February 2014- April 2014, Vol. 4, No. 2; 1637-1645. E- ISSN: 2249 –1929

Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

*Available online at*www.jcbsc.org

Section D: Environmental Sciences

CODEN (USA): JCBPAT Research article

Zinc Sorptivity of Selected soils of Southern Nigeria

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Received: 20 December 2013**; Revised:** 04 February 2014**; Accepted:** 08 February 2014

Abstract: Zinc sorptivity of selected soils of Southern Nigeria was evaluated by equilibrating 2 g soil sample with 20 ml 0.01M $CaCl_2$ solution containing graded concentrations (0, 10, 20, 30, 40, 50 and 60 mg kg^{-1}) of Zn and sorbed Zn determined. Sorbed Zn was fitted to the Langmuir, Freundlich and Temkin isotherms and sorption maximum (b), affinity constant (k), bonding energy (n), distribution coefficient (k_f) and equilibrium Zn concentration (EPCo) determined. Sorption mechanism was estimated using the Gibbs free energy (ΔG). Furthermore, relationships between b, k, n, k_f, EPCo and ΔG with soil properties (clay, OM, pH, P, ECEC and Fe) were determined using correlation analysis. Direct and indirect effects of soil clay, pH, OM, P and ECEC on b was determined using Path analysis. Langmuir isotherm conformed better to Zn sorption than the Freundlich and Temkim isotherms. Soil b, k, n, k_f,EPCo and ΔG ranged from 64.39-112.36 and 67.93-114.94 mg kg^{-1}, 0.24-3.76 and 0.25-5.14 L mg^{-1}, 0.28-84.76 and 0.28-28.57 L kg^{-1}, 3.85-16.07 and 3.19-18.88 L kg^{-1}, 0.20-0.32 and 0.18-0.33 mg L^{-1} and -4598.79-- -2859.83 and -4489.40- -2809.76J mol^{-1} for surface and subsurface soil depths repectively. Zinc sorption capacity using b increased in the order Bende < Ihiagwa < Ahoada < Okigwe for both soil depths while the affinity constant (k) was Okigwe < Ihiagwa < Ahoada < Bende for surface and Ihiagwa < Okigwe<Ahoada <Bende for subsoil. Sorption mechanism was spontaneous and exothermic. Correlation between b, k, $k_{f,}$ n, and ΔG with clay, ECEC, OM, pH and P but not Fe and that between EPCo and ECEC, OM, pH and P but not clay and Fe were significant ($P < 0.05$). Path analysis showed significant direct effects of clay (r = -0.55), available P (r = -0.53) and pH r = 0.92) and non-significant direct effect of ECEC (r = -0.09) and OM (r = - 0.05) on b.

Keywords: Zinc, Sorptivity, Soils, Equilibrium, Southern Nigeria.

INTRODUCTION

Zinc deficiency has been widely reported in most semiarid calcareous soils, highly weathered tropical soils and coarse textured soils of different agro-ecological zones[1]. It thus, constitutes one of crops most limiting nutrients in the intertropical zones[2, 3]. Deficiency of zinc is associated with sorption reaction by soil constituents[2].The potential for Zn sorption varies, with soils of the savanna being higher than those of the forest zones[4]. Two mechanisms, adsorption and precipitation control sorption process, with adsorption occurring at low and precipitation at high equilibrium ion concentrations. Studies of sorption processes could be undertaken using sorption isotherms, with the most frequently used types being the Langmuir, Freundlich and Temkin isotherms[2, 5].

Sorption processes are driven by certain energies, the extent and spontaneity of which could be elucidated using thermodynamics principles[2, 6]. For instance, the Gibbs free energy which is a measure of the force that guides the adsorption reaction or the force corresponding to the transfer of element from bulk solution into the appropriate site of the double layer or clay mineral lattice helps in the expression of sorption process[2, 6]. Soil properties especially pH, clay content, OM, Fe and Al oxides and CEC influence zinc sorption capacity, with the nature of the relationship often estimated using correlation analysis.

This provides information on whether the relationship is significant or not but does not indicate if the effect of soil properties on zinc sorption is direct or indirect. Another tool, the path analysis partitions correlation into direct and indirect effects and distinguishes between correlation and causation[7]. Its use has been extensive in the investigation of the relationship between soil properties and ions especially phosphorus and metal sorption[7, 8].

Few studies on Zn status of Nigerian soils have been reported[4, 9] but none contain information on the direct or indirect impacts of soil properties on Zn sorptivity. The objectives of the present study were therefore to estimate the Zinc sorption capacity, sorption mechanism and direct and indirect influence of selected soil properties on Zn sorption capacity of selected rainforest soils of southern Nigeria.

MATERIALS AND METHOD

Study Sites: The study sites were Ahoada, Bende, Ihiagwa and Okigwe and representing soils of different lithologies in Southern, Nigeria. Ahoada lies between Latitudes 5^0 03^1 and 5^0 05^1Nand Longitudes 6^0 26^1 and 6^0 39^1 E. Mean annual rainfalls of about 2680 mm and mean daily temperature of 26 ^{0}C.The soil type is Typic Dystropepts on recent alluvium parent material[10, 11]. Climax vegetation was a mixture of cassava/plantain interspersed with wild oil palm of more than 50 years old. Major economic activities of the area include farming, fishing and crude oil exploitation. Bende is located between Latitudes 5^0 25^1 and 5^0 52^1 N and longitudes 7^0 28^1 and 7^0 45^1 E, with mean annual rainfall and mean daily temperature of about 2400 mm and 27^0 C respectively[12]. Soil type is Typic- Haplustult derived from shale parent material[13].

Vegetation of the site consisted of cocoa, rice and cassava. Major economic activities include farming and trading. Ihiagwa is located between Latitudes 5^0 21^1 and 5^0 27^1N and Longitudes 7^0 02^1 and 7^0 15^1E, with mean annual rainfall of 2075mm and mean daily temperature of 28^0C.The soil type is Arenic Kandiudult underlain by coastal plain sands parent material[14]. Vegetation of the site was secondary forest. Major economic activities are farming, trading and artisanry. Okigwe (Lats. $5^045^{1'}$-$6^000^{1'}$N and longs. $7^015^{1'}$-$7^030^{1'}$E) has a mean annual rainfall of about 2250 mm and temperature of about 28^0C[13] .Its soil type is Typic Paleudult derived from false bedded sandstone[15]. Climax vegetation was cassava.

Sample Collection and Preparation: Three surface (0-15cm) and subsurface (15-30cm) soil samples each were collected from Ahoada, Bende, Ihiagwa and Okig were presenting soils formed over Alluvium, Shale, Coastal Plain sands and Sandstone parent materials respectively. The samples were air dried, sieved using 2 mm diameter sieve and the fine earth soil fractions analyzed for particle size [16], pH in 1:2.5 soil/H_20 ratio [17], organic matter[18], Total iron[19] and available P[20].

Sorption Studies: Sorption studies was conducted by equilibrating 2 g of the fine earth soil fraction in a 30 ml centrifuge tube with 20 ml of 0.01M $CaCl_2$ solution containing graded concentrations of Zn (0, 10, 20, 30, 40, 50 and 60 mg kg^{-1}) as $ZnSO_4$for 4 hrs. At the end of the equilibration period, the tubes were centrifuged at 5000 x g for 15 mins and the clear supernatant decanted into a 30 ml tube. Zinc concentration in the equilibrium solution was then determined using an AAS.

Calculations

1. Sorbed Zn

Sorbed Zn was obtained as:

Amount of Zn sorbed = Added Zn – Equilibrium solution Zn concentration … (1)

2. Zinc Sorption Parameters

i. Sorption maximum (b) and
ii. Bonding energy (k)) were obtained using the

Langmuir equation: $C/x = 1/k\,b + C/b$ … (2)

Where C = solution Zn concentration (mg ml^{-1}), x =Sorbed Zn (mg kg^{-1}), b = Zn sorption maximum (mg kg^{-1}) and k = a constant related to the bonding energy (L mg^{-1}). By plotting C/xvs. C, the slope is equal to 1/b and the intercept is equal to 1/k b.

i. Distribution coefficint or energy of adsorption (k_f)
ii. Intensity or energy of bonding was calculated using the Freundlich equation:

$$x = K_f C^{1/n} \quad \ldots (3)$$

Furthermore, the parameter (EPC_O) which is the solution Zn concentration when adsorbed and desorbed Zn is equal to zero was obtained using the equation:

$$EPC_O = S_o/Kd \quad \ldots (4)$$

Where S_o = initial or native sorbed Zn (mg kg^{-1}) and Kd a linear adsorption coefficient (L mg^{-1}).

By plotting a linear form (Xvs. C) of the equation,

$$S = Kd \times C - S_o \quad \ldots (5)$$

S_o could be obtained from the least square fit[21] as the intercept and Kd as the slope. Finally, the spontaneity of adsorption was calculated using the standard or

Gibbs free energy (J mol^{-1}) as:

$$\Delta G = -RT\ln K^o = RT(\log Ceq - \mathrm{Log}Co) \quad \ldots (6)$$

Where R is the universal gas constant (8.314J mol^{-1}), T is absolute temperature (kelvins), Ceq is the equilibrium Zn solution concentration and Co the added Zn.

Statistical Analysis: Simple correlation between soil properties and sorption parameters was performed using Genst at statistical package[22]. Soil properties that correlated significantly with sorption maximum (b) were partitioned into direct and indirect effects using Path analysis. The path diagram for the relationship between the selected soil properties and sorption maximum (b) is shown in **Fig. 1**.

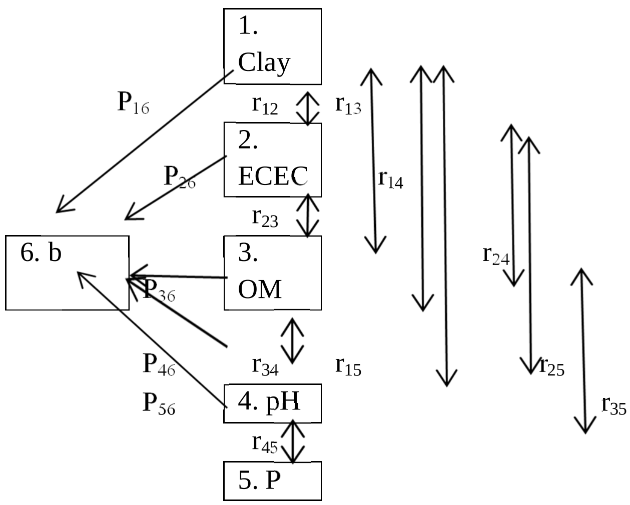

Fig 1: Path Diagram of the effects of soil properties on Zinc sorption maximum (b)

Direct effects are referred to as path coefficients and are standardized partial regression coefficients[7]. The direct effects of soil properties on b are represented by single headed arrows while the coefficients of inter-correlation between soil properties are indicated by double headed arrows. Indirect effects of soil properties on b are determined as the product of one double headed arrow and one single headed arrow. The independent variables considered included: clay content, ECEC, OM, P and soil pH. Also the relationship between sorption maximum and clay content, ECEC, OM, P and soil pH were considered. Path analysis results were then obtained from the following Path equations:

$$r_{16} = P_{16} + r_{12}P_{26} + r_{13}P_{36} + r_{14}P_{46} + r_{15}P_{56} \text{ --- } (1)$$

$$r_{26} = r_{12}P_{16} + P_{26} + r_{23}P_{36} + r_{24}P_{46} + r_{25}P_{56} \text{ --- } (2)$$

$$r_{36} = r_{23}P_{26} + r_{13}P_{16} + P_{36} + r_{34}P_{46} + r_{35}P_{56} \text{ --- } (3)$$

$$r_{46} = r_{34}P_{36} + r_{24}P_{26} + r_{14}P_{16} + P_{46} + r_{45}P_{56} \text{ --- } (4)$$

$$r_{56} = r_{45}P_{46} + r_{35}P_{36} + r_{25}P_{26} + r_{15}P_{16} + P_{56} \text{ --- } (5)$$

RESULTS AND DISCUSSION

Soil Characterization: All soil properties varied with parent materials **(Table 1).** Percent clay was higher in the surface (0-15 cm) relative to the subsurface (15-30 cm) soil, being better under shale and least under Alluvium parent materials. Soil organic matter, available phosphorus and ECEC followed similar pattern as the clay content, with soils under shale better than others probably due to its high fertility status. It has been indicated that fertility of tropical soils depends on their organic matter contents[23], and thus the high organic matter content under shale could be responsible for its high nutrient concentrations and fertility. Soils were generally acidic with the degree higher in the subsurface (15-30 cm) than surface (0-15 cm) soil and in soils under Alluvium than the other parent materials. Total Fe was better in the 15-30 cm soil depths, with concentrations under sandstone better than the other parent materials.

Table-1: Selected Properties of Soils of Dissimilar Parent materials in Southern Nigeria

Parent material	Location	Depth cm	Clay $g\ kg^{-1}$	OM	Avail P $mg\ kg^{-1}$	ECEC $cmol\ kg^{-1}$	Total Fe $g\ kg^{-1}$	pH (H_2O)
Alluvium	Ahoada	0-15	10.04	20.10	5.60	3.00	1.25	5.52
		15-30	20.04	0.89	2.80	2.56	1.27	5.38
Shale	Bende	0-15	450.04	3.75	11.20	8.90	0.40	6.65
		15-30	450.05	3.03	9.80	8.38	1.51	5.94
Ihiagwa	Coastal plain sands	0-15	270.14	1.41	4.20	4.66	0.48	5.61
		15-30	270.28	0.89	4.20	4.30	0.80	5.29
Okigwe	Sandstone	0-15	190.04	3.51	9.80	4.76	1.27	5.79
		15-30	330.04	1.86	5.60	4.66	1.43	5.61

OM =Organic matter, Avail P = Available phosphorus and ECEC = Effective cation exchange capacity

Zinc Sorption: Zinc sorption conformed to the Langmuir better than the Freundlich and Temkin isotherms, as reflected by the high R^2 values in the surface and subsurface soil depths(R^2 = 0.99 and 0.97, 0.96 and 0.94 and 0.91 and 0.89 for surface and subsoil using Langmuir, Freundlich and Temkin isotherms respectively).Sorption maximum (b) ranged from 64.39-112.36 and 67.93-114.94 mg kg^{-1}while the affinity constant (k) ranged from 0.24-3.76 and 0.25-5.14 L mg^{-1} in the surface (0-15 cm) and subsoil (15-30 cm) depths, respectively **(Table 2).** This showed that as b increased k also increased, with the subsoil better than surface soil. High b in the top soil and k for subsoil has been reported[6]. Zinc sorption capacity using the sorption maximum (b) increased in the order Bende < Ihiagwa < Ahoada < Okigwe for both soil depths while that for the affinity constant (k) was Okigwe < Ihiagwa< Ahoada < Bende for surface and Ihiagwa < Okigwe < Ahoada < Bende for subsoil. In both soil depths, Bende had the least Zn sorption maximum (b) but best affinity constants (k), indicating that sorbed Zn will be held with great tenacity in Bende than others. As affinity constant (k) increased, the energy of bonding (n) also increased, with best and least values being in Bende and Okigwe, respectively. The increase in k with n indicates that as the tenacity with which sorbed Zn increased, the bonding energy between soil and Zn also increased. The Freundlich distribution coefficient (k_f), a good index for characterizing the mobility and retention of Zn in soil solution [2] was related to the k and n.

According to[6], as$k_{f,}$ increases, mobility and the potential for environmental pollution decreases. Soil k_f ranged from 3.19-18.88L mg^{-1}, with Bende soil having the highest values of 16.07 and 18.88L mg^{-1} and Ihiagwa the least values of 3.85 and 3.19L mg^{-1} in the surface and subsoil, respectively. This signifies that Zn solubility and mobility and the potential for environmental pollution will be least in Bende soil with the highest k_f values. It has been reported that high k_f indicates low mobility and high retention of metals in soils while low values signify that most of the metals are soluble and available for transport, chemical processes and plant uptake[24]. The poor Zn mobility in Bende corroborated the low EPCo **(Table 2).** The EPCo refers to the metal or Zn solution concentration at which net sorption and desorption are equal to zero and is related to metal mobility. According to[25], as EPCo increases, metal solubility and mobility also increase. The EPCo values ranged from 0.20-0.32 and 0.18-0.33 mg L^{-1} for surface and subsurface soil depths, respectively.

Table-2: Sorption Parameters of the Soils

Location	Soil Depth cm	b mg kg^{-1}	k L mg^{-1}	EPCo mg L^{-1}	n Lmg^{-1}	k_f L mg^{-1}	ΔG (J mol^{-1})
Ahoada	0-15	101.01	0.28	0.25	0.35	8.02	-3034.91
	15-30	112.36	0.31	0.25	0.37	7.5	-2983.25
Bende	0-15	64.39	3.76	0.2	84.76	16.07	-4598.79
	15-30	67.93	5.14	0.18	28.57	18.88	-4489.4
Ihiagwa	0-15	98.04	0.25	0.32	0.28	3.85	-2859.83
	15-30	103.09	0.25	0.33	0.28	3.19	-2809.76
Okigwe	0-15	112.36	0.24	0.27	0.34	7.11	-3000.34
	15-30	114.94	0.27	0.27	0.32	5.96	-2949.25

Zinc sorption process was expressed using the Gibbs free energy (ΔG) **(Table 2)**,a thermodynamic parameter that measures the force corresponding to the transfer of an element from the bulk solution into the appropriate site of the double layer or clay mineral lattice or the force that guides sorption reaction[2]. The ΔG for the soils ranged between -2809.76 to -4598.79 $KJmol^{-1}$and similar to ranges obtained for some calcareous soils of Iran[2] but lower than ranges for some highly weathered Brazilian soils[6].

The values for the ΔG were negative indicating the feasibility of the spontaneity of Zn sorption with energy released for conversion of the less stable Zn forms in solution to adsorbed forms with greater stability[6]. Sorption parameters (b, k, $k_{f,}$ n, EPC_O) and process (ΔG) were affected by soil properties especially clay content, ECEC, OM, pH, P, and Fe **(Table 3).** Soil b, k, $k_{f,}$ n, and ΔG were significantly correlated with percent clay, ECEC, OM, pH and P but not Fe **(Table 3)**. Soil EPCo was significantly correlated with ECEC, OM, pH and P but not clay and Fe. Other workers have also reported correlations between kf and OM[2], kf and clay, ECEC and CCE[26], kf with pH and clay content [27], soil n with clay and ECEC[2, 26] , n with clay, pH and ECEC[28], b with clay content and ECEC[5]. No significant correlation has been reported between b and clay content, pH and OM[2].

Table-3: Simple Correlation between Selected Soil Properties and Sorption Parameters

	Sorption Parameters					
Soil Properties	**b**	**ΔG**	**EPCo**	**k**	**kf**	**n**
Clay	-0.45	-0.68	-0.33	0.71	0.54	0.48
ECEC	-0.57	-0.92	-0.63	0.93	0.81	0.66
OM	-0.31	0.73	-0.67	0.68	0.70	0.56
P	-0.47	-0.78	-0.68	0.76	0.76	0.58
pH	-0.38	-0.85	-0.68	0.89	0.75	0.87
Fe	0.31	0.11	-0.3	-0.26	0.13	-0.61

Path analysis partitioned each correlation (r) value of b versus soil properties into one direct and four indirect effects. Partitioning by path analysis showed significant direct effects by clay (r = -0.55), available P (r = -0.53) and pH (r = 0.92) on b. The direct effects of OM and ECEC on b were however not significant (p> 0.05).Path analysis also indicated that the indirect effects of clay (r = -0.50), available P (r = -0.46) and pH (r = 0.76) were responsible for the correlation between ECEC and b.

Similarly the indirect effects of clay (r = -0.43), available P (r = -0.46) and pH (r = 0.90) contributed to the correlation between OM and b. Hence clay, pH and P were the main factors for Zn sorption in the soils. Impact of clay included the increase in soil surface area and greater number of sorption sites [29]. Soil pH is related to the hydrolysis of metal ions and as it increased, the quantity of sorption sites with greater affinity for Zn sorption increases[6, 30].

According to[31] increase in Zn sorption with pH rise could be due to the complexation of Zn ions by OH^- and a higher net negative charge. Mechanism of P on Zn sorption includes the effect of P on the electrical potential of colloids which makes it more negative and thus facilitates sorption of metals such as Zn[3]. Also increase in soil pH with P addition could also increase Zn sorption. Due to the ability of oxyan ions such as P and as to form complexes with Fe and Al oxides, increase in Zn sorption with application of P has been linked to Fe oxide and other variables in soils with variable charges[3].

Table-4: Path Analysis of Direct (diagonal, underlined) and Indirect effects (off diagonal) of clay content, ECEC, OM, available P and soil pH on Zinc Sorption capacity of the soils

Response B	**Clay**	**ECEC**	**OM**	**Available P**	**pH**	**r**
Clay	-0.55	-0.08	-0.03	-0.34	0.56	-0.45
ECEC	-0.5	-0.09	-0.28	-0.46	0.76	-0.57
OM	-0.43	-0.27	-0.05	-0.46	0.9	-0.31
Available P	-0.29	-0.08	-0.36	-0.53	0.79	-0.47
pH	-0.46	-0.42	-0.08	-0.38	0.92	-0.38

CONCLUSION

Soil properties varied in relation to the parent materials. Zinc sorption conformed to the Langmuir better than the Temkim and Freundlich isotherms. Sorption maximum (b) was higher in the surface than the subsurface soil while the reverse was the case for the affinity constant (k). Zinc sorption capacity using sorption maximum (b) followed the order Bende<Ihiagwa<Ahoada<Okigwe for both soil depths while that for affinity constant (k) were Okigwe<Ihiagwa<Ahoada<Bende for surface and Ihiagwa<Okigwe<Ahoada<Bende for subsoil. Sorption mechanism using ΔG was negative indicating that it is spontaneous and exothermic. Zinc sorption was directly influenced by soil clay, pH and P but indirectly by the other factors.

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