Sorption of Zinc on Some Clay Soils in Malaysia

Ibrahim A. Al-Hawas[1]

ABSTRACT

Six soil samples represent the major soil series used for agricultural production such as Rubber, oil palm, cocoa and rice in Malaysia were sampled to study the adsorption capacity of zinc which consider as an environmental harmful metal. The objectives of this study were to report experimental results on adsorption of Zn and to determine the adsorption mechanism of these soils using different models. After soil characterization, sorption isotherms were prepared using the six different soils and initial zn concentrations ranged from 5 to 100 mg L^{-1}. The soils show different retention capacity. The highest sorption capacity was found in Melangit soil. Because of the presence of calcite and high pH, the precipitation of zinc was the dominate factor. Where the high Zn adsorption in Kundor soil attributed to the characterization of the soil. The high CEC and the clay content were the main factors. Zn adsorption isotherms corresponding to all soils adjusted to Langmuir and Freundlich empirical models. Results showed that Freundlich equation has highest value of correlation coefficient (r^2) comparison to Langmuir equations and that all soils have high affinity for Zn sorption. Therefore the main factors controlling the adsorption of Zn in these alluvial soil are precipitation and ionic adsorption.

Keyword: Zn, adsorption, Langmuir, Freundlich, calcite

INTRODUCTION

The behavior of heavy metals in soils has been extensively studied, and several review concerning retention phenomena have been published during the past 10 years (Uzun, and Guzel 2000; Muhamad 1998, Igwe, et. al., 2005). Adsorption isotherm analysis is useful in studying the retention process, because it provides a macroscopic view of the retention phenomena. Retention may be due to precipitation and / or adsorption (involving several molecular mechanisms) and depends on factors such as the nature of metal, nature of mineral and organic constituent of the soil, cation exchange capacity (Shuman, 1975) and the composition of soil solution. Most micronutrients (Fe, Mn, Zn, Cu, Co) are more readily available at a low pH. Many studies on adsorption of heavy metals by soils, pure mineral or organic adsorbents in suspension have shown that the pH is a master variable. Among potentially toxic trace metals, zinc (Zn) is one of the most widespread contaminants in the environment (Nriagu and Pacyna, 1988). It accumulates in soils by atmospheric deposition originating from smelting operations and by agricultural applications of sewage sludge and agrochemicals (Alloway 1990).

Zinc plays an essential role in cellular systems and enzymes (Silva and Williams, 1991). Zinc may be irreversibly fixed by clay through isomorphus substitutions or solid-state diffusion into the crystal structure of layer silicates (Adriano, 1986). Swift & McLaren (1991) reported that adsorption and desorption strongly affect the bioavailability of heavy metals and therefore toxicity in soil. The type and stability of metal sorption complexes formed at solution–particle interfaces depend on the solution conditions (pH and ionic strength) and the solid phase present (Maarten and Sparks, 2004).

For adsorption, cations are held either through electrostatic attraction, thus giving rise to exchange with the surrounding ions, or by specific adsorption through surface complexation on organic and mineral subsurface. Zachara et al., (1998) reported that uptake of Zn(II) by calcite in sorption experiments may include adsorption processes, incorporation of Zn(II) into the calcite structure, and the formation of Zn-hydroxy-carbonate precipitates. Whatever the mechanisms involved, retention in soils greatly determines the mobility and the behavaibiliy of heavy metals; it is therefore essential to improve our knowledge of this processes. In this study different type of soils have different chemical properties have been used. Our objectives were to:

(i) Identify the soil which has high capability to adsorbed Zn.

(ii) Understand adsorption mechanism of these soils using different models.

(iii) Established correlation between adsorption behavior and adsorption capacity of these soils.

MATERIALS AND METHODS

Soils:

Six surface (0-20 cm) soil samples represent the major soil series used for agricultural production in Malaysia were sampled. The soils classification present in Table (1). The soils were selected to be truly

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representative of the area and to give wide variation in soil properties. The soil samples were air dried and ground to pass through a 2 mm sieve.

Soil pH was determined using 1:2.5 soil/water ratio. Organic carbon (OC) by dichromate oxidation method (Nelson and Sommer, 1982). The cation exchange capacity (CEC) were determined by leaching with neutral ammonium acetate solution (Piper 1947). Ca-exchange of the soils was determined by extraction with 0.1M KNO_3 of the Ca sorbed from 0.025M $CaCl_2$ (Mackay et al., 1986). Mineralogical composition of the soils was determined using x-ray diffraction analysis (Page et al. 1982).

Table 1. The classification of the studied soils

Soil	Soil Classification	Latitude (N)	Longitude (E)
Sedu	Typic Sulfaquept	2° 30.238'	102° 48.505'
Segamat	Haplic Acrorthox	1° 56.287'	103° 11.533'
Kundor	Tropic Fluvaquent	1° 56.114'	103° 10.916'
Durian	Orthoic Tropudult	1° 50.443'	103° 07.343'
Melangit	Typic Paleudults	6° 05.287'	103° 20.148'
Betu Anam	Typic Paleudults	6° 31.097'	100° 10.468'

Sorption experiment:

Sorption isotherms were conducted at constant pH 7 and room temperature. The sorption of Zn was determined by adding 25 mL solution containing each of 0, 5, 10, 20, 40, 60, and 100 mg Zn as zinc chloride ($ZnCl_2$) in 0.01M $CaCl_2.2H_2O$ to 1 g soil in 50 ml polypropylene test tube. Triplicate samples were prepared for each solution concentration. The tubes were mechanically shaken for 24 hrs at 240 rpm and room temperature (25°C). Each sample was filtered through a Whatman No. 42 filter paper. The concentration of Zn in the filtrate was determined by ICP. The Zn sorption was calculated as difference between the Zn concentration in solution before and after equilibration. Two models, Freundlich and Langmuir isotherm models, have been used to study adsorption analysis. The Freundlich isotherm model was chosen to estimate the adsorption data according to the following formula:

$$x/m = AC^{bn}$$

where x/m is the amount of Zn retained by the soil in mg kg^{-1}, C is the equilibrium concentration of Zn in solution (mg L^{-1}), A is the maximum retention in m^3 kg^{-1} and the parameter b is bonding energy. A linear regression analysis was performed between Log C and Log (x/m). The slope and intercept were used to calculate b and A as well as to test differences among soils for Zn.

The Zn sorption isotherms were plotted using the mean quantity of Zn sorbed and mean Zn equilibrium concentration. The sorption data ere also plotted using the linear version of Langmuir equation:

$$C/(x/m) = 1/(k_1 k_2) + C/K_1$$

Where C is the equilibrium concentration of Zn in solution (mg L^{-1}), x/m is the quantity of sorbed Zn (mg kg^{-1}) on soil, k_1 is the adsorption maximum (mg kg^{-1}), and k_2 is a constant related to bonding energy of Zn to soil (m^{3}kg^{-1}).

A linear regression analysis was performed between C and C/x/m. The slope($1/k_1$) and intercept ($1/k_1 k_2$) were used to calculate k_1 and k_2 as well to test differences among soils for K_1 and k_2.

RESULTS AND DISCUSSIONS

Physico-chemical properties of soils:

General physico-chemical properties of soils, used in this study, were greatly differed (Table2). The soils were very acid to slightly alkaline with the lowest pH value at 3.00 (Sedu) and the highest pH is 7.3 at Melangit soil. The soils texture varied from silty to clayey. The highest clay content (870 g kg^{-1}) was found in Segamat series. Organic carbon range from 18 to 62 g kg^{-1} soil. The highest organic carbon was found in Durian series. The cation exchange capacity was relatively high ranged from 9.4 to 120 Cmol$_c$kg^{-1}. A very high CEC of Kundor soil (120cmol(+) kg^{-1}) is attributed to presence of high charge clay minerals and to the high content of organic matter. Exchangeable Ca range between 0.18 to 77Cmol$_c$kg^{-1}. The highest exchangeable Ca was found dominating the exchange site of the Kundor soils.

Table 2. Selected physical and chemical properties of the studied soils

Soil	Depth cm	pH in H_2O	Clay g Kg^{-1}	*Texture	Organic C g Kg^{-1}	CEC Cmol$_c$kg^{-1}	Exchangable Ca mmol$_c$kg^{-1}	Mineralogy of the clay fraction**
Sedu	0-20	3.0	490	SiC	18.8	38	2	K, Q, Gb, S, M, and J
Segamat	0-20	4.9	870	C	21.0	36	11	K, Q, Gb, and Go
Kundor	0-20	4.9	750	C	45.1	120	77	K, Q, M and S
Durian	0-20	4.4	480	SiC	62	31	2	K, Q, Gb, S, M, F, M+M-ML and M+S
Melangit	0-20	7.3	189.2	Si	5.4	9.4	0.18	K, Calcite
Betu Anam	0-20	5.4	630	C	15.7	42	21	K, Q, M and F

*C-clay, SiC- Silty clay, Si-silty

** K-Kaolinite, Gb- Gibbsite, Go- Goethite, F-Feldspar, M-Mica, Ml- Mixed layer, S-Smectite, Q-Quartz and J- Jarosite, CEC (Cation Exchange Capacity), O.C (Organic Carbon).

The studied soils varied in the clay mineralogy (Table 2). In general, smectite, kaolinite, and mica were the most common clay minerals in most soil samples. The clay fraction of soils Sedu, Kundor and Durian was dominated by smectite with a moderate amount of kaolinite and mica. In contrast, Melangit soil was dominated by kaolinite and calcite. Most of these soils considered highly weathered soils and hence, low amounts of 2:1 minerals present. The clay fraction of Betu Anam soils consisted of nonphylosilicate minerals such as feldspar. Goethite was detected only in Segamat soils, whereas gibbsite was found in three soil (Sedu, Segamat and Durian). However, quartz occurred in all studied soils in very low amounts.

Adsorption Mechanisms

The amount of sorbed Zn by soil greatly varied and depended on the physico-chemical properties of used soils. Sorption isotherms of Zn for studied six soils are shown in Figure(1). All used soils showed a high sorption capacity at low concentration of zinc (0-30 ppm). A sharp increase in the sorbed amount was noted with increasing of Zn concentration from 30 to 100 ppm in three soils Sedu, Durian and Batu Anam. The soil pH significantly affected the exhibited sorption, being maximum of Zn sorption was at soil with pH value of 4.5.

High increment in the amount of sorbed Zn by soils was in the order Melangit >Kundor > Segamat > Sedu > Durian > Batu Anam. The high adsorption of Zn in Melangit soil is attributed to the type of minerals present. Though, Melangit soil is silty with low CEC but, it has pH> 7, and dominated with calcite mineral these factors may have a high influence in increasing the retention of Zn. On the other hand, Kundor soil attributed to high content of clay fraction and exchangeable Ca and high CEC. Hanafi and Sjiola (1998) have shown that CEC is the most important factor controlling the adsorption of Zn in acid tropical soils. Whereas, Wahba and Zaghloul (2007) have reported a comparison between clay minerals and calcite and showed that calcite gave higher adsorption capacity compared with montmorillonite or kaolinite. For the $CaCO_3$ Papadopoulos and Rowell (2006) found that the precipitation of $CdCO_3$ on calcite predominates at higher Cd additions, whereas at low Cd additions an ideal surface solid solution is formed between $CdCO_3$ and $CaCO_3$.

Statistical parameter (r) was used to find the best fit of Zn sorption for three physicochemical equations Freundlich, Langmir and the second order equations. A comparison of the coefficient of regression (r^2) for the three isotherms is shown in Table3. For the Langmuir

isotherm r^2 have a range from 0.411 to 0.999 with an average value of 0.760. The range for r^2 by Freundlich is 0.349 to 0.926 and the average is 0.7205. For the second ordered equation isotherm the range of r^2 varied 0.366 to 0.997 with an average value of 0.774. Results obtained indicated that all equations showed similar average (r^2). Generally Langmuir equations was better to describe the relation between Zn concentration in equilibrium solution and its sorption by soils because of higher r^2 values compared to Freundlich equations (Table 3). Therefore, it could be concluded that Langmuir equations fits Zn sorption better. Al-Ameri (2001) in has study on the calcareous soils from Baghdad reported similar conclusions.

Table 3. Correlation using different equations Langmuir (L) and Freundlich (F) and second order equation

Soils	Isotherm		
	r^2 (F)	r^2 (L)	r^2
Sedu	0.903	0.821	0.845
Segamat	0.349	0.820	0.366
Kundor	0.857	0.999	0.755
Durian	0.551	0.514	0.785
Melangit	0.737	0.997	0.898
Betu Anam	0.926	0.411	0.997

The Adsorption coefficient (k_1-b) and bonding energy (log A – k_2) for both Freundlich and Langmuir are shown in (Table, 4). Zn adsorption showed the highest log A value was 2.865 m^3 kg^{-1} for Melangit soil and the lowest was 0.062 m^3 kg^{-1} for Betu Anam soil. The high value of log A indicated that the soil has high affinity to sorb Zn in comparison to the other soils with low value of Log A. In addition Melangit soil has pH > 7, and rich in calcite this could be an indication of precipitation of Zn as it explained by Ford and Sparks (2000) and Ford et. al. (1999). Who reported that at higher solute concentrations and pH > 6.5, Zn can be incorporated into neo-formed precipitates, formed at the surfaces of phyllosilicate minerals. These surface precipitates are formed at solution conditions undersaturated with respect to homogeneous precipitation. Metwally et. al.,(1993) suggested that aqueous Zn^{++}-$Zn(OH)_2$ aqueous controlled the solubility of zinc in soil and clay mineral suspensions at pH 7.5 - 9.0.

The bonding energy (b) values ranged from 0.269 to 1.1793. Most soils showed low b values except Betu Anam soil. The difference between soils could be related to the physiochemical properties such as acidity, fine texture and relatively high CEC. The low b indicate that Zn adsorbed on the surface in less than one layer and the bonding is could be Zn- Zn. Maarten and Sparks, (2004) suggested that in acidic to near
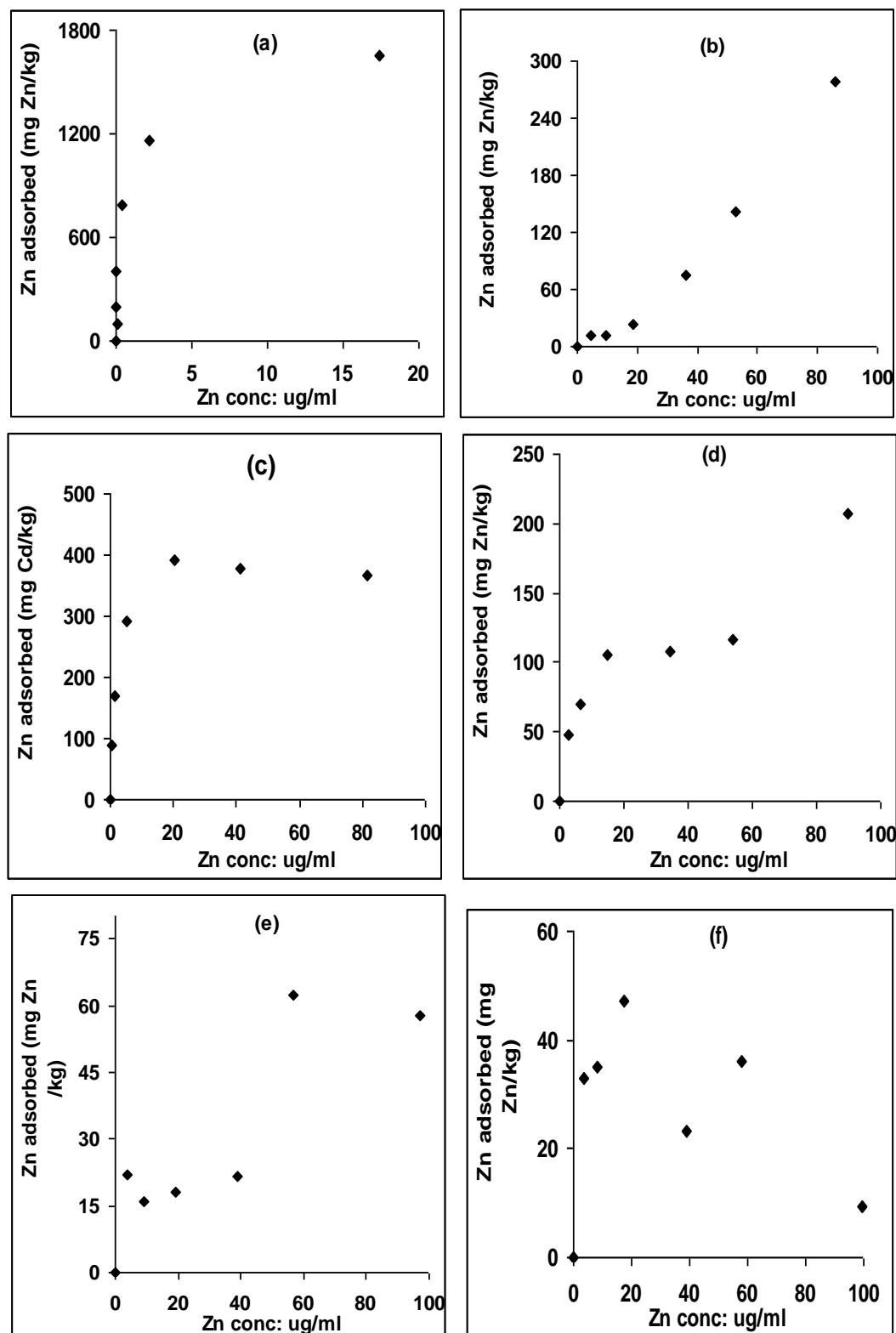
Figure 1. Zn sorption isotherms for (a) Melangite (b) Batu Anam (c) Kundur (d) Sedu (e) Durian (f) Segamat soils

Table 4. Adsorption coefficient (log A-k_2) and bonding energy (b-k_1) for both Freundlich and Langmuir equations

Soil Name	(Freundlich)		(Langmuir)	
	log A	b	K_2	K_1
Sedu	1.5466	0.3521	0.0548	0.207091
Segamat	1.7973	0.2686	0.7401	0.009812
Kundor	2.1441	0.2779	0.9539	0.376946
Durian	0.9457	0.3697	0.2295	0.078481
Melangit	2.8651	0.3850	1.8788	1.697217
Betu Anam	0.0621	1.1793	0.0067	0.212256

neutral environments, Zn partitioning to phyllosilicate surfaces mainly occurs by electrostatic interactions, due to a net negative structural charge developed within the octahedral layers of phyllosilicates and by specific chemical binding to hydroxyl edge sites.

Similar result was found with Langmuir equation where it shows that Melangit soil has the highest adsorption coefficient (k_1, 1.697), moreover, bonding energy (k_2) was higher in Langmuir than Freundlich equation for Melangit soil. Because of the Langmuir is liner equation it is better to explained the adsorption situation.

CONCLUSION

It is observed from the present study that zinc sorption varied greatly between soils. Evaluation of the adsorption isotherms tested, Langmuir can successfully be explained by a simple model that gave the best fit followed by Freundlich isotherm. The sorption process was found to be a physio-sorption process as seen from the apparent energy of adsorption.

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الملخص العربي

إمتصاص الزنك في بعض الترب الطينية في ماليزيا

إبراهيم بن عبدالرحمن الحواس

تم جمـع سـت عينـات تربـة تمثل المجموعـات الرئيسـة للـترب المستخدمة في الإنتاج الزراعي في ماليزيا, لدراسة قدرة إدمصاص الترب للزنك الذي يعتبر احد معادن البيئة الضارة. وكان الهدف من هذه الدراسة هو تحديد نتائج تجارب إدمصاص عنصر الزنك و تحديد آلية إدمصاص هذه الترب باستخدام نماذج مختلفة. وبعد تحديد خصائص التربة،تم الحصول على منحنى الإدمصاص عن طريق إضافة ستة محاليل تحتوي على تراكيز بين 5 و 100 مغلم/لتر من $ZnCl_2$. و لقد أظهـرت التربة قـدرات اسـتيعابية مختلفـة. و لقـد كانـت اعلى قـدرة إدمصاص في تربة ميلاجيت و نظرا لوجود الكالسيت وارتفاع درجة الاس الهيدروجيني, لذا فان العامل الرئيس للنسبة العالية هو ترسيب

الزنك. ولكن ارتفاع إدمصاص عنصر الزنك في تربة كوندور يعزى الى خصائص التربة. فالمحتوى العالي من الطين و السعة التبادلية الكاتيونية هـي الأسباب الرئيسـة. ولقـد تم توضيح نتـائـج الإدمصـاص لجميع الترب باستخدام النماذج التجريبية لمعادلة لانجومير وفريندليتش. وتبين النتائج التي تم الحصول عليها من معادله فريندلتش أن قيم خط الميول (R) أعلى من تلك التي تم الحصول عليها باستخدام معادلة لانجمير و أن جميع الترب لها قدرة عالية على إدمصاص عنصر الزنك. لذلك فإن العوامل الرئيسية التي تؤدي الى الإدمصاص العالي للزنك في هذه الترب الطينية هي الترسيب و الإدمصاص الأيوني.