short exposure time. Also, the use of higher concentrations of metals will be useful to observe the trend in the adsorption isotherms.

A.A. spectrometry is a very useful technique to determine the concentration of metals in solution, but since Fe is a common compound in some clays, more sensitive methods are recommended when determining the concentration of Cd and Zn, if there is the danger that Fe might be released from the clay. For the Pb desorption test, since the range of hours seems to be enough to complete the process, the reduction of exposure times to the range of minutes could give more insight about the desorption mechanism of Pb. For Pb and Zn, testing between 12 and 24 hours could help to establish the trend of the ratio of H^+ ions released to metals adsorbed as a function of time. Finally, since aluminium and silica sites seem to be participating in the reactions it would be useful to know the variation of concentration of aluminium and silica in the clay and in the solution.

5.4 Future Research

The results obtained in the thesis expand the knowledge about the adsorption of metals onto kaolinite. However, there are still some questions about the kinetics of the reaction and the adsorption mechanisms. Future researches could focus on the individual interactions between the clay elements and the metals salts to obtain the selectivity of the kaolinite (i.e. aluminium hydroxides, silica oxides and Fe oxides solutions with the metal salts). The follow up of the pH in these experiments will be also helpful to determine the pH changes present in this research. An insight of the polluted kaolinite structure will be helpful to understand how the Fe oxides are interacting with the solutions, as there is little information in how these elements are distributed in the clay structure. Finally, additional runs between 0.1 hour and 1 hour and between 12 and 24 hours could give more information about the kinetics of the reactions.

Appendix A

Adsorption and Desorption Raw Data

A.1 Adsorption Raw Data for Zinc

Dif= difference
F= final
K= kaolinite

Beaker #	Kaolinite	time	Solution	pH o	Zn Conc f	Zn f	pH f	dif Zn	Dif H+
	grs	hrs	mM/l		ppm	mM		mM/grs k	mM
A	2.0019	0.1	0.97	4.6	6.2	0.0190	3.7	0.0002	0.0035
B	1.9900	0.1	0.97	4.6	5.8	0.0177	3.8	0.0008	0.0027
1	2.0015	8	0.97	4.6	4.9	0.0150	3.2	0.0022	0.0115
2	1.9980	8	0.97	4.6	5.0	0.0153	3.2	0.0021	0.0100
7	2.0083	24	0.97	4.6	5.2	0.0159	3.5	0.0017	0.0058
8	2.0042	24	0.97	4.6	5.1	0.0156	3.4	0.0019	0.0061
13	2.0055	12	0.97	4.6	5.1	0.0156	3.5	0.0019	0.0051
14	2.0068	12	0.97	4.6	5.1	0.0156	3.5	0.0019	0.0051
19	2.0050	1	0.97	4.6	5.1	0.0156	3.6	0.0019	0.0040
20	2.0081	1	0.97	4.6	4.9	0.0150	3.6	0.0022	0.0040
25	2.0053	2	0.97	4.6	5.2	0.0159	3.4	0.0017	0.0073
26	2.0066	2	0.97	4.6	5.2	0.0159	3.4	0.0017	0.0063
31	2.0060	4	0.97	4.6	5.2	0.0159	3.4	0.0017	0.0071
32	2.0010	4	0.97	4.6	5.3	0.0162	3.4	0.0016	0.0075

Beaker #	Kaolinite	time	Solution	pH o	Zn Conc f	Zn f	pH f	dif Zn	Dif H+
	grs	hrs	mM/l		ppm	mM		mM/grs k	mM
C	1.9900	0.1	1.92	4.6	11	0.033644	3.7	0.0024	0.0035
D	1.9900	0.1	1.92	4.6	11.2	0.034256	3.7	0.0021	0.0035
3	2.0006	8	1.92	4.6	10.6	0.032421	3.5	0.0030	0.0057
4	2.0070	8	1.92	4.6	10.8	0.033033	3.6	0.0027	0.0051
9	2.0024	24	1.92	4.6	11.1	0.03395	3.8	0.0022	0.0031
10	2.0070	24	1.92	4.6	11.0	0.033644	3.6	0.0024	0.0050
15	2.0050	12	1.92	4.6	10.8	0.033033	3.6	0.0027	0.0043
16	2.0068	12	1.92	4.6	10.8	0.033033	3.5	0.0027	0.0053
21	2.0092	1	1.92	4.6	10.5	0.032115	3.5	0.0031	0.0055
22	2.0065	1	1.92	4.6	10.6	0.032421	3.6	0.0030	0.0051
27	2.0031	2	1.92	4.6	10.7	0.032727	3.5	0.0028	0.0058
28	2.0072	2	1.92	4.6	10.6	0.032421	3.6	0.0030	0.0048
33	2.0017	4	1.92	4.6	10.6	0.032421	3.4	0.0030	0.0073
34	2.0060	4	1.92	4.6	10.7	0.032727	3.5	0.0028	0.0057

Beaker #	Kaolinite	time	Solution	pH o	Zn Conc f	Zn f	pH f	dif Zn	Dif H+
	grs	hrs	mM/l		ppm	mM		mM/grs k	mM
E	2.0055	0.1	2.94	4.6	14.7	0.044961	3.6	0.0069	0.0045
F	1.9990	0.1	2.94	4.6	14.1	0.043126	3.6	0.0078	0.0045
5	2.0000	8	2.94	4.6	14.3	0.04373	3.6	0.0075	0.0041
6	2.0069	8	2.94	4.6	13.8	0.04220	3.7	0.0083	0.0039
11	2.0060	24	2.94	4.6	13.8	0.04220	3.7	0.0083	0.0039
12	2.0021	24	2.94	4.6	13.7	0.04190	3.7	0.0084	0.0034
17	2.0046	12	2.94	4.6	14.0	0.04282	3.7	0.0080	0.0033
18	1.9975	12	2.94	4.6	13.7	0.04190	3.7	0.0085	0.0032
23	2.0067	1	2.94	4.6	14.1	0.04312	3.7	0.0078	0.0034
24	2.0040	1	2.94	4.6	13.7	0.04190	3.7	0.0084	0.0033
29	2.0030	2	2.94	4.6	14.2	0.04343	3.7	0.0077	0.0037
30	2.0044	2	2.94	4.6	14.2	0.04343	3.7	0.0077	0.0033
35	2.0030	4	2.94	4.6	14.2	0.04343	3.6	0.0077	0.0045
36	2.0053	4	2.94	4.6	14.0	0.04282	3.6	0.0080	0.0049

A.2 Adsorption Raw Data for Cadmium

Dif= difference
F= final
K= kaolinite

Beaker #	Kaolinite	time	Solution	pH o	Cd Conc f	Cd f	pH f	dif Cd	Dif H+
	grs	hrs	mM/l		ppm	mM		mM/grs k	mM
A	1.9993	0.1	1.05	4.6	4.0	0.0178	3.8	0.0016	0.0027
B	1.995	0.1	1.05	4.6	4.0	0.0178	3.9	0.0016	0.0020
1	2.0038	1	1.05	4.6	3.9	0.0173	3.7	0.0018	0.0033
2	2.0035	1	1.05	4.6	4.1	0.0182	3.7	0.0014	0.0035
7	2.0069	2	1.05	4.6	4.2	0.0187	3.8	0.0012	0.0021
8	2.0000	2	1.05	4.6	4.2	0.0187	3.8	0.0012	0.0022
13	2.0057	4	1.05	4.6	4.3	0.0191	3.9	0.0009	0.0018
14	2.0020	4	1.05	4.6	4.1	0.0182	3.9	0.0014	0.0019
19	2.0031	8	1.05	4.6	4.4	0.0196	3.9	0.0007	0.0017
20	2.0057	8	1.05	4.6	4.3	0.0191	3.9	0.0009	0.0018
25	2.0066	12	1.05	4.6	4.4	0.0196	3.8	0.0007	0.0026
26	2.0047	12	1.05	4.6	4.1	0.0182	3.8	0.0014	0.0025
31	2.0060	24	1.05	4.6	4.3	0.0191	3.6	0.0009	0.0040
32	2.0059	24	1.05	4.6	4.4	0.0196	3.6	0.0007	0.0040

Beaker #	Kaolinite	time	Solution	pH o	Cd Conc f	Cd f	pH f	dif Cd	Dif H+
	grs	hrs	mM/l		Ppm	mM		mM/grs k	mM
C	1.9984	0.1	2.05	4.6	8.0	0.03558	3.7	0.0027	0.0035
D	1.9967	0.1	2.05	4.6	8.5	0.03781	3.7	0.0016	0.0035
3	2.0075	1	2.05	4.6	7.7	0.03425	3.7	0.0034	0.0040
4	2.0052	1	2.05	4.6	7.6	0.03380	3.7	0.0036	0.0039
9	2.0060	2	2.05	4.6	7.8	0.03469	3.7	0.0031	0.0033
10	2.0026	2	2.05	4.6	7.9	0.03513	3.7	0.0029	0.0033
15	2.0020	4	2.05	4.6	7.7	0.03425	3.8	0.0034	0.0029
16	2.0069	4	2.05	4.6	7.7	0.03425	3.8	0.0034	0.0029
21	2.0017	8	2.05	4.6	7.7	0.03425	3.8	0.0034	0.0027
22	2.0049	8	2.05	4.6	7.7	0.03425	3.8	0.0034	0.0028
27	2.0023	12	2.05	4.6	7.6	0.03380	3.7	0.0036	0.0034
28	2.0065	12	2.05	4.6	7.7	0.03425	3.7	0.0034	0.0034
33	2.0085	24	2.05	4.6	8.4	0.03736	3.5	0.0018	0.0054
34	2.0039	24	2.05	4.6	8.6	0.03825	3.5	0.0014	0.0053

Beaker #	Kaolinite	time	Solution	pH o	Cd Conc f	Cd f	pH f	dif Cd	Dif H+
	grs	hrs	mM/l		ppm	mM		mM/grs k	mM
E	2.0037	0.1	2.95	4.6	11.1	0.04937	3.6	0.0048	0.0045
F	2.008	0.1	2.95	4.6	11.2	0.04981	3.6	0.0046	0.0045
5	2.0008	1	2.95	4.6	10.4	0.04625	3.6	0.0064	0.0041
6	2.0080	1	2.95	4.6	10.9	0.04848	3.7	0.0052	0.0039
11	1.9988	2	2.95	4.6	10.7	0.04759	3.7	0.0057	0.0039
12	1.9992	2	2.95	4.6	10.8	0.04803	3.7	0.0055	0.0034
17	2.0008	4	2.95	4.6	10.5	0.04670	3.7	0.0061	0.0033
18	2.0064	4	2.95	4.6	10.6	0.04714	3.7	0.0059	0.0032
23	2.0055	8	2.95	4.6	10.7	0.04759	3.7	0.0057	0.0034
24	2.0044	8	2.95	4.6	10.6	0.04714	3.7	0.0059	0.0033
29	2.0000	12	2.95	4.6	10.6	0.04714	3.7	0.0059	0.0037
30	2.0072	12	2.95	4.6	10.8	0.04803	3.7	0.0055	0.0033
35	2.0031	24	2.95	4.6	11.9	0.05293	3.5	0.0030	0.0057
36	2.0030	24	2.95	4.6	12	0.05337	3.5	0.0028	0.0055

A.3 Adsorption Raw Data for Lead

Dif= difference
F= final
K= kaolinite

Beaker #	Kaolinite	time	Solution	pH o	Pb Conc f	Pb f	pH f	dif Pb	Dif H+
	grs	hrs	mM/l		ppm	mM		mM/grs k	mM
A	2.007	0.1	1	4.6	7.3	0.0176	3.7	0.0012	0.0035
B	2.0077	0.1	1	4.6	7.5	0.0181	3.6	0.0009	0.0045
1	1.9977	8	1	4.6	4.2	0.0101	3.2	0.0049	0.0115
2	2.0056	8	1	4.6	4.2	0.0101	3.3	0.0049	0.0100
7	2.0050	12	1	4.6	4.3	0.0104	3.5	0.0048	0.0058
8	2.0005	12	1	4.6	4.2	0.0101	3.5	0.0049	0.0061
13	2.0052	24	1	4.6	4.9	0.0118	3.6	0.0041	0.0051
14	2.0030	24	1	4.6	4.3	0.0104	3.6	0.0048	0.0051
19	2.0042	1	1	4.6	5.4	0.0130	3.7	0.0035	0.0040
20	2.0046	1	1	4.6	4.9	0.0118	3.7	0.0041	0.0040
25	2.0054	2	1	4.6	4.7	0.0113	3.4	0.0043	0.0073
26	2.0048	2	1	4.6	4.3	0.0104	3.5	0.0048	0.0063
31	2.0033	4	1	4.6	4.4	0.0106	3.4	0.0047	0.0071
32	2.0022	4	1	4.6	4.2	0.0101	3.4	0.0049	0.0075

Beaker #	Kaolinite	time	Solution	pH o	Pb Conc f	Pb f	pH f	dif Pb	Dif H+
	grs	hrs	mM/l		ppm	mM		mM/grs k	mM
C	2.0082	0.1	2.05	4.6	15.1	0.03644	3.5	0.0023	0.0058
D	2.0082	0.1	2.05	4.6	15.1	0.03644	3.5	0.0023	0.0058
3	2.0000	8	2.05	4.6	10.2	0.02461	3.2	0.0082	0.0113
4	2.0090	8	2.05	4.6	10.4	0.02510	3.3	0.0079	0.0107
9	2.0006	12	2.05	4.6	10.4	0.02510	3.3	0.0079	0.0089
10	2.0022	12	2.05	4.6	10.5	0.02534	3.4	0.0078	0.0084
15	2.0032	24	2.05	4.6	10.4	0.02510	3.4	0.0079	0.0076
16	2.0013	24	2.05	4.6	10.5	0.02534	3.4	0.0078	0.0076
21	2.0017	1	2.05	4.6	11.5	0.02775	3.5	0.0066	0.0058
22	2.0090	1	2.05	4.6	11.5	0.02775	3.5	0.0066	0.0057
27	2.0027	2	2.05	4.6	10.7	0.02582	3.4	0.0076	0.0080
28	2.0012	2	2.05	4.6	11.1	0.02679	3.4	0.0071	0.0076
33	2.0044	4	2.05	4.6	10.4	0.02510	3.4	0.0079	0.0080
34	2.0040	4	2.05	4.6	10.5	0.02534	3.4	0.0078	0.0078

Beaker #	Kaolinite	time	Solution	pH o	Pb Conc f	Pb f	pH f	dif Pb	Dif H+
	grs	hrs	mM/l		ppm	mM		mM/grs k	mM
E	2.0046	0.1	3.01	4.6	22.0	0.053089	3.4	0.0035	0.0075
F	2.0041	0.1	3.01	4.6	21.7	0.052365	3.4	0.0039	0.0075
5	2.0000	8	3.01	4.6	16.8	0.040541	3.6	0.0098	0.0041
6	2.0040	8	3.01	4.6	16.8	0.040541	3.7	0.0098	0.0039
11	1.9992	12	3.01	4.6	16.5	0.039817	3.7	0.0102	0.0039
12	2.0027	12	3.01	4.6	17	0.041023	3.7	0.0096	0.0034
17	2.0017	24	3.01	4.6	16.7	0.040299	3.7	0.0099	0.0033
18	2.0031	24	3.01	4.6	17.1	0.041264	3.7	0.0095	0.0032
23	2.0024	1	3.01	4.6	18.5	0.044643	3.7	0.0078	0.0034
24	2.0077	1	3.01	4.6	18.8	0.045367	3.7	0.0074	0.0033
29	2.0034	2	3.01	4.6	18.1	0.043678	3.7	0.0082	0.0037
30	1.9990	2	3.01	4.6	18.1	0.043678	3.7	0.0083	0.0033
35	2.0000	4	3.01	4.6	17.7	0.042712	3.6	0.0087	0.0045
36	2.0050	4	3.01	4.6	17.9	0.043195	3.6	0.0085	0.0049

A.4 Desorption Raw Data for Lead, Cadmium and Zinc

Dif= difference
F= final
K= kaolinite
D= desorption
O= initial

Beaker	Kaolinite	time	Pb o	Pb o	Pb o	Pb ads	Pb d	Pb d	% desorbed
	grs	hrs	ppm	mM/l	mM	mM/grs k	ppm	mM	
1	2.0060	1	3.5	0.4223	0.0084	0.0058	4.8	0.0116	100
2	2.0060	1	3.6	0.4344	0.0087	0.0056	4.7	0.0113	100
7	2.0085	2	3.5	0.4223	0.0084	0.0058	4.8	0.0116	100
8	2.0039	2	3.7	0.4464	0.0089	0.0055	4.5	0.0109	98
13	2.0038	4	3.6	0.4344	0.0087	0.0056	4.0	0.0097	85
14	2.0044	4	3.6	0.4344	0.0087	0.0056	4.5	0.0109	96
19	2.0038	24	3.5	0.4223	0.0084	0.0058	4.8	0.0116	100
20	2.0024	24	3.3	0.3982	0.0080	0.0060	4.8	0.0116	96
25	2.0046	12	3.5	0.4223	0.0084	0.0058	4.5	0.0109	94
26	2.0034	12	3.4	0.4102	0.0082	0.0059	4.7	0.0113	96
31	1.9990	8	3.6	0.1737	0.0035	0.0083	4.9	0.0118	72
32	2.0011	8	3.7	0.1786	0.0036	0.0082	4.9	0.0118	72

Beaker	Kaolinite	time	Zn o	Zn o	Zn o	Zn ads	Zn d	Zn d	% desorbed
	grs	hrs	ppm	mM/l	mM	mM/grs k	ppm	mM	
3	2.0035	1	5.4	0.8258	0.0165	0.0014	3.3	0.0100	350
4	2.0028	1	5.3	0.8105	0.0162	0.0016	3.4	0.0103	326
9	2.0034	2	5.3	0.8105	0.0162	0.0016	3.0	0.0091	288
10	1.9997	2	5.1	0.7799	0.0155	0.0019	3.0	0.0091	241
15	2.0042	4	5.3	0.8105	0.0162	0.0016	3.1	0.009482	297
16	2.0034	4	5.2	0.7952	0.0159	0.0017	3.2	0.009787	280
21	2.0036	24	5.1	0.7799	0.0155	0.0019	3.2	0.009787	257
22	2.0082	24	5.3	0.8105	0.0162	0.0016	3.2	0.009787	307
27	2.0082	12	5.1	0.7799	0.0155	0.0019	3.2	0.009787	257
28	2.0041	12	5.2	0.7952	0.0159	0.0017	3.2	0.009787	280
33	2.0010	8	5.1	0.7799	0.0155	0.0019	3.0	0.009176	241
34	2.0054	8	5.2	0.7952	0.0159	0.0017	3.1	0.009482	271

Beaker	Kaolinite	time	Cd o	Cd o	Cd o	Cd ads	Cd d	Cd d	% desorbed
	grs	hrs	ppm	mM/l	mM	mM/grs k	ppm	mM	
5	2.0050	1	4.4	0.9785	0.0195	0.0007	2.2	0.009786	685
6	2.0057	1	4.4	0.9785	0.0195	0.0007	2.1	0.009341	654
11	2.0025	2	4.5	1.0008	0.0200	0.0005	2.1	0.009341	949
12	2.0064	2	4.4	0.9785	0.0195	0.0007	2.0	0.008896	623
17	2.0043	4	4.5	1.0008	0.0200	0.0005	2.0	0.008896	904
18	2.0062	4	4.3	0.9563	0.0191	0.0009	2.0	0.008896	475
23	2.0018	24	4.3	0.9563	0.0191	0.0009	2.0	0.008896	475
24	2.0029	24	4.4	0.9785	0.0195	0.0007	2.0	0.008896	623
29	2.0070	12	4.3	0.9563	0.0191	0.0009	2.0	0.008896	475
30	2.0050	12	4.3	0.9563	0.0191	0.0009	2.0	0.008896	475
35	2.0022	8	4.4	0.9785	0.0195	0.0007	2.0	0.008896	623
36	2.0085	8	4.3	0.9563	0.0191	0.0009	1.9	0.008451	451

A.5 Error Analysis.

This section provides a sample of the error analysis calculated for the batch test data. The calculation of error was obtained followed the step taken by Coles (1998) where the amount of errors are added when there is the addition or subtraction of like quantities or the multiplication or division or like or unlike quantities.

The first step in the experiment was to prepare a metal solution. The salt used was $CdCl_2$, which has a molecular weight of 228.34 g/gmol, and the salt was dissolved in distilled water (D.W.). To obtained a 3 mmol/L solution of Cd, 0.6850 g of $CdCl_2$ were dissolved in DW.

$$\frac{0.6850\ g\ Cd\ \pm 0.14\%}{1\ lt\ \pm 5\%} x \frac{1}{228.34\ g/gmol} = 2.99\ mmol/g\ \pm 5.14\%$$

After the sorption of Cd onto kaolinite, the solution was diluted to read in the AAS.

$$\frac{2\ ml\ \pm 1\%}{50\ ml\ \pm 0.1\%} x2.99\ mmol/g\ \pm 5.14\% = \ 0.1199\ mmol/lt\ \pm 6.24\%$$

The data obtained in the AAS has a deviation of 0.5 ppm in the Cd readings. In this example, the value obtained is 10.8 ppm (which is 0.0967 mmol/lt).

$$0.1199\ mmol/lt\ \pm 6.24\% - 0.0967\ mmol/lt\ \pm 4.6\% = 0.02383\ \pm 11\%$$

The final step was to determine the amount of metal adsorbed per weight of kaolinite. The dilution factor of 25 is applied.

$$\frac{0.02383\ mmol/lt\ \pm 11\%}{2.0072\ g\ \pm 0.05\%} x25 = 0.02968\ mmol/gr\ kaolinite\ \pm 11\%$$

This means that the data obtained in the batch test are accurate within 11%.

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