Sorption of Zinc and Iron in Soils of Selected Areas in Southern Ethiopia

Abay Ayalew[1] Sheleme Beyene[1] Fran Walley[2]
1.Hawssa University, Ethiopia
2.University of Saskatchewan, Canada

Abstract

Sorption is one of the most important chemical processes in soils that determine the quantity of plant nutrients retained on soil surfaces and, therefore, affect transport of nutrients and regulate the concentration of nutrients in soil solution. A study was conducted in soils of Zeway, Alage, Butajira, Hawassa Zuria, Halaba and Taba in southern Ethiopia with the objective of evaluating the extent of Zn and Fe sorption. Surface soils (0-30cm depth) from the sites were collected, air dried and analyzed for particle size distribution, pH, EC, CEC, organic C, calcium carbonate equivalent, macro and micro nutrients using standard procedures. A 0.5 g soil sample was placed in a 100 ml plastic bottle and equilibrated with 0.01 M $CaCl_2$ overnight using a soil/solution ratio of 1:50 to determine the sorption of Zn and Fe. Stock solutions of $ZnSO_4$ and $FeSO_4$ with concentrations of 0, 2, 5, 10, 15 and 30 mg L^{-1}Zn Fe respectively were mixed with the soil-0.01 *M*$CaCl_2$ solution and equilibrated for 24 hours. The suspension was filtered, and the concentrations of Zn and Fe in the clear extract solution were determined using Atomic Absorption Spectrophotometer. The Langmuir and Freundlich adsorption equations were applied to determine the sorption relationships. The results indicated that the soils differ in physicochemical characteristics as well as Zn and Fe sorption capacities. Additionally, sorptions of the two micronutrients were high in all soils, except that of Zn in Hawassa soils, where added Zn was remained in the soil solution. Sorptions of Zn and Fe in the experimental soils followed Langmuir and Freundlich models, respectively. Zn adsorption was strongly related with soil organic carbon, calcium carbonate, iron and manganese contents of the soils, whereas iron was strongly related to clay. Fertilizer management for optimum crop production should therefore consider inclusion of Zn and Fe in the experimental sites, except Zn at Hawassa.

Keywords: Freundlich, Iron, Isotherms, Langmuir, Sorption, Zinc

Introduction

Sorption (adsorption) is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. Sorption is one of the most important chemical processes in soils that determine the quantity of plant nutrients, metals, pesticides and other organic chemicals retained on soil surfaces and, therefore, it is one of the primary processes that affect transport of nutrients and regulate the concentration of nutrients in soil solution (Dandanmozd and Hosseinpur, 2010). The distribution of a chemical substance between soil and aqueous phases is a complex process depending on a number of different factors: the chemical nature of the substance, the characteristics of the soil, and climatic factors such as rainfall, temperature, sunlight and wind. Thus, the numerous phenomena and mechanisms involved in the process of adsorption of a chemical substance by soil cannot be completely defined by a simplified laboratory model. However, even if this attempt cannot cover all the environmentally possible cases, it provides valuable information on the environmental relevance of the adsorption of an element. Adsorption is usually described through adsorption isotherms that is the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature (Da̧browski, 2001).

Langmuir and Freundlich isotherms are the most commonly and frequently used isotherms (Al-Degsa et al., 2006). Langmuir isotherm equation is the most common used due to its simplicity and ability to fit a variety of adsorption data. The Langmuir equation is intended for a homogeneous surface soils and a good fit of this equation reflects monolayer adsorption (Teng and Hsieh, 1998). It also enables to estimate maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface (Igwe and Augustin, 2007). In Langmuir adsorption model, a straight line is expected when equilibrium concentration divided by the amount of adsorption per unit adsorbent (x/m) is plotted against equilibrium concentration of adsorbate (Ce). Similar results are expected in the Freundlich model when log (x/m) is plotted vs. log Ce, and the comparisons among these models are based on the goodness of fit (Hussain et al., 2006).

Zinc and iron deficiencies are common in calcareous soils as a consequence of reaction taking place between soluble Zn/Fe in soil solution and solid phase leading to reduced availability of Zn/Fe to plants. Zinc and iron sorption by soils can be influenced by soil reaction, clay content, organic matter, carbonate content and amount of zinc applied (Al-Tamimi, 2006). Increasing soil pH increases the total number of negative sites on clay minerals and organic matter (OM), and therefore increases the capacity for Zn/Fe sorption (Dandanmozd and Hosseinpur, 2010). Availability of Zn decreases with increasing soil pH due to increased adsorptive capacity, the formation of hydrolysed forms of zinc, possible chemisorption on calcium carbonate and co-precipitation with iron oxides. At pH greater than 7.0 the hydrolyzed species Zn $(OH)^+$, $ZnHCO_3^+$, Zn $(OH)_3^-$ are present in sufficient amounts relative to Zn^{2+} to be important in adsorption reactions (Alloway, 2008). Availability of Fe also decreases with increasing soil pH as Fe is converted to less soluble forms, principally to the oxide (Fe_2O_3), and precipitated in to Fe $(OH)_3$, which is chemically equivalent to the hydrated, $Fe_2O_3.3H_2O$ (Fageria et al., 1990). The rate of Zn and Fe sorption from solution to solid surfaces is a dynamic factor that directly or indirectly regulates the amounts of the minerals in solution and their availability (Diatta and Kociałkowski, 1998). Adsorption and or precipitation on surfaces of soil solids decrease the concentration of Zn/Fe in solution phase. Sorption study is useful for generating essential information on the mobility of Zn/Fe and its distribution in the soil. It can be used in the prediction or estimation of the availability of Zn/Fe transformation and uptake by organisms and run-off from land surfaces into natural waters.

Abay et al. (2015) reported that the soils in the study sites had alkaline reactions with pH of more than 7.4, and the contents of Zn and Fe were low in most of the soils. The authors also indicated clay content of Taba, Halaba and Butajira soils, and calcium carbonate of Zeway, Hawassa, and Alage soils were high, which could adsorb more Fe and Zn. The available Zn and Fe contents of most of the soils were low, which could be attributed to sorption of these minerals by the soils (Abay et al., 2015).

Therefore, this study was conducted with the objective of determining Fe and Zn sorption capacity of soils in different parts of southern Ethiopia.

Material and Methods

The study was conducted with soils collected from Zeway, Taba, Butajira, Hawassa Zuria, Alage and Halaba in southern Ethiopia. One composite sample from 10 random surface soil samples (0-30cm depth) was collected from each study site. All samples were air dried at ambient temperature (25 °C), crushed and sieved to pass through a 2-mm sieve prior to soil analysis and sorption studies. Particle size analysis was carried out by the modified sedimentation hydrometer procedure (Bouyoucos, 1951). The pH of the soils was determined in H_2O (pH-H_2O) 1:2.5 soil to solution ratio using a pH meter. Organic carbon content of the soils was determined following the wet combustion method of Walkley and Black as outlined by Sahlemedhin and Taye (2000). Soil total nitrogen was analyzed by wet-oxidation procedure of the Kjeldahl method (Bremner and Mulvaney, 1982). Available phosphorus was analyzed using the Olsen sodium bicarbonate (pH 8.5) extraction method and determined using a spectrophotometer at 882 nm. Exchangeable basic cations and the cation exchange capacity (CEC) of the soils were determined using the 1*M*NH4OAc (pH 7) method as outlined by Sahlemedhin and Taye (2000). Exchangeable Ca and Mg in the leachate were determined using atomic absorption spectrophotometer (AAS), whereas K and Na were measured using aflame photometer. Available micronutrients (Fe, Mn, Zn, and Cu) contents of the soils were extracted by diethylene triamine pentaacetic acid (DTPA) method (Tan, 1996) and the contents in the extract were determined by AAS.

Stock solutions of Zinc and iron were prepared by dissolving $ZnSO_4$ and $FeSO_4$ in a 0.01 M calcium chloride ($CaCl_2$) solution, which was used as the aqueous solvent phase to improve centrifugation and minimize cation exchange (Dandanmozd and Hosseinpur, 2010). A 0.5 g soil sample collected from each site was placed in a 100 ml plastic bottle and equilibrated by shaking with 22.5 ml of 0.01 M $CaCl_2$ overnight (12 h). Then, 2.5 ml of the stock solution of the Zn and Fe was added in order to adjust the final volume to 25 ml. The concentrations of the stock solutions were 0, 2, 5, 10, 15 and 30 mg L^{-1}Zn and Fe. The mixture was shaken for 30 minutes and equilibrated for 24 hours. The suspension was filtered, and the concentrations of Zn and Fe in the clear extract solutions were determined using Atomic Absorption Spectrophotometer. One control sample with only Zn/Fe in 0.01 M $CaCl_2$ solution (no soil) was subjected to precisely the same steps as the test systems, in order to check the stability of the test substance in $CaCl_2$ solution and its possible adsorption on the surfaces of the test vessels. A blank run per soil with the same amount of soil and total volume of 25 ml 0.01 M $CaCl_2$ solutions (without Zn or Fe) was subjected to the same test procedure. This serves as a background control during the analysis to detect interfering compounds or contaminated soils. All the experiments, including controls and blanks, were performed in triplicate. The amount of Zn or Fe adsorbed was calculated as the difference between initial Zn or Fe concentrations and that remaining in solution after equilibration.

For studying the sorption relationship (for interpreting the reaction of zinc/iron with soil), the Langmuir and Freundlich adsorption equations were applied.

Langmuir equation: $Ce/qe = 1/Kb + Ce/b$,…………..Equation (1)

where Ce is the Zn or Fe concentration in the equilibrium solution (mg L^{-1}), qe is the amount of Zn or Fe adsorbed by the soil (mg kg^{-1}), b is adsorption maximum (mg kg^{-1}), and K is the bonding energy coefficient (L mg^{-1}).

Freundlich equation: $\log qe = \log Kf + 1/n \log Ce$, …………Equation (2)

where qe is the amount of Zn or Fe adsorbed by the soil (mg kg^{-1}), Ce is the Zn or Fe concentration in the equilibrium solution (mg L^{-1}), Kf is proportionality constant (mg kg^{-1}), and 1/n is slope of the curve, when log (qe) vs. log (Ce) was plotted.

The Langmuir adsorption maxima and bonding energy constant were obtained from slope and intercept, respectively, by regressing Ce/qe against Ce. An adsorption maximum is reciprocal of slope and bonding energy constant is the ratio of reciprocal of intercept to adsorption maxima.

Percent saturation was calculated as: %saturation = Amount of Zn or Fe adsorbed/Adsorption maxima.

The differential buffering capacity was calculated as: $DBC = b \times k/(1+kCe)^2$, …. Equation (3)

where, DBC - differential buffering capacity, b - adsorption maxima, k - bonding energy constant, Ce - equilibrium concentration of Zn/Fe in soil solution.

Results and Discussions

Physico-chemical properties of the soils revealed that the textures of the soils are loam and clay loam with a range of clay content from 21.20 to 36.70% (Table 1). All soils had alkaline reaction (pH ranging from 7.39 to 8.1). The carbon content varied from 2.05 to 3.63%, whereas the CEC values ranged from 20.70 to 44.40 cmolc kg^{-1}. The content of iron ranging from 0.31 to 2.66 mg kg^{-1} and that of zinc between 0.31 and 1.80 mg kg^{-1}. According to Maria and Yost (2006), the organic carbon content in all soils was medium but high in Zeway soils. The CaCO3 content of soils of Taba, Halaba and Butajira were low, whereas it was high in soils of Hawassa Zuria, Zeway and Alage (FAO, 2006). According to Landon (1991), the CEC of Hawassa Zuria, Taba and Halaba soils were medium but that of Butajira, Zeway, and Alage soils were high (Table1). The available Zn level in Zeway, Alage, and Butajira soils were low, whereas it was high in soils of Hawassa Zuria, Taba and Halaba. The available Fe was low in soils of all locations (Havlin et al., 1999). All these indicate the possibility of Fe and Zn to be adsorbed on the surface of the soils.

Table 1. Physico-chemical properties of the experimental soils

Soil properties	Zeway soil	Alage soil	Hawassa Zuria soil	Butajira soil	Halaba soil	Taba soil
Sand (%)	25.58	51.30	42.10	30.00	36.50	27.60
Silt (%)	49.50	23.70	36.70	37.00	34.00	35.70
Clay (%)	24.92	25.00	21.20	33.00	29.50	36.70
Textural class	Loam	Sandy clay loam	Loam	Clay loam	Clay loam	Clay loam
pH (H_2O)	8.1	7.51	7.39	7.4	7.70	7.47
Org. C. (%)	3.63	2.21	2.20	2.05	2.35	2.35
Exch.Ca (cmol kg^{-1})	29.60	17.00	12.35	25.10	13.30	14.10
Exch.Mg (cmol kg^{-1})	1.70	1.25	2.80	2.50	1.70	1.10
Exch.K (cmol kg-1)	1.35	2.45	2.20	0.60	1.65	1.70
Exch.Na (cmol kg^{-1})	0.85	0.60	1.65	0.50	0.60	0.85
CEC (cmol kg^{-1})	44.40	26.20	20.70	38.25	21.70	21.52
$CaCO_3$ (%)	19.00	5.25	2.65	1.90	1.50	1.50
DTPA Zn (mg kg^{-1})	0.31	0.46	1.21	0.49	1.33	1.80
DTPA Fe (mg kg^{-1})	0.31	0.62	2.66	1.26	1.60	1.50
DTPA Cu (mg kg^{-1})	0.35	0.19	0.23	1.38	0.26	0.25
DTPA Mn (mg kg^{-1})	0.59	0.41	3.74	4.80	4.50	3.91
Total N (%)	0.30	0.21	0.26	0.34	0.24	0.16
Available P. (mg kg^{-1})	12.20	8.21	12.25	12.13	10.00	14.30

The adsorption isotherms showed different curves for the soils of the six locations (Fig 1). The order for Zn sorption followed a decreasing trend; Zeway > Alage > Butajira > Taba > Halaba > Hawassa Zuria (Table 3), i.e. the lowest levels of sorption were observed in the Hawassa Zuria soil (with CEC = 20.70), and the highest in the Zeway soil (with CEC = 44.40). Both the adsorption maxima of Langmuir isotherm (except for Zeway and Alage soils) and the proportionality constant of Freundlich isotherm (for all soils) followed the same trend for zinc sorption capacity (Table 2). The relatively high Freundlich Kf values for Zeway and Alage soils indicate the higher sorption capacities these soils compared to those from the other sites. The highest proportionality constant of Freundlich Kf (47.86) was recorded in Zeway soil, whereas the lowest (2.01) was calculated from that of Hawassa, indicating that Zeway and Hawassa soils have the highest and the lowest zinc sorptions, respectively.

Table 2. Parameters of Freundlich and Langmuir isotherms for Zn sorption

Soils	Freundlich isotherm				Langmuir isotherm				
	kf	1/n (slope)	R^2 (%)	Y-intercept	a_{max} (b)	k	R^2 (%)	Y-intercept	Slope
Zeway soil	47.86	1.13	37.69	1.68	-23.93	-0.94	7.00	0.044	-0.042
Alage soil	29.51	1.05	48.04	1.47	-22.59	-0.71	9.00	0.0624	-0.044
Hawassa Zuria soil	2.01	0.39	84.38	0.303	7.19	0.56	92.00	0.4904	0.139
Butajira soil	10.71	0.54	72.67	1.03	34.048	0.28	77.00	0.0523	0.0294
Halaba soil	5.29	0.49	94.44	0.723	24.137	0.26	60.00	0.1624	0.0414
Taba soil	8.0	0.57	98.61	0.903	29.49	0.462	90.00	0.0734	0.0339

Table 3. Influence of Zn additions on the equilibrium concentration (Ce, mg L^{-1}), adsorption (qe, mg kg^{-1}), and differential buffering capacity (DBC) and percent saturation of the soils.

Soil		Initial zinc concentration in solution (mg/L)				
		2	5	10	15	30
Zeway soil	Ce	0.15	0.22	0.14	0.16	0.56
	qe	1.85	4.78	9.86	14.84	29.44
	DBC	30.45	35.63	29.70	31.23	101.70
	%saturation	-	-	-	-	-
Alage soil	Ce	0.207	0.207	0.138	0.4715	0.783
	qe	1.793	4.793	9.862	14.529	29.217
	DBC	22.04	22.04	19.71	36.24	81.33
	%saturation	-	-	-	-	-
Hawassa Zuria soil	Ce	0.54	2.438	4.4965	10.833	23.345
	qe	1.46	2.562	5.5035	4.167	6.655
	DBC	1.52	0.71	0.39	0.12	0.04
	%saturation	20.31	35.63	76.54	57.96	92.56
Butajira soil	Ce	0.184	0.092	0.437	1.541	4.692
	qe	1.816	4.908	9.563	13.459	25.31
	DBC	15.67	17.25	12.31	5.49	1.45
	%saturation	5.33	14.41	28.09	39.53	74.33
Halaba soil	Ce	0.10	0.70	2.84	5.05	8.80
	qe	1.90	4.30	7.16	9.95	21.21
	DBC	5.95	4.49	2.08	1.17	0.58
	%saturation	7.86	17.81	29.66	41.23	87.84
Taba soil	Ce	0.09	0.30	1.43	2.08	6.67
	qe	1.91	4.70	8.57	12.92	23.33
	DBC	12.49	10.48	4.95	3.54	0.82
	%saturation	6.47	15.94	29.07	43.81	79.11

A Kf can be related to both plant uptake and environmental pollution. Low Kf values indicate that most of the metals present in the system remain in the solution and are available for transport, chemical processes and plant uptake, whereas high values show lower mobility and higher retention of metal in the soil (Dandanmozd and Hosseinpur, 2010). The lowest Zn mobility in Zeway soil could be attributed to the high CEC, pH and $CaCO_3$ contents of the soil, as these factors contribute to Zn adsorption. Slope of the Freundlich model (1/n) is a measure of the heterogeneity of a system. A more homogeneous system will have slope value approaching unity, whereas heterogeneous system will have 1/n value approaching zero (Hussain et al., 2006). The results showed Freundlich slope (1/n) approaching unity for Zeway and Alage soils indicating they were more homogenous, whereas the other soils having lower Freundlich slope are relatively heterogeneous.

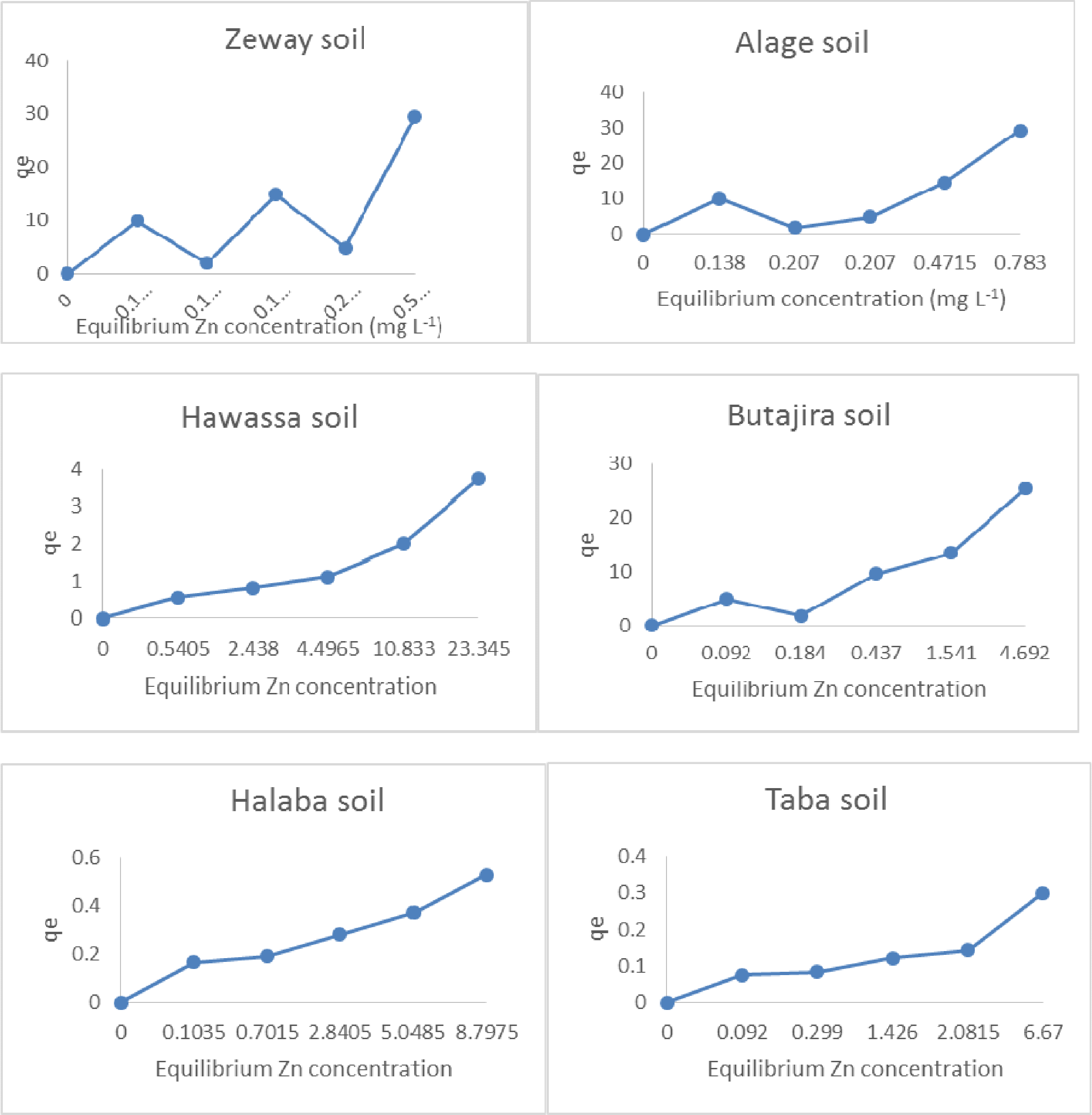

Fig 1. Zinc adsorption isotherms of the experimental soils

Adsorption of zinc increased with increasing initial zinc concentration in all soils (Fig 2). Similar finding was reported by Moreira & Alleoni (2010). The lowest Zn sorption was obtained when the lowest Zn concentration was added to the soil, whereas the highest was recorded with the highest Zn concentration in all soils showing increments of Zn sorption with increasing application until full percent saturation (100%) is achieved. At the lowest and highest concentration of zinc (2 and 30 mg/L), a noticeable difference in the adsorption of zinc by the different soils occurred, which is in agreement with the result obtained by Diatta and Kociałkowski (1998). Soils of Zeway and Alage adsorbed almost equal quantities of Zn added. Soils of Butajira, Halaba and Taba adsorbed most of the added Zn, but soil of Hawassa Zuria adsorbed far below the quantities of Zn added indicating the high affinity of Zn by the adsorption sites of Butajira, Halaba, and Taba soils (Moreira & Alleoni, 2010).

The data indicated that 98.12, 97.39, 84.36, 77.77 and 70.86% of the added Zn were adsorbed by soils of Zeway, Alage, Butajira, Taba and Halaba respectively, whereas only 22.18% of the added Zn was adsorbed by the Hawassa Zuria soil. These show that almost all the applied Zn were adsorbed by the soils of Zeway and Alage, as was also reported by Moreira and Alleoni (2010). Thus, Alage and Zeway soils require application of Zn fertilizer for sufficient availability for plant growth after satisfying the sorption requirement. Similar findings were also reported by Mustafa et al. (1988) on Zn sorption by soils.

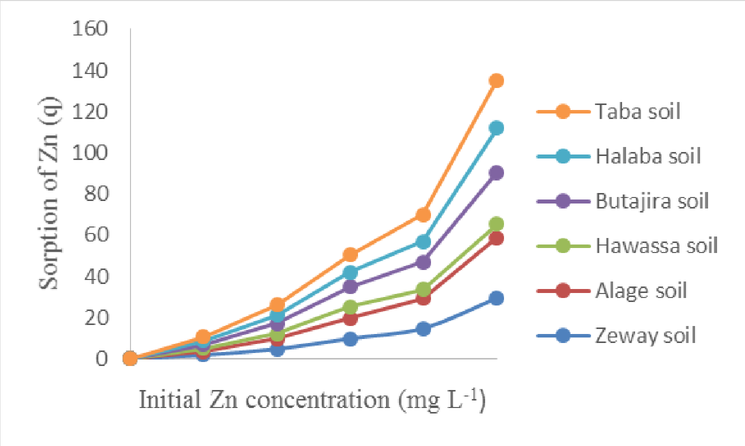

Fig 2. Effect of initial Zn concentration on Zn sorption capacity

Despite the differences between Zeway and Alage soils in terms of selected physicochemical properties (Table 1), the Zn sorption capacities of the two soils were more or less similar, which might be attributable their similar clay contents (Table 1). On the other hand, the similarity in Zn sorption of Butajira, Halaba and Taba soil might be attributed to their $CaCO_3$ and organic carbon contents, which is in agreement with the findings reported by Hussein et al. (2002). The lowest Zn sorption capacity in soil of Hawassa might be attributed to the lowest contents of clay (21.20%), pH (7.39), OC (2.20%) and CEC (20.70 cmol kg^{-1}). About 16, 22 and 29% of the added Zn could be available in soils of Butajira, Taba and Halaba, respectively, implying the requirement of Zn fertilizer for optimum crop production. Zeway and Alage soils did not fit Langmuir isotherm for zinc adsorption, which is indicated by the non- straight line, the negative values of the Langmuir parameters (Igwe and Abia, 2007) and the low values of coefficient of determination (R^2 <10) (Table 2). However, they better fitted to the Freundlich isotherm (Fig 4).Their coefficients of determination increased from 6.5 to 37.69% for Zeway and from 8.8 to 48.04% for Alage soils when Freundlich model was used (Table 2). The other four soils, Halaba, Butajira, Taba and Hawassa Zuria soils, fitted the Langmuir isotherm for zinc adsorption (Fig 3) indicating the adsorption is a mono layer (Teng and Hsieh, 1998).

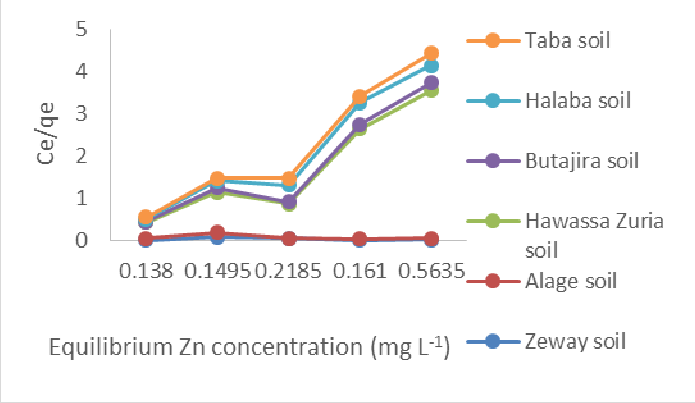

Fig 3. Langmuir isotherms of the soils for Zn

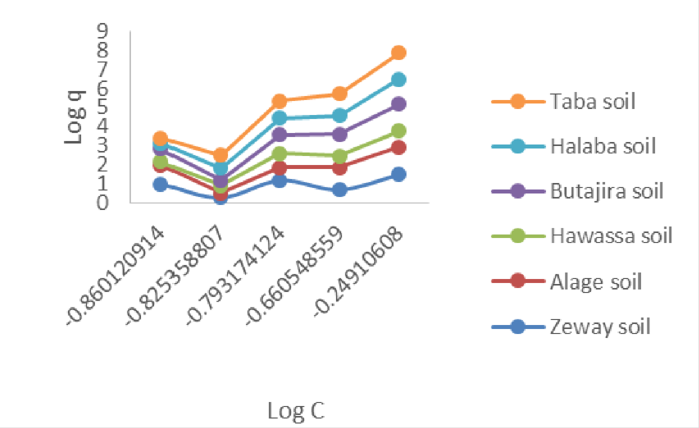

Fig 4. Freundlich isotherms of the soils for Zn

Additionally, the calculated percent saturation indicated that the adsorption sites on the adsorbent are not saturated and adsorption is increasing with increasing initial Zn concentration implying the adsorption is a monolayer. Taba and Halaba soils were best fitted the Freundlich model as compared to that of Langmuir. The coefficients of determination of these two soils in the case of Langmuir model is 59.8% for Halaba soil and 90% for Taba soil. But when they were analyzed using Freundlich model, the coefficients of determination were increased from 59.8 to 94.44% for Halaba soil and from 90 to 98.61% for Taba. Hawassa and Butajira soils best fitted the Langmuir isotherm compared to Freundlich (Table 2).

Equilibrium Zn concentration (Ce) in the soils, which is equivalent to the DTPA Zn in the soil solution, increased with increasing application of zinc, except in Zeway and Alage soils. Similarly, with the increasing equilibrium concentration (Ce) an increase in the adsorption of zinc (qe) was also noted in Hawassa Zuria, Butajira, Halaba and Taba soils as reported by Diatta and Kociałkowski (1998). But, such trend was not observed in sorptions of Zeway and Alage soils with increasing equilibrium Zn concentrations (Fig. 1).

Soils with high sorption capacity had low DTPA Zn content (Table 2) indicating more of the applied Zn might be adsorbed by the soils as compared to those with low sorption capacity. Similar to the DTPA Zn content, equilibrium Zn concentration was also decreased with increasing of Zn sorption capacity of soils, which is in agreement with a results reported by Diatta and Kociałkowski (1998). As indicated in Table 3, the highest Zn sorption capacity and the lowest equilibrium Zn concentration were recorded in Zeway soil. On the other hand, the lowest Zn sorption capacity and the highest equilibrium Zn concentration were observed in Hawassa soil.

A high adsorption maxima (a $_{max}$) value (34.05 mg kg^{-1}) found for Butajira soil is perhaps related to the higher clay content that enhance soil cation exchange capacity. Adsorption maxima was correlated (but not significantly) with clay (r = 0.72), which is in line with Diatta and Kociałkowski (1998). Correlation between some soil properties with Langmuir constants (Table 4) showed that Zn adsorption maxima and bonding energy were positively (not significantly) correlated with clay, r = 0.72 and r = 0.38, respectively, but negatively (not significantly) correlated with pH, CEC, organic carbon and CaCO3. Mustafa et al. (1988) also reported similar findings on Zn sorption by calcareous soils. These Langmuir constants were positively correlated with Zn, Fe, and Cu. Adsorption maxima and bonding energy were significantly correlated with Mn. r = 0.97*** and r =0.92**, respectively, which shows Zn sorption was strongly related to Mn contents in the soils. On the other hand, the correlation between these soil properties and Freundlich constants showed that proportionality constant (Kf) was negatively correlated with clay (r = -0.31), but positively with pH (r = 0.77) and CEC (r = 0.73). Freundlich slope was negatively correlated with clay (r = -0.28) but positively correlated with pH, OC, CEC and $CaCO_3$ with r = 0.65, 0.66, 0.59 and 0.78, respectively. Kf was significantly correlated with OC (r = 0.80*), $CaCO_3$ (r = 0.91*), Fe (r = -0.87*) and Mn (r = -0.88*) indicating that Zn sorption that followed Freundlich model (Zeway and Alage soils) was strongly related to these soil properties.

Table 4. Correlation coefficients between soil properties and sorption parameters

Soil properties	kf	n	b	k
Clay	-0.31	-0.28	0.72	0.38
pH	0.77	0.65	-0.55	-0.70
OC	0.80*	0.66	-0.59	-0.68
CEC	0.73	0.59	-0.33	-0.62
$CaCO_3$	0.91**	0.78	-0.74	-0.81*
Zn	-0.73	-0.69	0.61	0.76
Fe	-0.87*	-0.90**	0.55	0.88*
Cu	-0.12	-0.21	0.47	0.18
Mn	-0.88*	-0.94**	0.97***	0.92**

The relative amount of Zn adsorbed was dramatically higher at a low concentration than at a higher concentration. This suggests that the reaction between zinc and the soil was rapid on initial contact; perhaps as low available Zn content results in high adsorption potential at the surface. Similar observations have been reported elsewhere on phosphorus by Tsado et al. (2012).

Saturation percentage increased with added Zn concentration. At initial Zn concentration, saturation percentage was highest in Hawassa Zuria soils but adsorption maxima was the least indicating sorption was lowest in these soils as compared to the others (Table 2). As indicated in Table 3, differential buffering capacity (DBC), which is an indicator of the resistance to change in ions of the soil solution is inversely correlated with initial (added) zinc concentration, equilibrium zinc concentration and percent saturation indicating concentration of Zn in solution phase will increase (Diatta and Kociałkowski, 1998). From these studies it is apparent that Zeway and Alage soils with comparatively high proportionality constant and buffering capacities have a greater affinity for added zinc and thus, they will require higher rates of zinc (Diatta and Kociałkowski, 1998).

Iron sorption followed a similar trend in all soils and it was increased with increasing equilibrium Fe concentrations (Fig 5 and Table 6) and initial Fe concentrations in all soils (Fig 6). In Butajira and Taba soils, the percentage of sorption was higher at lower initial concentrations. Similar findings were reported by Karthikeyan et al. (2005) on adsorption of Fe on chitin. But in the rest of the soils, sorption percentage was higher at higher Fe concentration. The adsorption was 86% at the lowest Fe concentration (2 mg L^{-1}) and it was reduced to 81% at the highest Fe concentration (30 mg L^{-1}) in Taba soils. Similarly, it went down in Hawassa Zuria soil from 82.5% at lowest Fe concentration to 76.5% at highest Fe concentration. In Zeway, Alage, Butajira and Halaba soils, the adsorptions were increased from lowest (2 mg kg^{-1}) to highest (30 mg kg^{-1}) Fe concentrations from 60.2 to 78.97, 79.5 to 83.07, and 81 to 89.87, 76.54 to 85.46%, respectively. The difference in CaCO$_3$, CEC and organic carbon did not strongly influence the sorption of iron. Iron sorption in all soils, but in Taba soils, did not fit Langmuir isotherm (Fig 8), which is indicated by the non-straight lines, the negative values of the adsorption maxima (Table 5). But it better fitted Freundlich isotherm (Fig 7) similar to that described by Sheta et al. (2003). The adsorption maxima in Hawassa Zuria soils was positive, but the non-straight line and the lower coefficient of determination (R^2) confirmed that it does not follow Langmuir model.

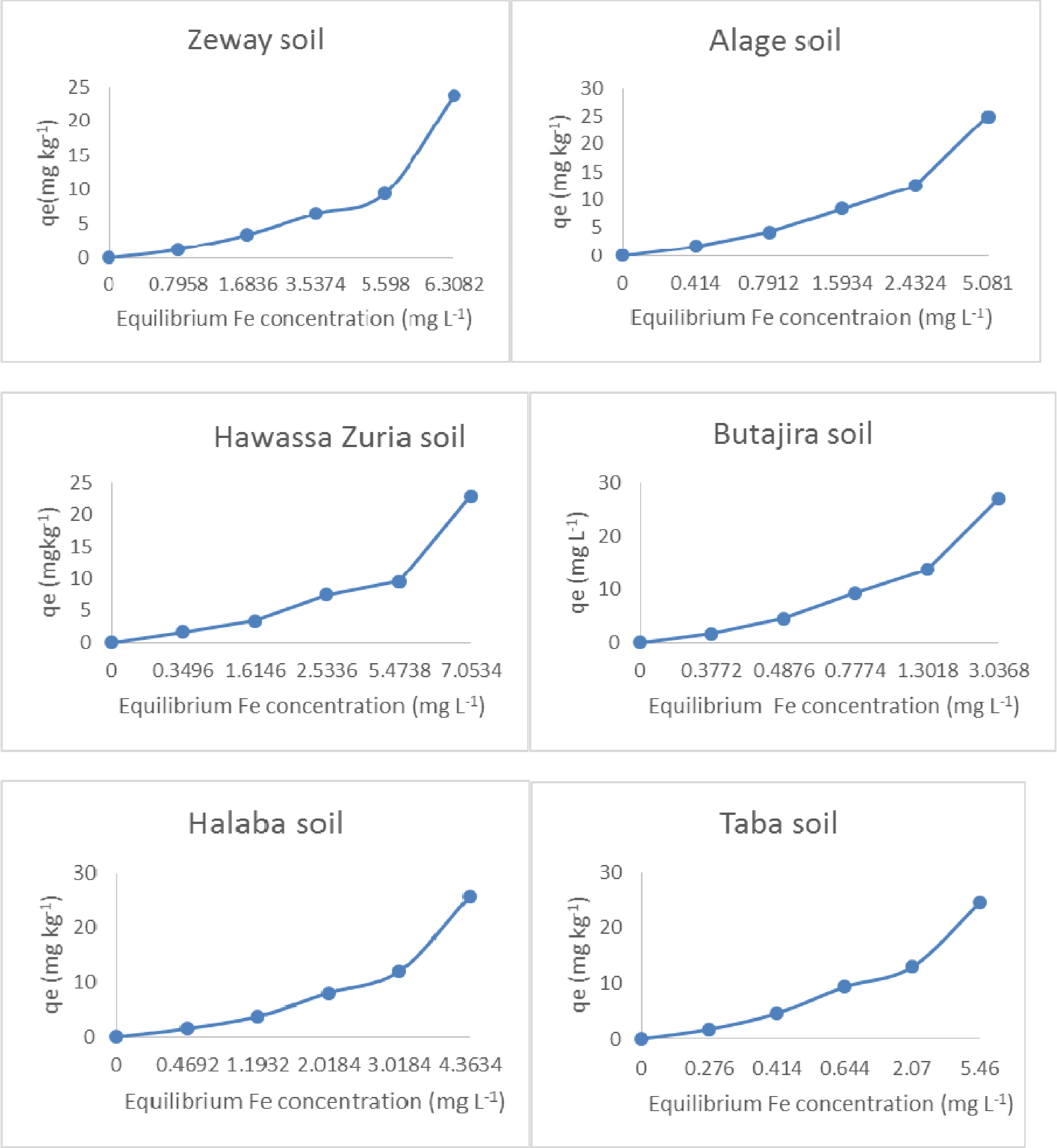

Fig 5. Iron adsorption isotherm of six types of soils

The Freundlich slopes in all soils were approaching unity (around one) indicating the soils were more homogenous (Table 5). Freundlich Kf, stated by Hussain et al. (2006) as extent of adsorption, ranged from 1.59 to 8.71 mg kg^{-1}. As low Freundlich Kf values indicate low Fe adsorption capacities at low Fe concentrations, Zeway, Alage, Hawassa Zuria and Halaba soils had lower adsorption capacity at low Fe concentrations.

Table 5. Parameters of Freundlich and Langmuir isotherms for Fe sorption

Soils	Freundlich isotherm				Langmuir isotherm					
	kf	1/n (slope)	R^2 (%)	Y-intercept	a_{max} (b)	kb	k	R^2 (%)	Y-intercept	Slope
Zeway soil	1.59	1.24	21.2	0.20	-25.13	1.59	-0.06	39.92	0.66	-0.04
Alage soil	4.73	1.08	37.81	0.674	-194.18	4.59	-0.02	9.68	0.22	-0.01
Hawassa Zuria soil	3.25	0.80	4.60	0.51	60.168	3.07	0.05	13.50	0.33	0.02
Butajira soil	8.71	1.23	16.25	0.94	-5.59	6.76	-1.21	10.45	0.15	-0.18
Halaba soil	3.49	1.23	13.23	0.54	-28.14	2.96	-0.11	89.94	0.34	-0.04
Taba soil	7.70	0.77	25.20	0.89	44.50	9.95	0.22	63.48	0.10	0.022

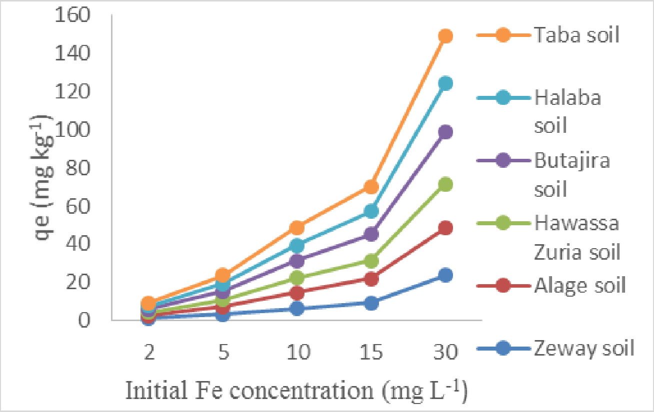

Fig 6. Effect of initial Fe concentration on Fe sorption

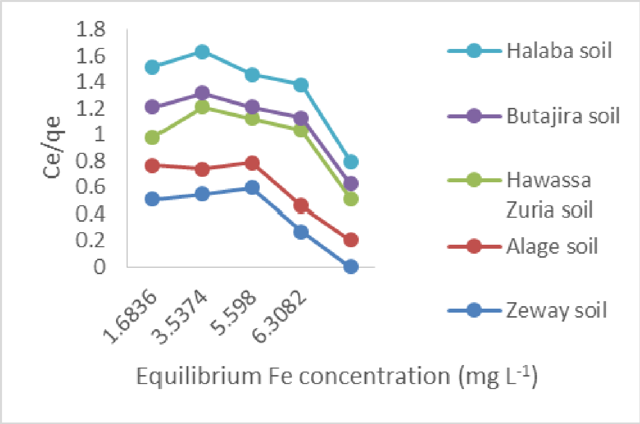

Fig 7. Langmuir isotherm for Fe

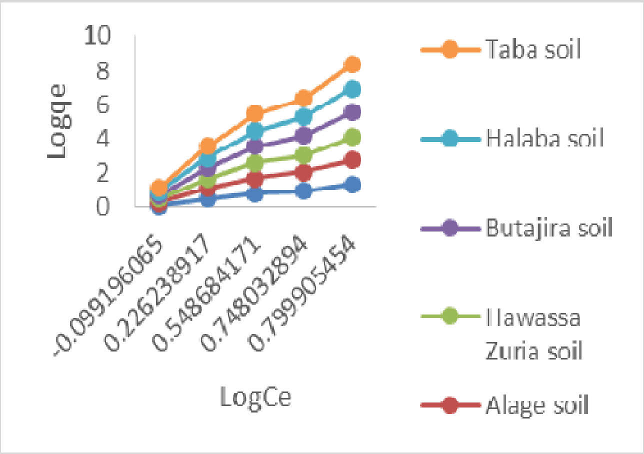

Fig 8. Freundlich isotherm for Fe

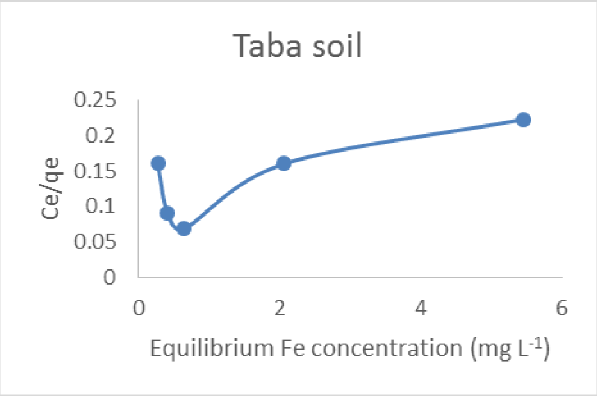

Fig 9. Langmuir isotherm for Fe.

Table 6. Influence of Fe additions on the equilibrium concentration (Ce, mg L^{-1}) and adsorption (qe, mg kg^{-1}) for the six soils.

Soil		Initial iron concentration in solution (mg L^{-1})				
		2	5	10	15	30
Zeway soil	Ce	0.7958	1.6836	3.5374	5.598	6.3082
	S	1.204	3.3164	6.463	9.402	23.691
Alage soil	Ce	0.414	0.7912	1.5934	2.4324	5.081
	S	1.586	4.209	8.407	12.568	24.919
Hawassa Zuria soil	Ce	0.3496	1.6146	2.5336	5.4738	7.0534
	S	1.65	3.385	7.466	9.526	22.947
Butajira soil	Ce	0.3772	0.4876	0.7774	1.3018	3.0368
	S	1.6228	4.512	9.223	13.698	26.963
Halaba soil	Ce	0.4692	1.1932	2.0184	3.0184	4.3634
	S	1.5308	3.807	7.9816	11.98	25.637
Taba soil	Ce	0.276	0.414	0.644	2.07	5.46
	S	1.724	4.586	9.356	12.93	24.54

Freundlich kf and bonding energy (k) were significantly correlated with caly, r = 0.79* and r = 0.84*, respectively, but not significantly correlated with the other soil properties indicating clay was strongly related with Fe sorption. Freundlich slope (1/n) and adsorption maxima were not significantly correlated with pH, CEC, OC, $CaCO_3$. Zinc, Fe, Cu, Mn, and Freundlich and Langmuir parameters (Table 7).

Table 7. Correlation coefficients between soil properties and sorption parameters

Soil properties	kf	n	b	k
Clay	0.79*	-0.04	0.24	0.84*
pH	-0.68	0.55	-0.13	-0.59
OC	-0.64	0.34	0.02	-0.50
CEC	-0.09	0.66	-0.12	-0.27
$CaCO_3$	-0.63	0.40	-0.15	-0.56
Zn	0.23	-0.69	0.57	0.49
Fe	0.10	-0.61	0.65	0.11
Cu	0.63	0.43	0.14	0.27
Mn	0.53	-0.18	0.67	0.41

Conclusions

Physico-chemical properties of the soils revealed that the content of OC was medium; $CaCO_3$ ranged from low to high, CEC ranged from medium to high, available Zn ranged from low to high, and available Fe was low. Though adsorption isotherms showed different curves for the soils of the six locations, the soils had high capacities of zinc and iron sorption except that Hawassa Zuria soil had low zinc sorption. Adsorption of zinc increased with increasing initial zinc concentration in all soils. Soils with high sorption capacity had low DTPA Zn content indicating more of the applied Zn might be adsorbed by the soils as compared to those with low sorption capacity. The relative amount of Zn adsorbed was dramatically higher at a low concentration than at a higher concentration. This suggests that the reaction between zinc and the soil was rapid on initial contact. Iron sorption followed a similar trend in all soils and it was increased with initial Fe concentrations in all soils. Most of the soils better fitted the Langmuir isotherm for zinc adsorption, indicating the adsorption is a mono layer, but for iron sorption they better fitted Freundlich isotherm. Amounts of zinc adsorbed were strongly related to soil organic carbon, calcium carbonate, iron and manganese contents of the soils, whereas amounts of iron adsorbed were strongly related to clay. The amount of Zn and Fe fertilizers to be applied for their availability to crop growth in the study soils should consider the sorption capacities of these nutrients in the soils.

References

Al-Degsa, Yahya S., Musa I. El-Barghouthia, Ayman A. Issaa, Majeda A. Khraishehb, Gavin M. Walkerc 2006. Sorption of Zn (II), Pb (II), and Co (II) using natural sorbents: Equilibrium and kinetic studies, Water Research 40 (2006) 2645 – 2658.

Alloway, B. J. 2008. Zinc in Soils and Crop Nutrition**,** Second edition, published by IZA and IFA, Brussels, Belgium and Paris, France

Al-Tamimi, R. A. 2006. Zinc sorption by some Torrifluvents soil of Sub-Saharian region south of Libya, Emir. J. Agric. Sci. 18 (2): 01-10.

Bouyoucos GJ, 1951. A re-calibration of the hydrometer methods for making mechanical analysis of soils. Agron. J. 43: 434-438.

Bremner JM, Mulvaney CS, 1982. Nitrogen – total. In Page et al. (ed.) Methods of soil analysis. Chemical and microbiological properties. SSSA, Madison, Wisconsin. 2: 595-642

Da̧browski, A. 2001. Adsorption _ from theory to practice, Advances in Colloid and Interface Science 93 135_224.

Dandanmozd, F. and A.R. Hosseinpur 2010. Thermodynamic parameters of zinc sorption in some calcareous soils, Journal of American Science 6(7).

Diatta, J. and W. Kociałkowski 1998. Adsorption of Zinc in Some Selected Soils. Polish Journal of Environmental Studies Vol. 7, No. 4, 195 – 200

Fageria, N.K., V.C. Baligar, and R.J. Wright. 1990. Iron nutrition of plants: An overview on the chemistry and physiology of its deficiency and toxicity, Pesq. Agropec. Bras., Brasilia, 25(4):553-570.

FAO, 2006. Guidelines for soil description. Fourth edition, Food and Agricultural Organization of the United Nations, Rome.

Havlin JL, Beaton JD, Tisdale SL, Nelson WL, 1999. Soil fertility and fertilizers. Prentice Hall, New Jersely. pp. 345-355.

Hussain, A., A. Ghafoor and G. Murtaza 2006. Use of Models for Phosphorus Adsorption on Some Sodic Soils of Punjab, International Journal of Agriculture & Biology 1560– 8530/2006/08–2–241–248, *Pakistan*

Hussein, Ahlam A., Elamin Abdelmagid Elamin and Yousif Elgorashi El Mahi. 2002. Zinc Sorption in Two Vertisol and One Aridisol Series as Affected by Electrolyte Concentration and Sodium Adsorption Ratio, *U. of K. J. Agric. Sci. 10 (1),* Shambat, Sudan.

Igwe, Jude C. and Augustin A. Abia 2007. Equilibrium sorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions detoxification from waste water using unmodified and EDTA- Modified maize husk, Journal of Biotechnology ISSN: 0717-3458 Vol.10 No.4.

Karthikeyan, G., N. Muthulakshmi Andal and K. Anbalagan 2005. Adsorption studies of iron (III) on chitin, *J. Chem. Sci.*, Vol. 117, No. 6, November 2005, pp. 663–672, Indian Academy of Sciences.

Landon JR, 1991. Booker tropical soil manual. A handbook for soil survey and agricultural land evaluation in the tropics and sub tropics. John Wiley and Sons, New York. pp. 94-95.

Maria, R.M. and R. Yost, 2006. A survey of soil fertility status of four agro-ecological zones of Mozambique, Soil Science Vol. 171, No. 11, Lippincott Williams & Wilkins, Inc. USA.

Moreira, C. S. and Luís Reynaldo Ferracciú Alleoni 2010. Adsorption of Cd, Cu, Ni and Zn in tropical soils under competitive and non-competitive systems, Sci. Agric. (Piracicaba, Braz.), v.67, n.3, p.301-307.

Mustafa, M.A., I.A. Ayed and O.A. Mahgoub 1988. Zinc Sorption by some Saudi Calcareous Soils, Arab Gulf J. Scient. Res. Agric. Biol. Sci. B6 (1). Pp. 9-20.

Sahlemedhin Sertsu and Taye Bekele, 2000. Procedures for Soil and Plant Analysis. Technical Paper N0. 74.

Sheta, A.S., A.M. Falatah, M.S. Al-Sewailem, E.M. Khaled, A.S.H. Sallam 2003. Sorption characteristics of zinc and iron by natural zeolite and bentonite, Microporous and Mesoporous Materials 61 127–136

Tan KH, 1996. Soil sampling, preparation, and analysis. Marcel Dekker, Inc. New York, USA.pp. 68-78.

Teng, Hsisheng and HSIEH, Chien-To. Influence of surface characteristics on liquid-phase adsorption of phenol by activated carbons prepared from bituminous coal. Industrial and Engineering Chemistry Research, September 1998, vol. 37, no. 9, p. 3618-3624.

Tsado P.A., Osunde O.A., Igwe C.A., Adeboye M.K.A., and Lawal B.A. 2012. Phosphorus sorption characteristics of some selected soil of the Nigerian Guinea Savanna**,** International Journal of AgriScience Vol. 2(7): 613-618.