

Sorption-Desorption of Zn by a Rhodic Khandiustult in the Northern Guinea Savanna of Nigeria

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Abstract: Zinc adsorption at concentrations between 0-50 mg Zn l⁻¹ was evaluated in surface and subsurface samples of a basaltic soil in the Northern Guinea Savanna, a Rhodic khandiustult. After adsorption, 3 consecutive extractions (desorption) in sequence were performed to the samples by using 25 mL of 0.1 NHCl. The results showed that the Ap and Bt horizons have large capacities to adsorb zinc. While the desorption showed that the sorbed zinc was not rigidly bound. The amount of zinc released in the Ap horizon was slightly more than that released in the Bt horizon, i.e., Zn was more difficult to release in the Bt horizon than in the Ap horizon. The adsorption data did not fit the linear form of either the Langmuir or the Freundlich isotherms. The amount of Zn needed to be added to give a critical level of 1.0 mg kg⁻¹ was estimated to be 20 mg kg⁻¹ of Zn and above in the Ap horizon. Whereas it was estimated to be 40 mg kg⁻¹ and above for the Bt2 horizon. The examined soil could offer an effective way to increase or decrease zinc ions concentration.

Key words: Sorption, desorption, langmuir isotherm, freundlich isotherm, zinc, rhodic khandiustult

INTRODUCTION

The Nigerian Savanna covers an area of about 780,000 km² and has a wide range of climatic conditions. Basaltic soils are found around the Jos plateau, Jema' plateau of Kaduna, Biu and Mambilla plateau. Basalts approach gabbro in chemical composition (Vilenskii, 1960). Their structure is variable and for most parts, they are minutely granular. The basaltic soil colours range from dark through brown to red and thick depending on its vegetation, slope and drainage (Jamice, 1968). Basaltic soils contain high proportion of micronutrients including Zn, B, Cu, Fe, Mn, Mo, Co and Cl (Nyle, 1974).

To that end, widespread Zn deficiency for different crops has been observed in different parts of the world including from Nigeria. Correction of such Zn deficiency is often accomplished by applying Zn to the soil as fertilizer. Its availability to crops as well as its concentration in soil solution is controlled by sorption-desorption reactions at the surfaces of soil colloidal materials Swift and McLaren (1991) cited by Mandal *et al.* (2000). Although desorption rather than adsorption likely controls the amount and rate of release of Zn into soil solution for plant uptake, only a few studies have examined the process in detail (Brunner *et al.*, 1983; Dang *et al.*, 1994). Desorption of Zn into soil solution is controlled by the energy with which it is adsorbed onto the soil colloidal surfaces. This in turn depends on the

soil characteristics, particularly pH, Cation-Exchange Capacity (CEC), the nature and content of the clay and different oxides of Fe, Al and Mn and CaCO₃ (Harter, 1991; Razra and Biswapati, 1996). Zinc adsorption on the other hand is the process by which Zinc is made present in the soils as a mineral and also held by exchange sites and solid surface this adsorption affects zinc availability to plants. The activity of zinc ions in the ambient soil solution bathing plant roots is controlled by simultaneous equilibra of several competing reactions such as specific bonding, surface exchange, lattice penetration, precipitation reaction and the processes leading to desorption of surface and lattice bound ions. Characterization of the solid phase supply of Zinc in relation to surface chemical reaction provides the net effect of all simultaneous equilibra controlling the activity of zinc ions in the ambient soil solution. This enables calculations of such parameters as quality intensity and buffering capacity of the soil which when combined into a united expression called supply parameter can be related to the uptake of zinc by crops (Khasawneh and Copeland, 1973). The process that control the mobility of zinc in soils include: the desorption of zinc from exchange complex solution, release of zinc from organic matter crystalline minerals as well as other precipitates of the solution phase. However, the sequential desorption of zinc by water in different electrolytes, complexing agents and mineral acids provide a measure of different chemical

pools of zinc in soils. Such pools have been referred to as water-soluble, exchange, specifically adsorbed, chelated and complexed-zinc and zinc in secondary and primary minerals (Keefer and Estep, 1971; Smith and Shoukry, 1968; Tiller *et al.*, 1972; Sinha *et al.*, 1975). Contribution of these forms to the available pool of zinc may vary depending on the physical and chemical properties of soils. Several factors have been found to influence the available zinc status of the soil (Macias, 1973). The sandy leached Inceptisols and Ultisols or Oxisols of the southern savanna and derived savanna were described as low in available zinc (Lombin, 1983) stated that the organic matter serves as the main reservoir of plant available zinc in these Nigerian savanna soils in view of the small amount of clay content.

Responses to zinc application in soils and its corresponding effects on plants have been obtained in several locations within Nigerian savanna zone (latitude 7°30'-14°0'N). It was observed that plant responses has also been quantified in terms of Phytoremediation which has emerged as an alternative technique for removing toxic metals from soil and offers the benefits of being *in situ*, cost-effective and environmentally sustainable (McGrath and Zhao, 2003; Banuelos, 2006). A laboratory study was undertaken to determine the zinc retention and release capacity of a Rhodic kandiuult as well as to determine if zinc adsorption by basaltic soils conforms to Langmuir and Freundlich Isotherms and based on the results make recommendations on how zinc could be best economically maintained or increased in the soils.

MATERIALS AND METHODS

Environment of study/location: Soil samples used in the study of adsorption and desorption of zinc came from a basaltic soil profile from Manchok on the Jema'a Platform, Kaduna state. Manchok is in the Northern Guinea Savanna zone. Two samples, one from the A horizon (surface horizon; Ap; 0-16 cm), the other from the Bt2 horizon (65-106 cm). The samples had already been prepared by air drying, grinding and sieving through a 100 mesh sieve and stored in clean cellophane bags for laboratory analysis.

Table 1 shows the physical and environmental set-up of the study area and soil classification while Table 2 shows the analytical properties of the soil. The low content of gravel and sand may be due to popular contention that quartz does not usually form in basalts as a result of low silica content of basaltic lava. Clay content of the basaltic savanna soil is high in both the Ap horizon (61%) and Bt2 horizon (73%). The soil is strongly acidic

Table 1: Soil sampling site, environmental set up and soil classification

Location	Gizagnoi village at Manchok (Latitude 09°40'N and Longitude 08°30'E)
Taxonomic classification	Rhodic Kandiuult (USDA) Haplic Acrisol (FAO/UNESCO)
Soil parent material	Saprolite from Newer basalts
Geology	Basement complex
Geomorphology	Nearly level plain with isolated basaltic cones in inselberg landscape
Topography	Crest, 0-1% slope
Ecological zone	Northern Guinea Savanna
Main grass species	<i>Hypprenia</i> sp.
Land use	Sorghum (<i>Sorghum bicolor</i> L.), millet (<i>Pennisetum</i> sp.), cassava (<i>Manihot</i> sp.), sweet potatoes (<i>Ipoemia batatas</i>)
Soil erosion hazard	None at profile site
Drainage	Well drained
Kparmwang (1993)	

Table 2: Summary of soil analytical properties of a rhodic Kandiuult on the Jema'a platform, Nigeria

Soil properties	Ap horizon	Bt2 horizon
Gravel (%)	0.00	1.00
Sand (%)	16.00	12.00
Silt (%)	23.00	15.00
Clay (%)	61.00	73.00
Textural class	Clay	Clay
pH (H ₂ O)	5.20	5.40
pH (CaCl ₂)	3.70	5.00
Ca (cmol(+) kg ⁻¹)	1.85	1.85
Mg (cmol(+) kg ⁻¹)	0.79	0.72
Na (cmol(+) kg ⁻¹)	0.05	0.03
K (cmol(+) kg ⁻¹)	0.17	0.07
Exchangeable acidity (cmol(+) kg ⁻¹)	0.50	0.10
CEC (soil) (cmol (+) kg ⁻¹)	13.00	9.00
CEC (clay) (cmol (+) kg ⁻¹)	12.70	11.70
Base saturation (%)	22.00	27.00
Organic carbon (%)	15.00	3.90
Total N (%)	1.30	0.60
Available P (mg kg ⁻¹)	9.50	0.50
Available S (mg kg ⁻¹)	11.80	2.30
Fe _p	0.01	0.02
Fe _{ox}	0.73	0.70
Fe _a	6.80	6.90
Al _{ox}	0.10	2.00
Al _d	0.15	2.00
Kparmwang (1993)		

(pH 5.2 and 5.4), low in exchangeable bases, base saturation and the CEC of the clay fraction but the CEC of the soil is relatively high. The organic carbon, total N contents are moderately high in the Ap but available P is low while available S is high in the Ap horizons but low in the Bt2 horizon.

Adsorption studies were carried out by weighing 5 g each of the Ap and Bt2 horizon soil samples into 40 different centrifuge tubes, 20 tubes for each of the Ap and Bt2 horizon. Dried Zinc sulphate solution (ZnSO₄) i.e., 2.51 g in 1000 mg (Zn L⁻¹) and water were then added to make a stock solution. The stock solution was further diluted to get the working solution (50 mL Zn L⁻¹) by pipetting 50 mL of the stock solution into a 1000 mL flask

and making to mark with distilled water. The centrifuge tubes were labeled A1-A20 for the A horizon and B1-B20 for the Bt2 horizon. This preparation was duplicated for A11-A20, respectively. The above preparation was also duplicated for B11-B20, respectively. All the preparations were made in duplicate (Arias *et al.*, 2005). Similarly, the standard solutions A1-A7 were also prepared. After the addition of the solutions as indicated above, the tops of the centrifuge tubes were closed with cellophane before working them to avoid spillage when shaking the tubes in a mechanical shaker.

They were now packed into the mechanical shaker and shaken vigorously for 5 h within a cumulative period of 24 (Wu *et al.*, 1999). The 47 centrifuge tubes containing the samples were now taken and centrifuged for 30 min at a high speed of 40 rpm (revolutions per minute) after which the soil samples settled at the bottom and the clear supernatant liquid obtained. Within 24 h, complete equilibration was attained (Arias *et al.*, 2005) and the solution (clear liquid) now filtered into glass containers and numbered properly A1-A20 and B1-B20 and the blank samples C1-C7. The clear extracts were now taken to the laboratory for reading on the Atomic Absorption Spectrophotometer (AAS) to read the concentration of the element zinc in the sample. The amount of zinc adsorbed was calculated by subtracting the amount of zinc in the supernatant solution after equilibration from the amount of zinc added (Arias *et al.*, 2005). Statistical analysis was made using the SAS (1988) statistical program.

RESULTS AND DISCUSSION

Zinc adsorption: The results showed that adsorption of Zn increases as the amount of Zn added increases both in the Ap and the Bt2 horizon (Fig. 1). Shuman (1976) reported similar findings. The Bt2 horizon adsorption was found to be higher than in the Ap horizon. This may be due to higher clay content of the Bt2 horizon (Table 2) which confers higher adsorptive capacity. This is however, contrary to the results obtained for the A and the Bt2 horizons of a Decateur soil (Rhodic Paleudult) by Shuman (1976) where the Bt2 horizon had lower adsorption capacity compared to the A horizon, even though it had higher clay content than the A horizon. The A however had higher Fe content than the Bt horizon. Hence, the researchers concluded that high clay content sometimes had to do with adsorptive capacities per unit clay. The soil studied however, had similar contents of Fe in the Ap and Bt2 horizons therefore, clay is likely to be the likely factor affecting the capacities of the Ap and Bt2

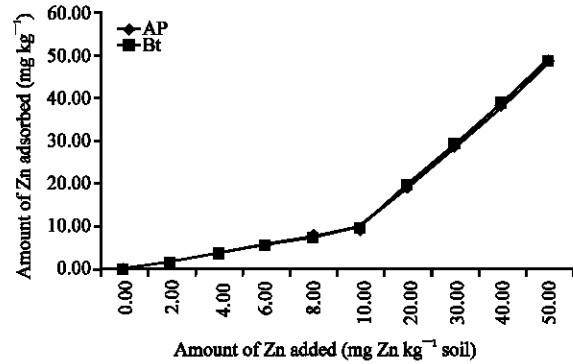


Fig. 1: Graph of amount of Zn adsorbed against amount of Zn added for both Ap and Bt horizons

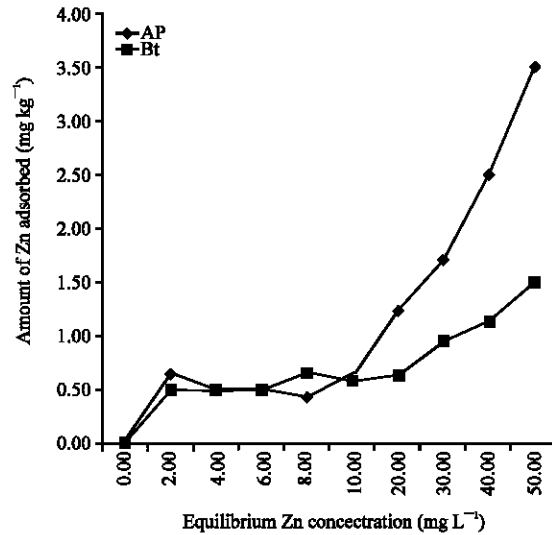


Fig. 2: Graph of amount of Zn adsorbed against equilibrium Zn concentration

horizons to adsorb Zn. This observation was further highlighted by Al-Qunaibit *et al.* (2005) and Erdem *et al.* (2004). They suggested that the adsorbent colloidal materials can be clay minerals, organic matter, iron and aluminium oxides, organomineral associations or natural zeolites and therefore, behaviour of heavy metals in soils therefore depends on the type of soil.

The statistical analysis was done using paired t-test procedure to compare the Ap and the Bt2 horizons adsorption. The adsorption data showed that there was no significant difference at 0.05% between the Ap and Bt2 horizons. This means that there is no much difference in amount of Zn adsorbed in concentration Zn L⁻¹ at both the Ap and Bt2 horizon profiles (Fig. 1). The trend in Fig. 2 showed that as the amount of Zn adsorbed increases, the equilibrium Zn concentration also increases (Fig. 2). For example, from 2-10 mg kg⁻¹ Zn added, the

amount of Zn adsorbed was almost equal in both the Ap and Bt2 horizons. This may be due to the low pH of the Bt2 horizon. Hawari *et al.* (2009) obtained similar adsorption equilibrium at low pH and therefore, concluded that maximum adsorption capacity of zinc was at pH value of 5. Further, Xue *et al.* (2009) found out that at pH 6, maximum adsorption of most metals occurred with zinc leading the sequence using a basic oxygen furnace slag. Similar pH was obtained in this study. However, a little variation was when 20-50 mg kg⁻¹ Zn was added, the Bt2 horizon adsorbed more Zn than the Ap horizon. This may be attributable to the higher clay content which imparts a higher capacity for it to adsorb Zn as against the higher organic carbon content of the Ap horizon, it was further observed that Zn adsorbed as organic colloids is more readily released than that adsorbed on inorganic colloids. In general it was observed that the equilibrium Zn mean concentration for the Ap horizon was higher than in the Bt2 horizon. This is an advantage, since the Ap horizon supplies most of the nutrients including Zn required by the plants.

Adsorption isotherms: The Freundlich equation Giles *et al.* (1974) cited by Arias *et al.* (2005) is:

$$X = K_F C^{1/n}$$

Where:

X = The adsorbed metal concentration (mg kg⁻¹)

C = The concentration of the metal in solution at equilibrium (mg L⁻¹)

K_F and 1/n = Constants

The Langmuir equation Giles *et al.* (1974) cited by Arias *et al.* (2005) is:

$$X = K_L X_m C / (1 + K_L C)$$

Where:

X_m = The maximum adsorbed metal concentration

K_L = The constant related to the energy of adsorption

These two equations were applied to the data and the results showed that the data obtained failed to conform to both the Langmuir and Freundlich isotherm as 2 attempts to fit the data to the 2 isotherms failed and hence were not presented. This was probably because the parameters of the equation had no physico-chemical meanings in the soil (Sposito, 1979; Barrow, 1985). The curves were erratic because the q and c values are low; a situation also encountered by Syers *et al.* (1973) with very low P adsorption values. Further, this observation was partially supported by the findings of (Arias *et al.*, 2005) in their

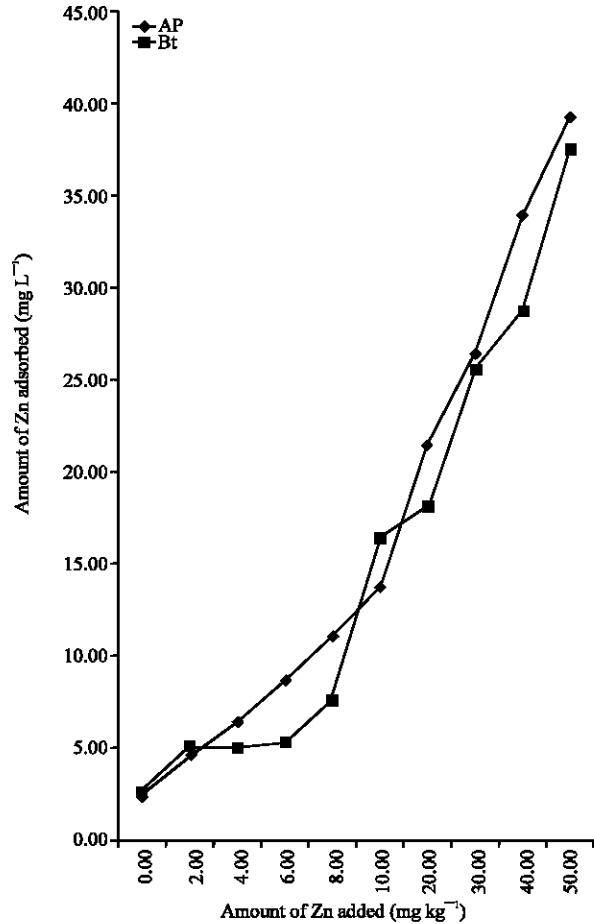


Fig. 3: Graph of amount of Zn desorbed against amount added for both ap and Bt horizons

own investigations; they found out that the data did not fit the Langmuir equation except the variation in the Freundlich equation which fitted the zinc data. Further, they concluded that the Freundlich equation is often useful for modeling adsorption onto solids with heterogeneous surfaces (Stumm and Morgan, 1981) and has frequently proved to be superior to the Langmuir equation.

Zinc desorption studies: The results showed that desorption increases with increase in amount of Zn added. Similar findings were obtained by Sidhu *et al.* (1977) using 0.1 M HCl for four different soils. There was lower desorption of Zn in the Bt2 horizon (15.13 mg kg⁻¹) than in the Ap horizon (16.69 mg kg⁻¹) (Fig. 3). This may be due to the higher clay content of the Bt2 horizon than the Ap horizon and also, the higher organic carbon content of the Ap horizon as earlier explained. In contrast (Yang *et al.*, 2007) observed that desorption was not

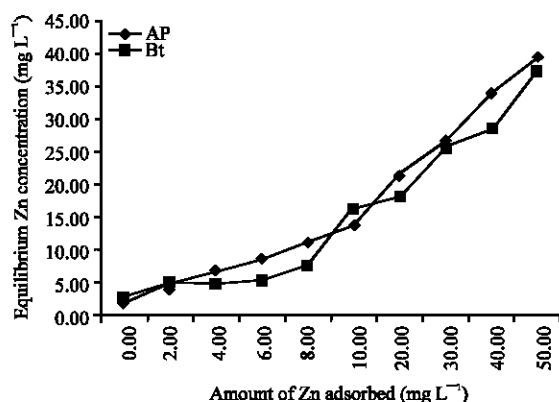


Fig. 4: Graph of amount of Zn desorbed against equilibrium concentration of Zn

possible and they attributed this to the ultrafine nature of the particles used for the studies. When the amount of Zn desorbed (equilibrium concentration) was related to the amount adsorbed as shown in Fig. 4, the Bt2 was found to be higher than the Ap horizon. This property is probably due to the higher retentive capacity of the Bt2 horizon. The statistical analysis carried out using paired t-test between the Ap and the Bt2 horizon for T1, T2 and T3; the desorption was found to be non-significant statistically. However, the summation of the Ap horizon for the 3 stages of desorption was higher than that of the Bt2 horizon, confirming the fact that Zn desorption in the Ap horizon was easier than in the Bt2 horizon. It is important to note that in the 2nd stage of desorption, the Bt horizon mean was higher than the Ap horizon indicating higher desorption in the Bt2 2nd stage but as stated this was not statistically significant.

Similarly, using the Analysis of Variance procedure (ANOVA) to compare the amount of Zn desorbed at the 3 stages within the Ap and Bt2 horizons, it was observed that at the Ap horizon, the 1st desorption (9.028) was statistically higher than the 2nd desorption (4.681) and 3rd desorption (2.980). The latter two were the same statistically. Thus, desorption was in the descending order of means as follows: replicate 1 > replicate 2 > replicate 3 but in the statistical order of replicate 1 > replicate 2 = replicate 3. For the Bt horizon, replicate 1 (7.163) is statistically similar to replicate 2 but different from replicate 3. However, replicate 2 (5.279) and replicate 3 (2.667) were found to be statistically similar.

CONCLUSION

Zinc adsorption and desorption studies were conducted in the Ap (0-16 cm) horizon and Bt2

(65-105 cm) horizon of a Rhodic Khandiustult. The amount of zinc adsorbed increases as the amount of zinc added increases, implying that zinc adsorption is concentration dependent. The statistical analysis showed that there was no significant difference between the amount of Zn adsorbed in the Ap and that of the Bt2 horizons but the mean amount of Zn adsorbed in the Bt2 horizon was higher than that of the Ap horizon. For desorption there was also no significant difference between the Ap and Bt2 horizon but the mean amount of Zn desorbed was higher in the Ap than in the Bt2 horizon. The summation of the three sequential desorption were as follows: for Ap: replicate 1 (90.28) > replicate 2 (46.81) > replicate 3 (29.28) while the Bt2 were: replicate 1 (71.63) > replicate 2 (52.97) > replicate 3 (26.67). However, for the replicate 2, Bt2 was higher than the Ap summation implying higher adsorption in the Ap horizon.

In comparing desorption within the Ap and within the Bt2 horizons, replicate 1 was statistically different from replicate 2 and replicate 3 which are the same for the Ap horizon. While in the Bt2 horizon, replicate 1 was not significantly different from replicate 2 but different from replicate 3 which was similar to replicate 2 statistically. The adsorption data did not fit either the linear form of the Langmuir or the Freundlich equation. Hence, the graphs were not presented. The soil was low in available Zn (Kparmwang *et al.*, 1998). But this study showed that the soils had a higher capacity to adsorb Zn. The study also showed that for the soil solution to have enough zinc above the critical available level of 1.0 mg Zn kg⁻¹ soil, then 20-50 kg⁻¹ Zn would need to be added for both the Ap and Bt2 horizon.

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