



Effect of Farmyard Manure (FYM) and Zinc Fertilizer Rates on Zinc Adsorption by Sandy Clay Loam Soil of Gongulong-yerima, Jere, Borno State, Nigeria

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ABSTRACT

Laboratory experiment was carried out in Soil Science Laboratory, University of Maiduguri to study the effects of Farmyard manure (FYM) and Zinc fertilizer rates on Zinc adsorption by Sandy clay loam soil of Gongulong-yerima of Jere, Borno state from November 2019 to February, 2020. One (1) kg of prepared soil was incubated with four levels of FYM; at 0, 5, 10 and 15 tha^{-1} equivalent to 0, 2.5, 5.0 and 7.5 g kg^{-1} soil for three months with optimum moisture and used for adsorption experiment. Adsorption data were interpreted with adsorption isotherms and Langmuir and Freundlich models. Results obtained showed that Zn adsorption by the soil increased with increase in Zn levels from 0-100 mg kg^{-1} Zn. FYM applied at 5 and 10 tha^{-1} decreased Zn adsorption while further addition (15 tha^{-1}) increased Zn adsorption. Adsorption isotherm plotted showed similar trend in Zn adsorption with 0, 5 and 10 tha^{-1} but differed quantitatively. Adsorption was found to be higher with soils untreated with FYM than those treated with FYM. The adsorption data fitted into both Langmuir and Freundlich adsorption isotherms. It was concluded that Zn adsorption by the soil increased with increase in Zn levels from 0-100 ppm and application of FYM at 5 and 10 tha^{-1} decreased Zn adsorption while adsorption was increased with application of 15 tha^{-1} FYM. Adsorption data of the soil studied fitted to both Langmuir and Freundlich adsorption models.

Keywords: adsorption, Zinc, Farmyard manure, Langmuir, Freundlich

1.0 Introduction

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface (Brownfield and Land Revitalization Technology Support Centre, 2009). Harter (1991), in a review of the subject, concluded that, adsorption isotherms have provided the majority of information about micronutrient adsorption by soils. Barrow (1993) stated that Zn adsorption was decreased by organic ligands as strong complexes of Zn are formed by humic acids. These complexes are more soluble forms of zinc in soils and become highly mobile and plant available. Reduced Zn adsorption onto mineral surface is caused by Zn complexation with organic ligands (Harter, 1991). The Zn adsorption-desorption reactions between the solution and solid phases control Zn concentrations in soil solution and the availability of Zn to plants (Catlett *et al.*,

2002), which depend on the pH, organic matter, soil minerals, and co-existing ions as well as the distribution into various fractions (Alloway, 2008c).

Zinc availability reduces at higher soil pH due to increased adsorption, formation of hydrolyzed Zn, chemisorption on CaCO_3 and co-precipitation in Fe oxides (Alloway, 2008b). With the addition of organic matter in soil, Zn availability is enhanced which form soluble, mobile and plant roots absorbable organic-zinc complexes. Imtiaz *et al.* (2006) reported Zn was greatly adsorbed by soils with high CEC, CaCO_3 , organic matter and fine texture. Covelo *et al.* (2004) inferred that Zn adsorption is affected by acidic pH and oxides.

Increasing soil pH increases the total number of negative sites on clay minerals and organic matter, thereby increasing the capacity for Zn sorption (McBride, 1989). Saha *et al.* (2001) showed that the adsorption of Zn and Cd on the hydroxyaluminum- and hydroxyl aluminosilicate-montmorillonite complexes is very strongly pH-dependent. Substantial fractions of these two metals were also adsorbed on complexes with a pH below 5. As the pH rose above 5, Cd and Zn adsorption on the complexes steeply increased, reaching plateau levels of almost 100% when the pH was between 6 and 7. Soil pH exercised the largest influence on Zn buffer power (Dang *et al.*, 2010); with increase in pH, zinc buffer power increased tremendously.

The rate of zinc sorption from solution to solid surfaces is a dynamic factor that directly or indirectly regulates the amounts of Zn in solution and its availability (Taylor *et al.*, 1995). Diatta and Kocialkowski (1997) concluded that with the addition of increasing amounts of zinc there was a simultaneous increase in the equilibrium concentration, adsorption, and percent saturation of adsorption capacity and supply parameter of zinc.

Farmyard manure refers to the decomposed mixture of dung and urine of farm animals along with litter and left over material from roughages or fodder fed to the animals. Organic matter plays a key role in governing the availability of soil Zn (Chami *et al.*, 2013). Exogenous organic materials not only release free Zn into soil solutions by decomposition, but also change the original solubility and mobilization of soil Zn by the formation of Zn organic complexes (Smith, 2009). Organic amendments were shown to alter the distribution of Zn precipitated by calcium carbonate, which is supposed to be a major factor in the loss of Zn availability in calcareous soil (Jalali and Khanlari, 2008). In addition, the adsorption and fixation of Zn takes place by the slow diffusion of available Zn into iron (Fe) and manganese (Mn) oxides and clay minerals, and this is also closely related to the change in the amount of Zn bound to organic matter (Pérez-Esteban *et al.*, 2012).

FYM is one of the most common sources of organic amendments used. Bolan *et al.* (2004) and Sial *et al.* (2007) reported that FYM determines many soil properties such as nutrients availability, aggregate stability, aeration, and favorable water uptake and retention characteristics.

1.1 MATERIALS AND METHODS

1.1.1 Soil of the Study

Soil for the experiment was collected at Gongulong-yerimari agricultural area between Latitude (11.923100°N and 11.919042°N) and Longitude (13.228927°E and 13.221758°E) of Jere Local Government Area, Borno state and was set out in Soil Science Laboratory, Faculty of Agriculture, University of Maiduguri.

Borno state is characterized with annual mean rainfall and temperature of 552 mm and 35°C and record high and low temperatures of 47°C and 5°C in the month of May and December (Climate Charts, 2017).

The vegetation of Gongulong-yerimari falls to Sudan Savannah. The vegetation includes trees like *Acacia nilotica*, *Acacia senegal*, *Acacia seyal*, *Mangifera indica*, *Azadirachta indica*, *Ziziphus spp* and *Balanites aegyptiaca*. There are also weed grass species present in the area that mostly cover uncultivated areas.

The land in the location is mostly devoted for agricultural uses especially in the cultivation of vegetables; onion, pepper, water melon, cereals; rice, wheat, sorghum, legumes; groundnut, cowpea and tree plantation; mango. Fishing is also done in the area. Based on information available, scanty fertilizer application is practiced in the area.

Sufficient 0-15cm soil was collected at Gongulong-yerimari agricultural area. Cow dung FYM was collected from Animal Science Research Farm, University of Maiduguri and used for the experiment. Stones and unwanted particles were removed from the soil and FYM. The soil and FYM collected were separately air

dried, bulked and mixed and finally sieved through 2mm stainless steel sieve. Portion of the soil sample and FYM were prepared for adsorption studies and laboratory analysis.

1.1.2 Soil and Farmyard Manure Analysis

Composite soil sample collected was analysed before the experiment for physico-chemical properties and DTPA extractable Zn. The particle size distribution was determined using hydrometer method (Bouyoucos, 1962). Soil pH was determined in soil-water ratio of 1:2.5 using glass electrode pH meter. The suspension used in the determination of pH was used for the determination of EC following the same process with the use of an EC meter.

Percentage organic carbon of the soil was determined by the use of Walkley and Black (1934) dichromate wet oxidation method as described by Nelson and Sommers (1982). Exchangeable cations of the soil was determined by using 1N NH_4OAc (pH7.0) saturation method (Chapman, 1965). Sodium and potassium were determined using flame photometric method while calcium (Ca) and Magnesium (Mg) were determined by titration method against EDTA using eriochrome black TEA indicator. Exchangeable acidity was extracted with 1N KCl and measured according to the procedure of Mclean (1982). Total nitrogen was determined by micro-Kjeldahl digestion method (Jackson, 1962), while available phosphorus was determined using Bray II method as described by Olsen and Sommers (1982). The analysis of FYM was done following the method of plant analysis by Marr and Cresser (1983). 0.2g of prepared cow dung FYM was weighed into a beaker and 2.5ml concentrated H_2SO_4 and HClO_4 acid and placed on a hot plate and heated at 180-200 $^\circ\text{C}$ until a clear digest was obtained from which NPK was determined. For Zn analysis, 500mg of the ground sample was weighed into a digestion tube and mixture of HNO_3 and perchloric acid were added. The content was heated and after getting a clear digest, the content was transferred into a 50ml volumetric flask and made up to mark and used for determination of Zn with an Atomic Absorption Spectrophotometre model number VGP210 at Adamawa State University, Mubi.

Soil zinc was extracted using diethylene triamine penta acetic acid (DTPA); 10g of soil was shaken with 20ml of DTPA extractant (0.005M, DTPA and 0.01M CaCl_2 +0.1M triethanol amine adjusted to pH 7.3) (Lindsay and Norvell, 1978) and then determined using VGP 210 atomic absorption spectrophotometre.

1.1.3 Zinc Adsorption Studies

The effect of FYM on Zn adsorption by Sandy clay loam soil of Gongulong-yerimari was evaluated in the Department of Soil Science laboratory, University of Maiduguri in March, 2019. Bulk soil sample of 1 kg were incubated with four levels of FYM: 0, 5, 10 and 15 tonnes of FYM per hectare equivalent to 0, 2.5, 5.0 and 7.5 g FYM per Kg soil for three months kept under field capacity moisture and covered. They were then air dried and sieved through 2 mm before the commencement of adsorption studies. Exactly 2g of the sieved soil were weighed into series of bottles. 25mls of 0, 50, 100, 150 and 200 ppm Zn were added to the soils with different levels of FYM. 25mls of 0.02M CaCl_2 was then added to the bottles. Final concentration of CaCl_2 was 0.01M and final Zn concentrations were 0, 25, 50, 75 and 100 ppm. The bottles were shaken for one hour and equilibrated for 24 hours and filtered. Zinc concentrations in equilibrium solutions were determined using Atomic Absorption Spectrophotometer (AAS). The amount of adsorbed Zn was calculated by the difference between Zn added and that remained in the equilibrium solutions multiplied by soil solution ratio. The obtained results of adsorption experiments were interpreted in the light of Langmuir and Freundlich adsorption isotherms. Langmuir equation is as follows:

$$C/X = 1/Kb + C/b,$$

Where C and X are the equilibrium ion concentration and the amount of ion adsorbed and the constants b and k are related to the adsorption maximum and bonding strength of the adsorbent, respectively. Using the Langmuir isotherm, a graph of C/X against C was plotted where the slope (1/b) and intercept (1/Kb) from which both binding energy (K) and maximum adsorption (b) can be found.

Freundlich adsorption equation is as follows:

$$X=KC^n$$

Where X is the amount of substance adsorbed per unit weight of adsorbent, C is the equilibrium concentration of the adsorbate, K and n are empirical constants. Using Freundlich isotherm, a graph of Log X versus Log C was plotted giving a straight line from which the slope (n) as adsorption intensity and intercept (Log K) can be used to obtain the adsorption constant (K) by taking the antilog for soils that have conformed to the model.

1.3 RESULTS

1.3.1 Characteristics of the Experimental Soil

The physicochemical properties of the soil used are presented in Table 1. The textural class of the soil was Sandy clay loam with clay 304 gkg⁻¹ soil, silt 114 gkg⁻¹ soil and sand 582 gkg⁻¹ soil. The pH of the soil was 7.20 which is slightly alkaline. The soil had EC of 0.02 mmhos/cm which is non saline. Phosphorus (16.10 mgkg⁻¹), organic carbon (12.99 gkg⁻¹), potassium (0.50 Cmol(+)/kg and sodium (0.48 cmol(+)/kg soil) were all moderate. Base saturation (94.86%) and calcium (24.4 cmol(+)/kg) were very high. Cation exchange capacity (38.78 Cmol(+)/kg soil) was high, total nitrogen (0.76%) was very low and DTPA extractable zinc (1.12 mgkg⁻¹) was moderate.

1.3.2 Characteristics of Cow Dung Farmyard Manure Used

The composition of cow dung FYM used is presented in Table 2. The content of N, P, K and Zn were 3.22, 0.38, 0.43 % and 1.84 µgg⁻¹ respectively.

Table 1: Physico-chemical properties of the soil sample

Characteristic	Value
Sand	582
Silt	114
Clay	304
Textural class	Sandy clay loam
<u>Chemical properties</u>	
pH 1:2.5 (H ₂ O)	7.20
EC (mmhos/cm)	0.02
Organic carbon (gkg ⁻¹)	12.99
Total N (gkg ⁻¹)	7.60
C:N ratio	1.71
Available P (mgkg ⁻¹)	16.10
Available Zn (mgkg ⁻¹)	1.12
<u>Exchangeable cations (Cmol/kg)</u>	
Ca	24.40
Mg	13.40
K	0.50
Na	0.48
Exchange acidity (H +Al)	2.10
CEC	38.78
ECEC	40.88
Base saturation (%)	94.86

Table 2: Characteristics of cow dung Farmyard manure used

Nutrient	Content
N (%)	3.22
P (%)	0.38
K (%)	0.43

Zn (μgg^{-1})	1.84
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1.3.3 Zinc Adsorption Studies

Table 3 shows the results obtained from the effect of FYM and Zn fertilizer application on the adsorption of Zn by the soil studied. There was no Zn adsorption for treatments receiving 0 tonnes/ha FYM and 0 ppm Zn. Amount of Zn adsorbed (X) increased with increase in Zn levels from 0 to 100 ppm Zn but not at a steady rate. For example, when 5 tonnes of FYM and 0, 25, 50, 75 and 100 ppm Zn were applied, Zn adsorption were 0, 429.75, 519.00, 417.00 and 635.50 μgg^{-1} respectively.

Amount of Zn adsorbed was also shown to be affected by application of FYM at different levels. Application of FYM at 5 and 10 t/ha decreased adsorption of Zn while 15 t/ha increased Zn adsorption compared to other levels but not in a steady rate. For example when FYM was applied at 0 t/ha and 25 ppm Zn fertilizer applied, adsorbed Zn was 564.75 μgg^{-1} while it was 453.50 μgg^{-1} for 10 t/ha at same 25ppm level of Zn.

Adsorption was observed to be high in soils without FYM than soils receiving 5 and 10 t/ha FYM but it differs in case of 15 t/ha FYM which showed increased Zn adsorption at 75 and 100ppm. The highest adsorption (1122.75 μgg^{-1}) was recorded with 15 t/ha FYM and 100ppm Zn application and lowest with 15 t/ha and 50 ppm Zn.

For all the levels of FYM, increasing addition of Zinc to the soil resulted in an increase in the equilibrium Zn concentration. Also, an increasing trend in the amount of Zn adsorbed was observed. Application of 5 and 10 t/ha FYM had relatively lower amounts of Zn adsorbed compared to the 0 t/ha FYM soil.

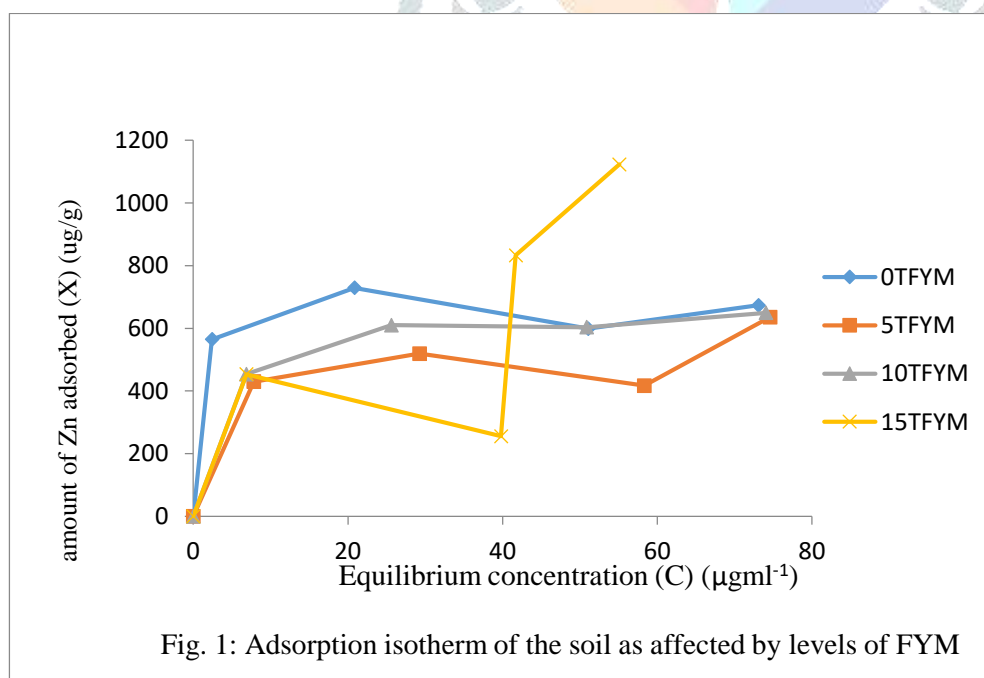
Table 3: Zinc adsorption data of Gongulong-yerimari soil studied

Treatment		Initial Zn concentration (μgml^{-1})	Equilibrium concentration (μgml^{-1})	(C) Equilibrium concentration- Zero concentration (μgml^{-1})	(X) Amount of Zn adsorbed (μgg^{-1})	C/X	Log X	Log C
FYM levels (t/ha)	Zn levels (ppm)							
0	00	0	0.03	0.00	0.00	0.00	0.00	0.00
0	25	25	2.44	2.41	564.75	0.0043	2.75	0.38
0	50	50	20.86	20.83	729.25	0.0286	2.86	1.32
0	75	75	51.09	51.06	598.50	0.0853	2.78	1.71
0	100	100	73.09	73.06	673.5	0.1085	2.83	1.86
5	00	0	0.04	0.00	0.00	0.00	0.00	0.00
5	25	25	7.85	7.81	429.75	0.0182	2.63	0.89
5	50	50	29.28	29.24	519.00	0.0563	2.72	1.47
5	75	75	58.36	58.32	417.00	0.1399	2.62	1.77
5	100	100	74.62	74.58	635.5	0.1174	2.80	1.87
10	00	0	0.03	0.00	0.00	0.00	0.00	0.00
10	25	25	6.89	6.86	453.50	0.0151	2.66	0.84
10	50	50	25.64	25.61	609.75	0.0420	2.79	1.41
10	75	75	50.90	50.87	603.25	0.0843	2.78	1.71
10	100	100	74.05	74.02	649.50	0.1140	2.81	1.87
15	00	0	0.02	0.00	0.00	0.00	0.00	0.00
15	25	25	6.89	6.87	453.25	0.0152	2.66	0.84
15	50	50	39.80	39.78	255.5	0.1557	2.41	1.60
15	75	75	41.71	41.69	832.75	0.0501	2.92	1.62
15	100	100	55.11	55.09	1122.75	0.0491	3.05	1.74

Adsorption isotherm of the soil is shown in Fig. 1. Adsorption pattern of 0, 5, 10 t/ha FYM were similar in trend but quantitatively differed in amount of Zn adsorbed. Initially, 0 t/ha FYM was higher, followed by 10, 5 and 15 t/ha FYM. Langmuir and Freundlich adsorption isotherms for the soil as affected by FYM are given in Figures 2-5 and Figures 6-9. The maximum adsorption and binding energy for Langmuir isotherm and the adsorption constant and adsorption intensity are given in Table 4. Plotting C/X against C gives the Langmuir adsorption Model. This is presented in Figures 2-4 for 0, 5, 10 and 15t/ha FYM levels. 0, 5 and 10 t/ha FYM conformed to the model as the plots were linear and had higher r^2 values that can be relied upon. For example, with 5 and 10 t/ha FYM levels, the r^2 values were 0.91 and 1.00. But with 15t/ha FYM, the adsorption did not conformed to the model as the r^2 value was low (0.33) and therefore did not satisfy the Langmuir model.

Freundlich linear adsorption model are presented from Figures 6-9. This was done by placing $\log X$ on the Y-axis and $\log C$ on the X - axis by which a linear graph together with higher r^2 value shows conformity to the model. Both FYM treated and untreated soils (Figures 6-9) had conformed to the model considering the r^2 values. For example r^2 value was 0.78 and 0.77 when 5 and 10 t/ha FYM were applied. Saleem *et al.* (2016) also found similar trend on Zn adsorption as affected by FYM, biochar and poultry manure.

Table 4 shows Langmuir and Freundlich constants. Langmuir maximum adsorption for Zn was 666.67 which were the same for 0, 10 and 15 t/ha FYM levels applied. The higher adsorption maximum and binding strength values closely determine the strength of attachment with which Zn is bonded to soil particles (Bahl *et al.*, 1986). Langmuir binding strength was higher (18.76) for soil untreated with FYM which suggests that the Zn adsorbed by untreated soils was very strongly retained by the soil compared to soils receiving FYM. For example 5t/ha FYM with binding strength of 0.38 was lower (Table 4). Freundlich adsorption constant (K) which gives the affinity for adsorption was higher for soils without FYM treatment. When 0 t/ha FYM was applied Freundlich adsorption K was 11.89 while with 15 t/ha FYM applied Freundlich adsorption K was 2.81. Freundlich adsorption intensity (n) was higher for soils receiving FYM application which suggests slower increase in adsorption with soils treated with FYM. For example this was highest (1.52) for 15 t/ha FYM application and lowest (1.11) for soil untreated with FYM (Table 4).



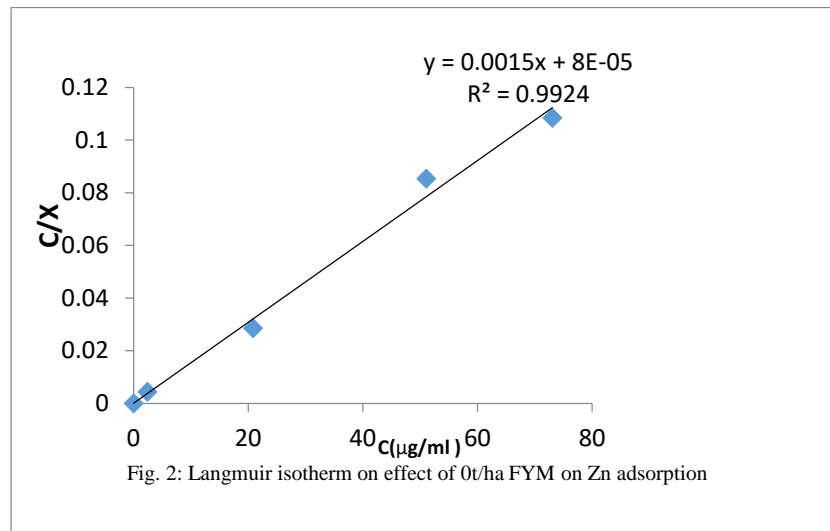


Fig. 2: Langmuir isotherm on effect of 0t/ha FYM on Zn adsorption

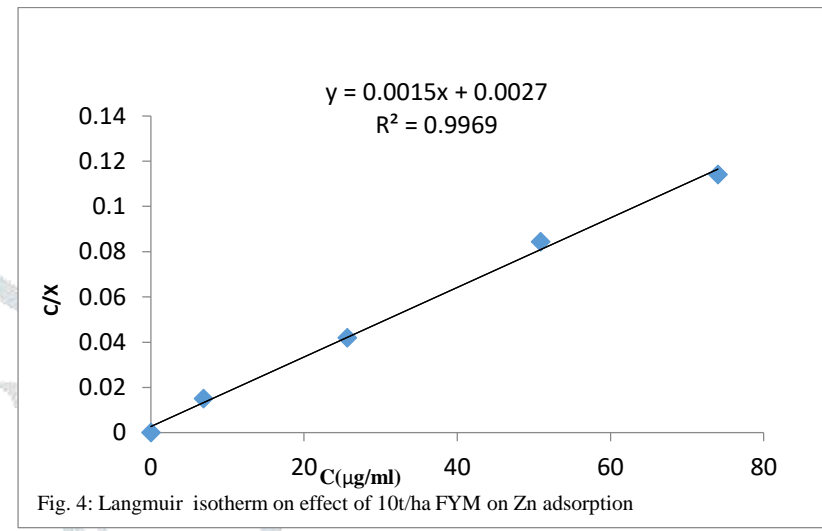


Fig. 4: Langmuir isotherm on effect of 10t/ha FYM on Zn adsorption

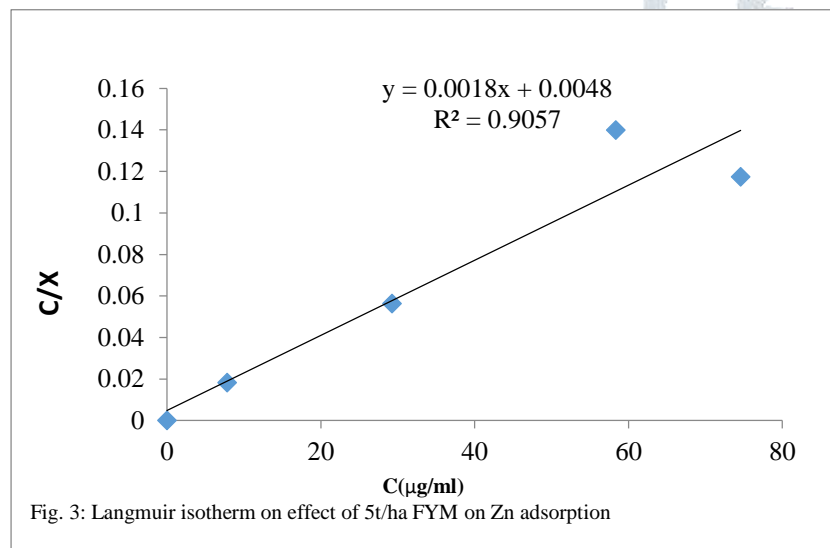


Fig. 3: Langmuir isotherm on effect of 5t/ha FYM on Zn adsorption

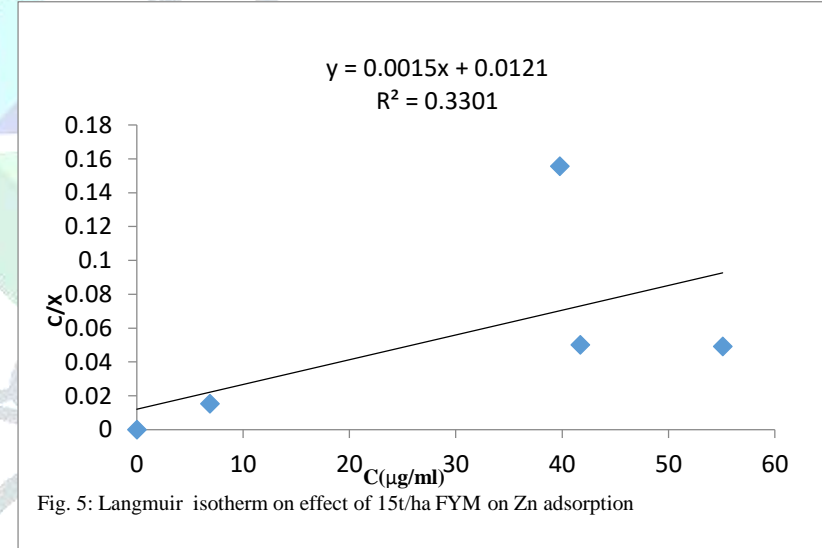


Fig. 5: Langmuir isotherm on effect of 15t/ha FYM on Zn adsorption

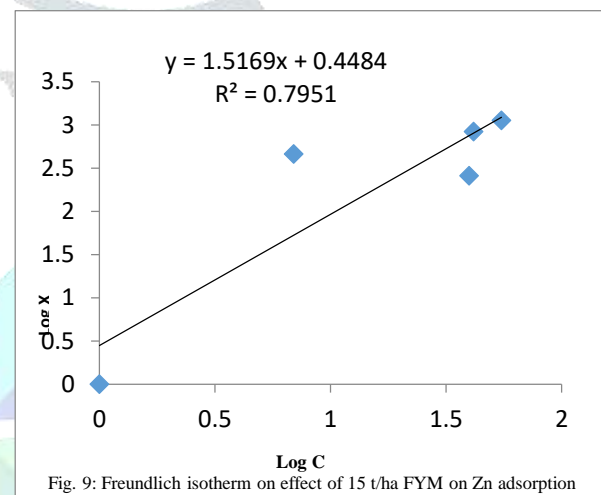
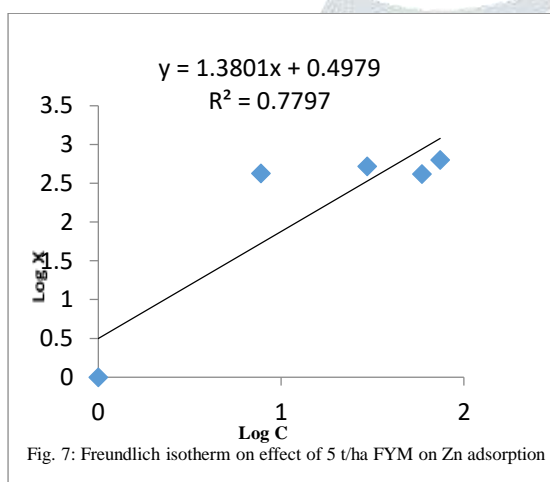
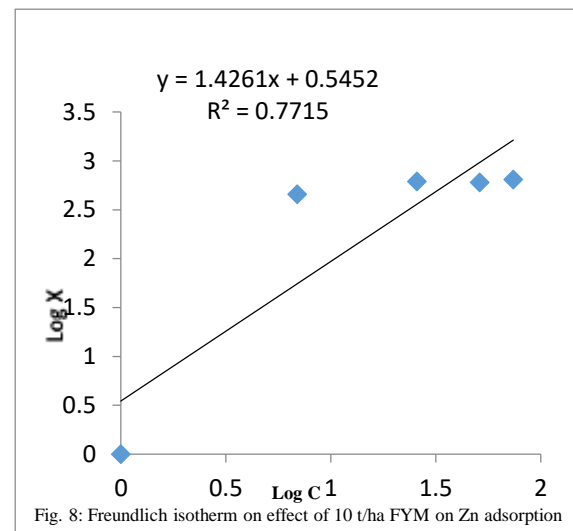
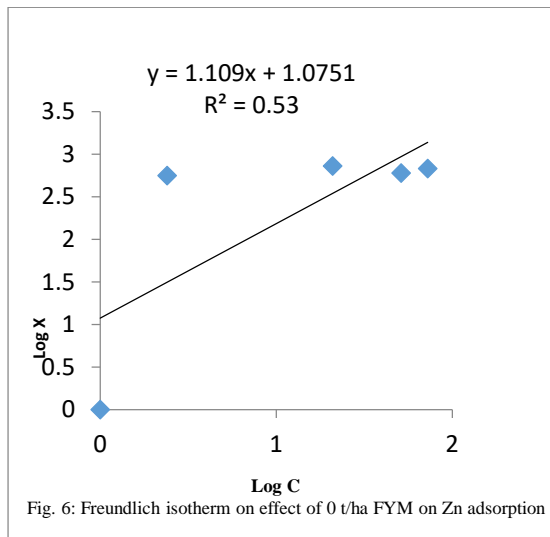


Table 4: Maximum adsorption and binding energy for Langmuir isotherm and adsorption constant and adsorption intensity for Freundlich and their regression coefficient

FYM rates (t/ha)	Langmuir			Freundlich		
	Maximum adsorption (b) ($\mu\text{g g}^{-1}$)	Binding strength (K)	r^2	Adsorption constant (K)	Adsorption intensity (n)	r^2
0	666.67	18.76	0.9924	11.89	1.11	0.5300
5	555.56	0.38	0.9057	3.15	1.38	0.7797
10	666.67	0.56	0.9969	3.51	1.43	0.7715
15	666.67	0.12	0.3301	2.81	1.52	0.7951

1.4 DISCUSSION

1.4.1 Zn Adsorption by the Soil Studied

Adsorption of Zn and equilibrium Zn concentration increased with increase in level of FYM for all the treatments with differing pattern. This is similar to the findings of Saleem *et al.* (2016) who stated that the Zn adsorption and equilibrium Zn increased with increase in applied Zn levels in both treated and untreated soils but with different patterns.

Adsorption isotherms have provided information about micronutrients adsorption by soils (Harter, 1991). Amount of Zn adsorbed (X) was plotted against the equilibrium concentration of Zn (C) to obtain the isotherms. Application of FYM at different levels had also affected equilibrium Zn concentration and Zn adsorption. With regards to Zn adsorption by the soil, adsorption was initially high in 0t/ha FYM followed by 10, 5 and 15 t/ha FYM. With increase in Zn concentration, adsorption was still higher in 0, followed by 10, 5 and 15 t/ha in this order. Further increase of Zn fertilizer from 75 - 100 ppm, 15 t/ha had the highest Zn adsorption followed by 0, 10 and 5 t/ha FYM. In general, adsorption was found to be higher in soils without FYM treatments than those treated with FYM which goes with the findings of Jalali and Jalali (2011), that the addition of organic amendments reduces the adsorption potential of Zn and increase Zn solubility and plant uptake (Tarkalson *et al.*, 1998). However, the implication of more adsorption by non-treated soil implies that, more Zn fertilizer application is needed in case of fixing Zn related problem in the soil. Adsorption data recorded for all the treatments were plotted in Langmuir and Freundlich isotherms. Langmuir Isotherm was best fitted to the data compared to Freundlich Isotherm as the r^2 values were higher for Langmuir Model.

With Langmuir adsorption isotherm, 0, 5 and 10 t/ha FYM treatments fitted to the model, as the r^2 values were higher. The bonding energy (K) and maximum adsorption (b) were also calculated. The K was higher for soils without FYM (18.76) than for the FYM treated soils which shows possibly more adsorption by the untreated soils. The maximum adsorption ranged from 555.556 - 666.667 $\mu\text{g g}^{-1}$ with 5t/ha having the lowest and 0, 10 and 15 t/ha FYM maintaining same value of 666.667 $\mu\text{g g}^{-1}$ respectively. The higher adsorption maximum (b) and bonding energy (K) closely determine the strength of attachment with which Zn is bonded to soil particles (Bahl *et al.*, 1986).

The adsorption data had fitted to Freundlich model but not as that of Langmuir as the linear relationship (r^2) (Table 4) were lower. Adsorption constant /coefficient (K) was 11.888 for untreated soils which was higher than the soils treated with FYM which shows more adsorption in soils without FYM. This is supported by the findings of Saleem *et al.* (2016) who found similar results to this in studying effect of amendments on Zn adsorption when Freundlich equation was applied.. This implies that presence of FYM can reduce the rate at which Zn is adsorbed by the soil studied. The adsorption intensity (n) were higher for soils with FYM which shows that adsorption was faster in soils without FYM treatment. According to Gregory *et al.* (2005), lower n value indicates more heterogeneity supporting that application of inorganic amendments increased the heterogeneity of the soil, though, adsorption intensity increases with increase in applied FYM level applied from 0-15 t/ha as soil surface increasingly become heterogeneous.

1.5 CONCLUSION

Zn adsorption increased with increasing Zn levels from 0-100ppm and farmyard manure decreased Zn adsorption at 5 and 10 t/ha FYM and increased Zn adsorption at 15 t/ha FYM and the adsorption data of the soil studied conformed to Langmuir and Freundlich adsorption models.

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