

Adsorption-desorption Study of Heavy Metals on Sandy-loam Soil of Sapele Metropolis

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Abstract: Adsorption – desorption processes controls the fate and bioavailability of heavy metals in soils. In this study, adsorption-desorption characteristics of aggregated soil samples from Sapele was studied using batch process in order to ascertain how heavy metals cations (Mn, Cu, Zn, Pb, Cd & Cr) are adsorbed and desorbed onto and from soil solid phase in a competitive situation. For all metals, we noted a general increase in metal adsorbed as equilibrium concentrations increases. The distribution coefficients (K_d) also increases with decrease concentration of soil solution. K_d values for Zn, Cu, and Mn were particularly higher compared to Pb, Cd, and Cr suggesting that soil loading of the later group are of greater environmental concern in this soil, than the former; and that the latter could easily be leached to nearby waters and aquifers. The adsorption isotherms were fitted to the Freundlich and Langmuir equations with the Freundlich given a better fit. The three adsorption sequences found for the soil were: Zn > Cu > Mn > Pb > Cd > Cr; Cu > Zn > Mn > Pb > Cd > Cr; and Cu > Mn > Zn > Pb > Cd > Cr. Neither electronegativity, electrostatics, Misono softness parameter nor hydrolysis properties could explain explicitly any of these orders. The soil parameters such as clay type and contents, Fe and Al oxides as well as organic content of the soil seems to have a major function in dictating the orders of adsorption. Adsorption of metals by soil increases with increase in hour of contact time and decrease with increase concentration of EDTA in soil solution. Desorption of metals from soil follow a similar pattern of initial fast phase reaction followed by slow phase reaction observed for the adsorption of metal onto soil. However, within the time frame, desorption was not completely reversible suggesting an evidence of hysteresis.

Key words: adsorption, desorption, distribution coefficients, heavy metals, sandy-loam, Sapele.

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I. Introduction

Adsorption-desorption processes controls the fate and bioavailability of heavy metals in soils. It determines the mobility and availability of plant nutrients and other contaminants retained in soil surfaces. Trace elements adsorption capacity of soil varies with the amount of sorptive phases (i.e, reactive oxide content, and organic matter content) and chemical property (i.e, pH) of the soil. Both physical and chemical forces are responsible for adsorption of solutes from solution. The physical forces include vander waal-force (e.g dispersion, a dipolar interaction and partitioning) and electrostatic outer-sphere complexes (e.g. ion exchange). Covalent bonding, hydrogen bonding and inner [sphere complexation involving a ligand exchange are forms of chemical forces [1]. Gomes et al [2], cited various models proposed by different authors to explain adsorption of metal cations, among such are; the exchange of H^+ for M^{n+} , the preferential adsorption of hydrolyzed products, the induced hydrolysis of cations on the surface of hydroxides and the affinity of cations for the surface O which usually correlate with electronegativity. The determinant nature of electronegativity in the preferential sorption of trace metals is well buttressed by [3]. McBride [3] also, emphasized the role of electrostatics in determining the ability of metals to chemisorb and predicted that the strongest bond would be for metals with the greatest charge-to-radius ratio. Others ascribed the major force governing the adsorption of metals cations to pH [4], [5]. Sposito [6], using the Misono softness parameter (quantified by ionic radius and the ionization potential), defined the tendency of metals to form covalent bonds and related this tendency to the ability of the metals cations to form strong complexes base.

The selectivity sequence for most studies have not all followed a definite pattern; however there seems to be a strong agreement between adsorption sequence and the hydrolysis properties of the heavy metal cations. Differences in adsorption and desorption isotherm typically show significant hysteresis and evidence that the process is not simply a competitive ion-exchange between metal ions and protons or hydroxyls. Some adsorbed metal is not readily desorbed being strongly bonded to the soil components. A major discrepancy that causes errors in predicting the potential toxicity of a contaminant is that researchers often ignore desorption characteristics. This is regrettable since once a soil is contaminated, desorption is an important process that

controls the bioavailability of the contaminant. If accurate assessment of the fate of metals in soils are to be gained, it is crucial that desorption behaviour be considered as well as sorption behaviour. The mobility and fate of metals in soil environment are directly related to their partitioning between soil and soil solution and therefore, are directly related to their distribution coefficients. Distribution coefficient is a useful parameter for comparing the sorptive capacities of different soils or materials for any particular ion, when measured under the same experimental conditions [7]. The objective of this study is to characterize sorption and desorption property of some heavy metals (Zn, Cu, Cr, Pb, Mn, & Cd) in a sandy-loam soil of Sapele metropolis.

II. Materials and Methods

The study area - Sapele metropolis - is situated between longitude 5°38'E and 5°55'E and latitude 5°33'N and 5°57'N. The aggregated soil sample for the study was obtained by compositing soil samples from ten sites which is representative of most common soil in the metropolis. The sample was air-dried, sieved through 2mm (10 mesh) stainless sieve and the physico-chemical properties were determined using standard methods [8], [9]. Adsorption characteristics of the aggregated soil was studied by preparing 50ml of cocktail solutions containing concentrations of 0, 5, 15, 25, 35, and 50mgL⁻¹ of all heavy metals' cations (Mn, Cu, Zn, Pb, Cd & Cr) in the same concentrations (the metals' cations were applied in the forms; MnCl₂. 4H₂O, CuCl₂.H₂O, Zn(NO₃)₂.4H₂O, Pb(NO₃)₂, CdCl₂, and CrCl₃.6H₂O). 5g of soil was added to each solution, agitated and equilibrated at room temperature (27°C) for 1hr. The solution was then separated from soil by filtration (using Whatman 42 filter Paper). Analyses of heavy metals cations concentration in each Filtrate was done by Atomic absorption spectrophotometry (Model 210 VGP). The differences between the initial amount of metals in solutions and the amount remaining after the reaction period were assumed to be adsorbed by the soils. The experiment was repeated with 25mgL⁻¹ of cations in solution and the effect of contact time (1, 3, 6, 9, 24, and 48hrs) was examined. The effects of the presence of ligand (EDTA) under varying concentrations (0.001, 0.002, 0.003 and 0.004M) were also studied using 25mgL⁻¹ cations in EDTA solutions. The desorption of heavy metals from soil was studied by using the residue of heavy metals enriched- soil separated from the supernatant solution of 50mgL⁻¹ heavy metals equilibrated for 48hrs. 50ml of distilled (deionized) water was added to the soil residue. The suspension was shaken for 1hr at room temperature (27°C) then; the soil was separated from the solution by centrifugation. The supernatant liquid obtained after centrifugation was analysed and the heavy-metals cations (Mn, Cu, Zn, Pb, Cd & Cr) desorbed into solution were ascertained by atomic absorption spectrophotometry. In order to estimate the affinity of heavy- metals to the soil, the desorption process was repeated six times (1, 3, 6, 9, 24 and 48hrs). The non extractant Fraction of the adsorbed heavy- metals in soil were obtained by difference between the total adsorbed heavy-metals and the total recovered heavy- metals by six successive extractions

III. Results and Discussion

The physicochemical properties of the soil and results of metals adsorbed under varying concentrations of solution for 1hour are as presented in Table 1 and Fig. 1.

Table 2: Some physico- chemical properties of the sandy-loam soil

Parameters	Results ± SD
pH	5.97± 0.02
Clay(%)	11.45± 1.10
Silt(%)	8.45±1.20
Sand(%)	80.10±3.30
TOC(%)	1.08±0.30
OM(%)	1.85± 0.30
P(mg/Kg)	28.94± 7.40
CEC(cmol/Kg)	13.27±0.45
Zn(mg/Kg)	11.80±1.40
Mn(mg/Kg)	4.49±1.10
Pb(mg/Kg)	1.45±0.00
Cu(mg/Kg)	15.68±3.00
Cr(mg/Kg)	0.20±0.00
Cd(mg/Kg)	0.02±0.00

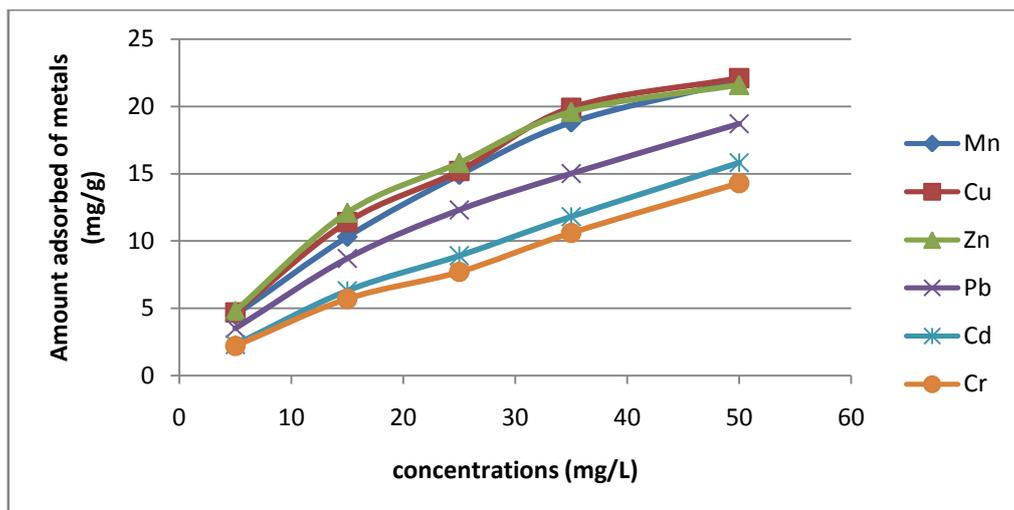


Fig 1: Metals adsorbed from solution under varying concentrations of solutions for 1hr.

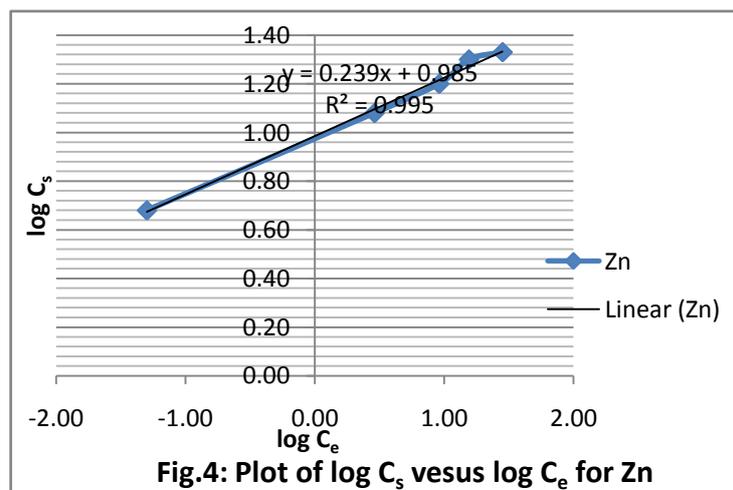
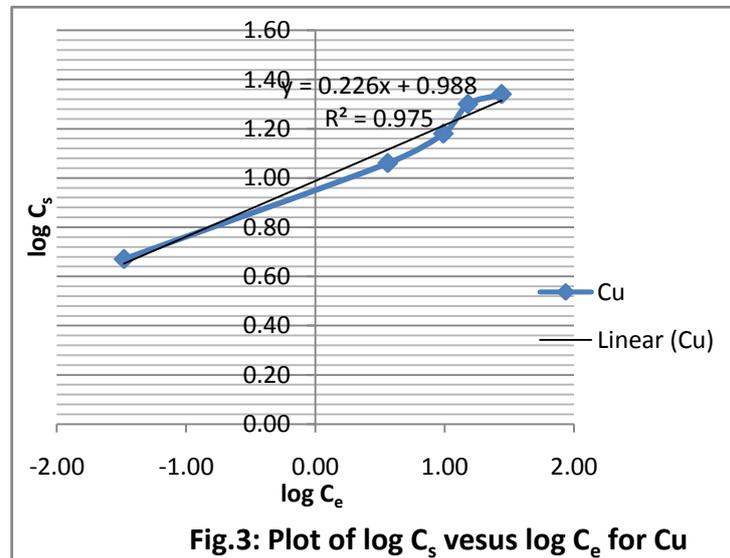
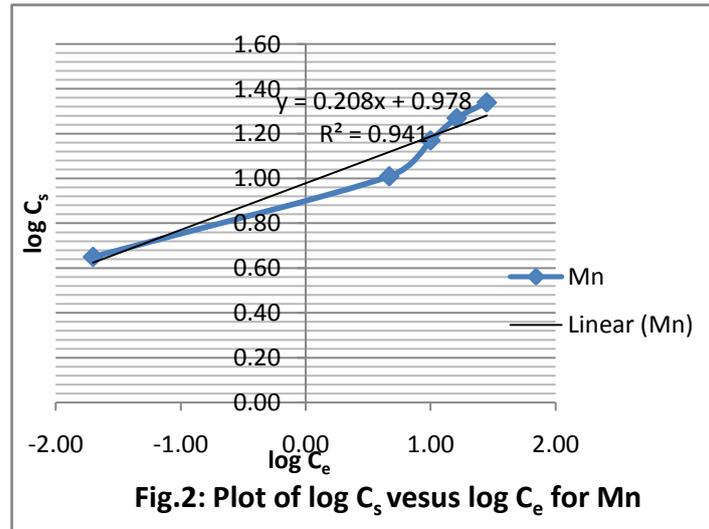
For all metals, we observed an increase in metal adsorbed as solution concentrations increases. The low concentrations of metals in the original soil use in the study must have induced less of inter-elemental competition for sites such that each metal tended to be increasingly adsorbed in the face of the others. Gomes et al [2], carried out a similar competitive adsorption on heavy metals (Cd, Cr, Cu, Ni, Pb, & Zn) noticed that Cadmium and Zinc tended to decrease after getting to maximums due to inter- elemental competition for sites.

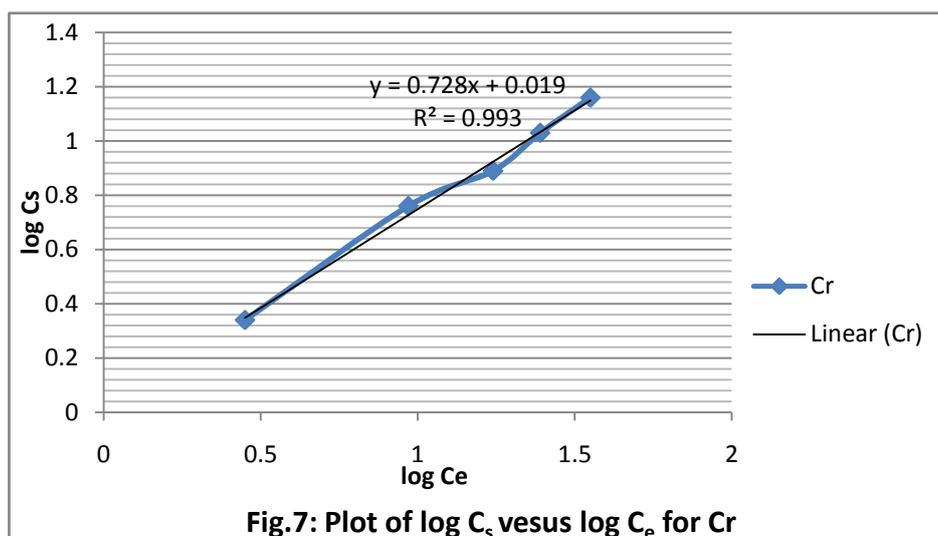
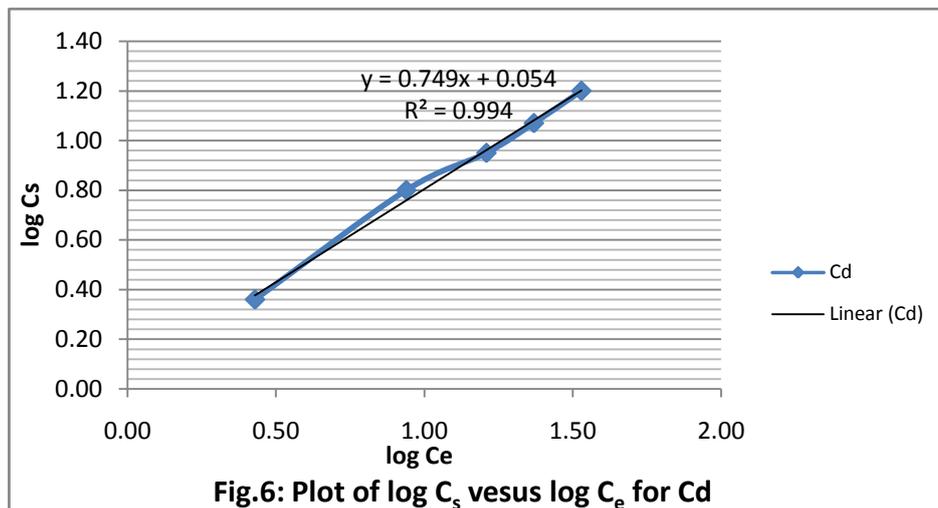
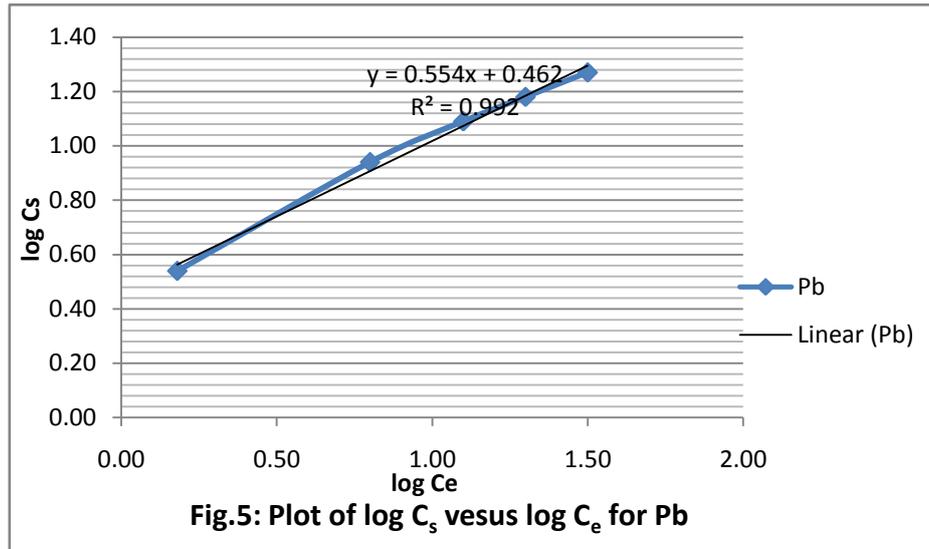
Table 2; show the distribution coefficients (K_d) for the different added concentrations. K_d indicate the sorption affinity of metal cations in solution for the soil solid phase and can be used as a valuable tools to study metal-cation mobility and retention in soil systems. According to [10], high values of K_d indicate that the metal has been retained by the solid phase through sorption reactions, while low values of K_d indicate that a large fraction of the metal remains in solution.

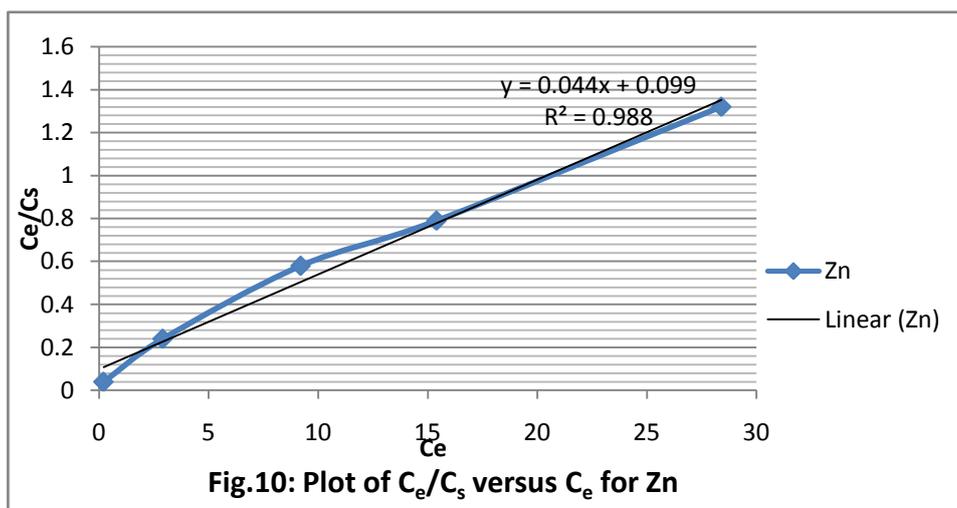
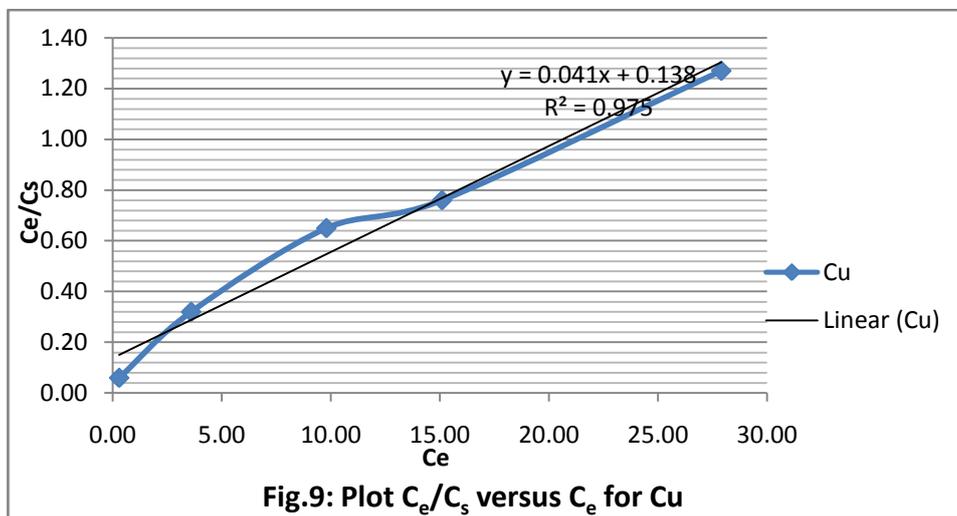
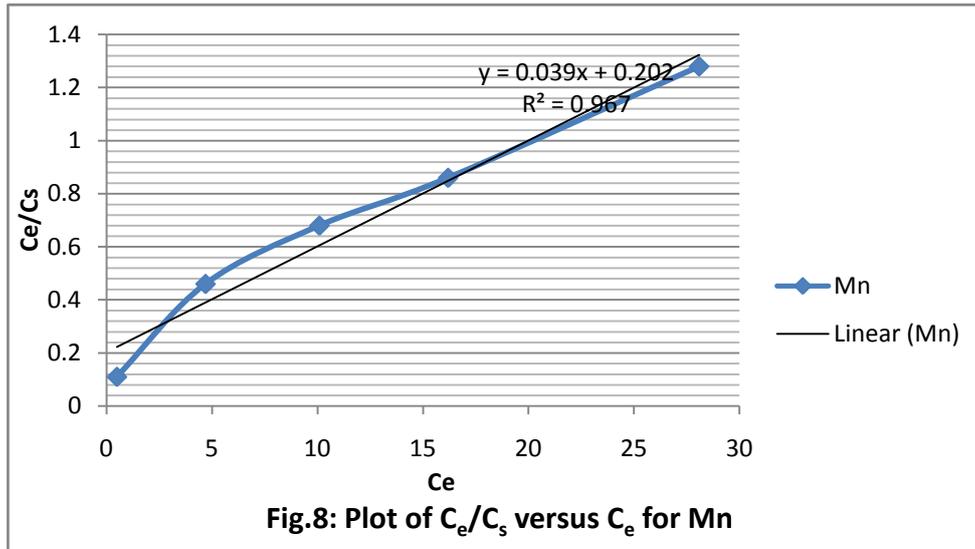
Table 2: K_d Values for the different concentrations of solution

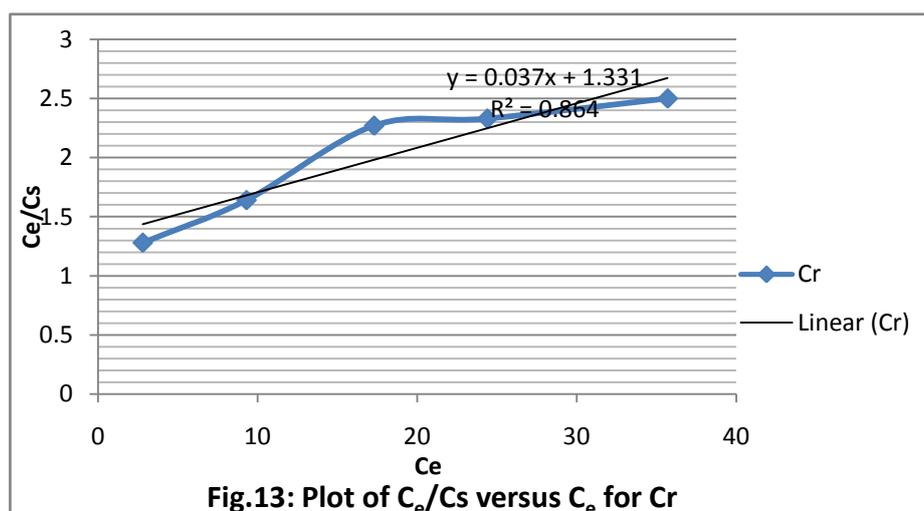
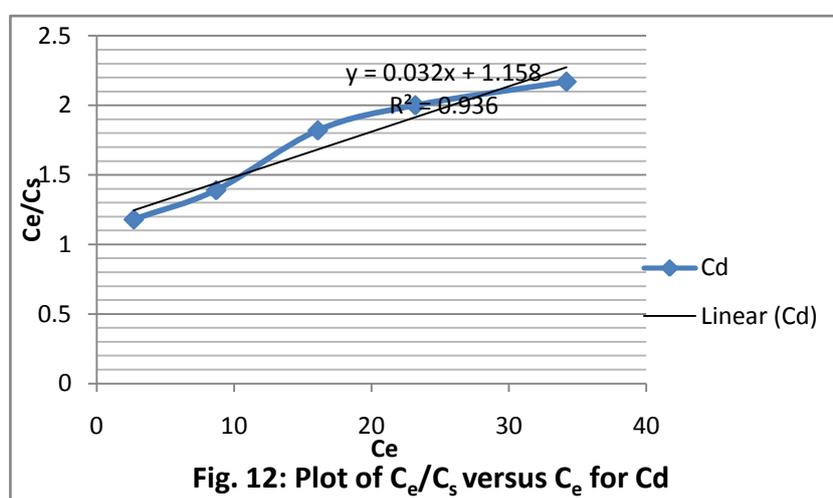
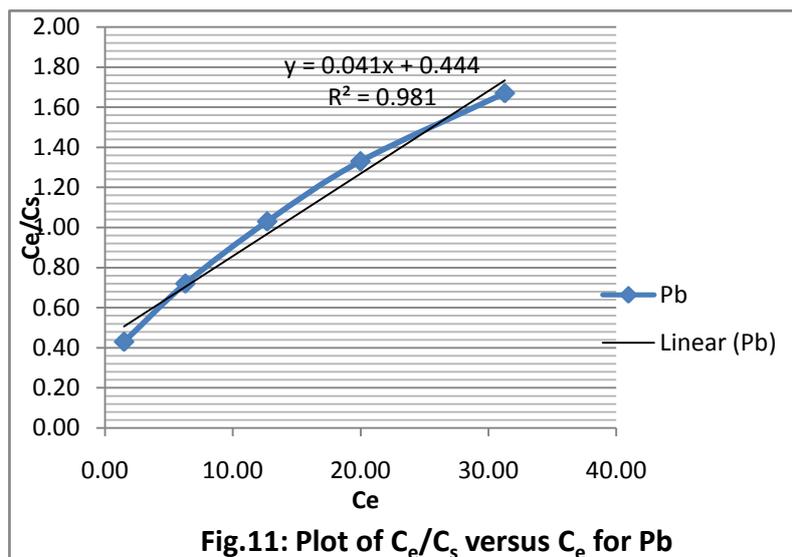
Concentrations (mg/L)	Mn	Cu	Zn	Pb	Cd	Cr
5	9.00	15.67	24.00	2.33	0.85	0.78
15	2.19	3.17	4.17	1.38	0.72	0.61
25	1.48	1.55	1.72	0.97	0.55	0.44
35	1.16	1.32	1.27	0.75	0.50	0.43
50	0.78	0.79	0.76	0.60	0.46	0.40

From Table 2, it can be seen that K_d values for all metals decrease with increase concentration of solution and that K_d values for Zn, Cu, and Mn were higher compared to Pb, Cd and Cr. This suggests that soil loading of Pb, Cd, and Cr is of greater ecological threat in this soil, than Zn, Cu, and Mn and that the first group could be easily leached to nearby waters and aquifers. The smaller concentrations of metals in soil used in this study perhaps did not induce a strong competition among the metal cations studied. Therefore, plots of the logarithm concentration of metal adsorbed ($\log C_s$) versus logarithms of the equilibrium concentration of metals in solutions ($\log C_e$) as well as that of equilibrium concentration of metals in solution over concentrations of metal adsorbed (C_e/C_s) versus equilibrium concentration of metals in solution (C_e) gave a near fit to the Freundlich and Langmuir equations with $R^2 > 0.97$ and 0.86 respectively. (Fig. 2-13) These results are in line with those of [11] for simultaneous sorption of metal cations. These data were better fitted by the Freundlich equation than by the Langmuir equation, possibly due to the heterogeneity of the adsorbent surfaces. These results is consistent with the conclusion of [12] that in variable- charge soils, the Freundlich model better describes the adsorption behaviour of heavy metal than the Langmuir model.









The Freundlich adsorption isotherm equation given by: $C_s = K_d \times C_e^{1/n}$ where C_s is amount of heavy metal adsorbed at equilibrium concentration C_e . K_d is the Freundlich distribution coefficient and n is a correction factor [5], gives the following values of K_d : 9.73, 9.66, 9.51, 2.90, 1.13, and 1.05 respectively for Cu, Zn, Mn, Pb, Cd, and Cr, while the corresponding n values were: 4.42, 4.18, 4.81, 1.80, 1.33 and 1.37 respectively. This is characteristic of a weak affinity of the soil for Pb, Cd and Cr. Work done by [2], shows

that the sorption affinity of Cd and Cr were mainly influence by pH, while Pb tended to be influenced by pH and Cation Exchange Capacity (CEC). The pH of this soil (pH =5.97) perhaps did not allow for much adsorption of these metals. The fact however, that the metals were added in equal mass, rather than equimolar amounts, introduces a possible bias in the comparison of the metals. There would be a bias in favour of the higher atomic mass elements, Cd and Pb, because of the decrease in K_d values at higher concentrations, while at the same time there would be a bias against, these elements because they are at a competitive disadvantages for a finite number of sites. The direction of the overall bias is not predictable but would show up in apparent selectivity at different concentrations of the metals.

The Langmiur adsorption isotherms equation: $C_e/C_s = C_e/C_m + 1/C_m \cdot L$ where C_s (mg/g) is the amount of heavy metal adsorbed at equilibrium concentration C_e (mg/L), C_m (mg/g) is the maximum adsorption capacity of the adsorbent, and L (L/mg) is the Langmiur constant, which is related to the free energy of adsorption [13]. C_m and L were calculated from the linear plot of C_e/C_s versus C_e (Fig. 8-13) Table 3.

Table 3: Values C_m and L for metals in Soil

	Mn	Cu	Zn	Pb	Cd	Cr
C_m	25.64	24.39	22.73	24.39	31.25	27.02
L	0.0193	0.2971	0.4442	0.0923	0.0277	0.0278

The maximum adsorption capacity of the soil after 1 hour of contact time (Table 3) for Cd, Cr, and Mn appears to be higher than that for Cu, Pb, and Zn. However the Langmiur constants which indicate the soil affinities for the metals were in the order: $Zn > Cu > Pb > Cr > Cd > Mn$. Although, the soil has a high maximum adsorption capacity for Cd and Cr, they were least retained because of their low affinities for the soil in presence of other metals. They thus, have the lowest K_d Values. The three adsorption sequences found for the different concentrations of solutions (Table 2 & K_d from the Freundlich equation isotherms) were: $Zn > Cu > Mn > Pb > Cd > Cr$; $Cu > Zn > Mn > Pb > Cd > Cr$; and $Cu > Mn > Zn > Pb > Cd > Cr$. None of these sequences exactly followed the order of the electronegativity of the metal cations, which is, according to [3], Cu(1.9), Pb(1.8), Cd(1.7), Zn(1.6), Cr(1.6), and Mn(1.5) (Paulings electronegetivities) The presence of Zn as one of the most retained cations, in spite of its lower electronegativity than Pb and Cd could be adduce to smaller ionic radius(0.75) compared to 1.18 and 0.95 of Pb and Cd respectively. The positions of Cu, Zn, and Mn tended to followed that based on electrostatics which is $Cr > Cu > Zn > Mn > Cd > Pb$, emphasizing that electrostatics play a role in bonding of divalent metals to soil particles and organic matter [3]. The order however, was faulted by the position of Cr being least adsorbed and Pb being more adsorbed than Cd in all the series. The Misono softness parameter which is based on the ability of metals cations to form covalent bonds ($Pb > Cd > Cu > Cr > Mn > Zn$) is perhaps a reason for Pb been more adsorbed than Cd and Cr [6]. McBride [14], using K_d values to indicate the potentials for leaching losses of some elements, found Cr, with a very high K_d value, to be the least mobile element. The reverse obtained in this study may due to different soil parameters such as pH, clay type and contents, Fe and Al oxides as well as organic content of the soil which seems to have a major function in dictating the orders of adsorption.

Chemical contaminants in soils can take several pathways, including rapid leaching into ground waters, uptake by plants, volatilization to the atmosphere, and storage and retention by soil [15]. Therefore, an important characteristic of many soils is their ability to adsorbed and store heavy metals. Fig. 14 show the amount of metals (mg/g) adsorbed from 25mg/L cations solution under varying hours of contact time.

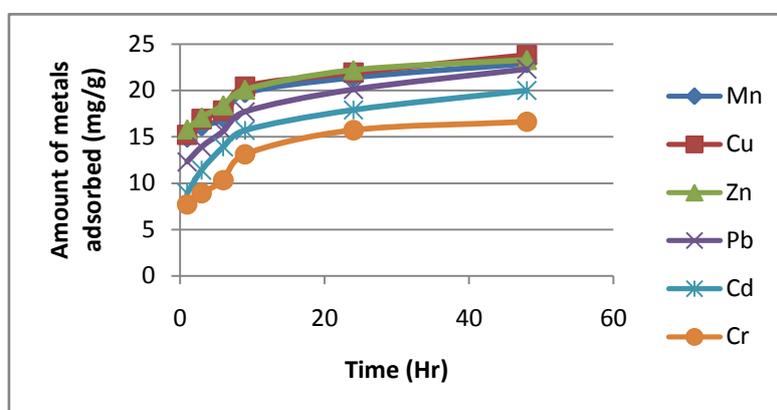


Fig. 14: Plot of metal adsorbed from 25mg/g cations solution under varying hours of contact time.

In all cases, there is sharp increase in adsorption (fast sorption reaction) from the 1st hour to the 10th hour, after which the slope of the adsorption tended to decrease markedly (slow sorption steps) The two stage time – dependent metal sorption behaviour is similar to the results observed on pure components and soils obtained by other researchers [16], [17], [18], [19]. The fast reaction is most likely adsorption via electrostatic attraction, and/or inner-sphere complexation with functional groups present on the soil components. It is Likely that several mechanisms are responsible for the slow sorption reactions, such as: slow interparticle diffusion in porous minerals and organic matter, formation of precipitates on surfaces and/or sorption reactions on sites that have higher activation energy than the fast sorption sites [19], [20], [21].

The effect of the presence of Ligand – EDTA – in solution on heavy metal adsorption by soil was study using different concentrations of EDTA (Fig. 15).

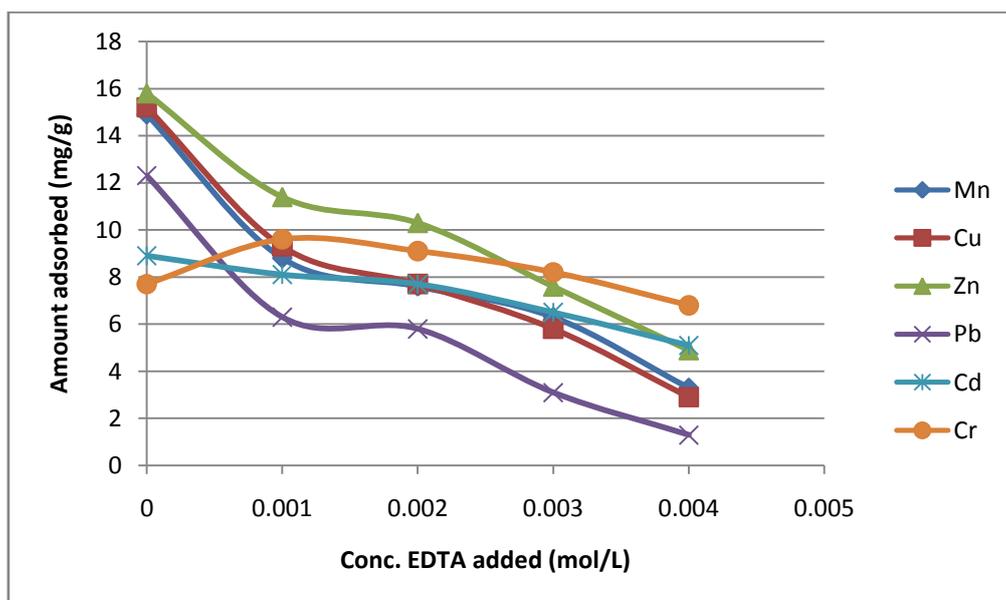


Fig.15: Plot of metal adsorbed (mg/g) from 25mg/L cations solutions under varying concentrations of EDTA

It could be seen that there is a general decrease in adsorbed metals as the concentrations of EDTA in soil solution increases. The conversion of the ions into coordination complexes must have resulted in a substantial change in solubility which affected the adsorption of these cations. Fig. 16 show the amount of cumulative metals desorbed (mg/g) after varying hours of contact time; from the 50mg/L cations enriched soil.

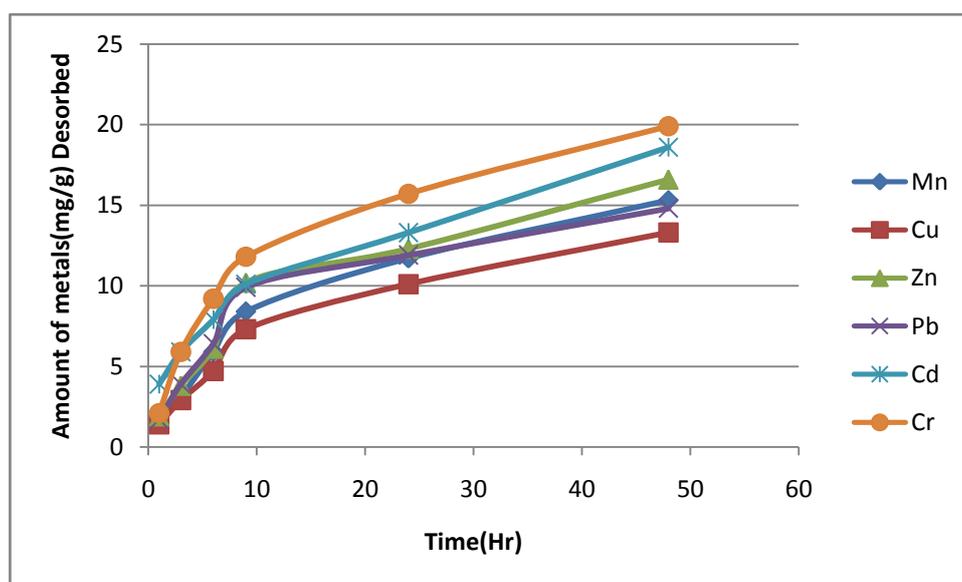


Fig. 16: Plot of Cumulative metal desorbed versus contact time

The rate of desorption was high for the first ten (10) hours after which it diminishes. The pattern of desorption was similar to that of adsorption isotherm (Fig.14). However after 48 hours of desorption, noticeable amount of metals adsorbed were still left undesorbed (Fig.17).

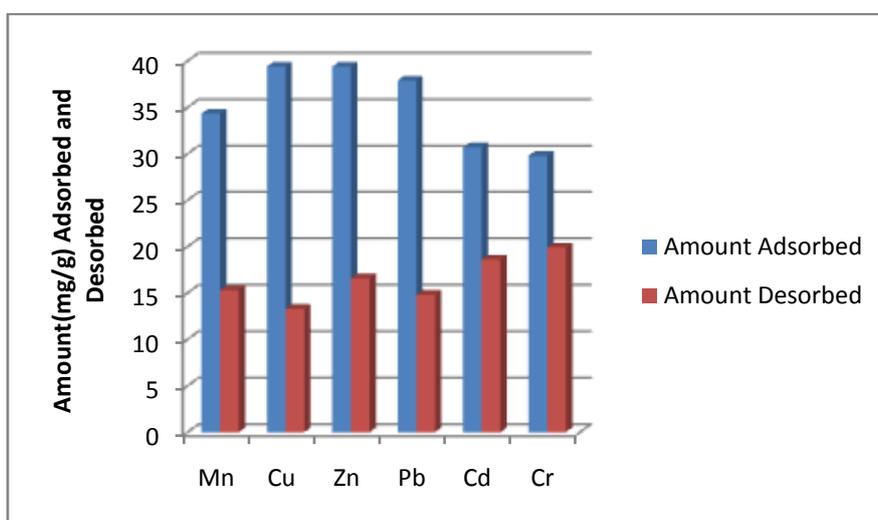


Fig. 17: Amount adsorbed and desorbed from 50mg/L cations solution after 48hours

This is an evidence of hysteresis, indicating that physical processes alone, cannot account for the sorption of these metals onto soil. Chemosorption is involved. Cu and Pb, tended to be more irreversibly adsorbed onto the soil. Approximately, 33.76 and 39.05% of the adsorbed Cu and Pb was respectively desorbed by six successive extraction compared to Cd and Cr with respective 60.59 and 66.78% desorption. 44.61% and 42.13% of adsorbed Mn and Zn were respectively desorbed from the soil. These high irreversible adsorptions of Cu and Pb onto this soil suggest that Cu and Pb forms high energy bonds with soil colloids, while the high percentage desorption of Cd and Cr is indicative that most of the adsorbed Cd and Cr are bioavailable within a short time of adsorption. Adsorption – desorption reactions of metals at the soil colloidal surface affect their soil solution concentration and consequently, their availabilities to plants [22].

IV. Conclusion

Adsorption – desorption reactions of metals at soil colloidal surfaces affect their soil solution concentration and consequently their availability to plants and their leaching potential to contaminate nearby aquifers. The adsorption pattern found for the soil under competitive situation as reflected in their distribution coefficients (K_d) values show that Zn, Cu and Mn were more adsorbed than Pb, Cd, and Cr suggesting that soil loading of the later group are of greater ecological threat in this soil than the former; and that the later group could easily leached to nearby waters and aquifers. Results obtained from desorption studies however, show that far lesser percent of the adsorbed Pb and Cu is desorbed compared to Cd and Cr. Adsorption of metals by soil increases with increase in hour of contact time and the effect of the presence of ligand – EDTA – in soil solution in decreasing the amount of adsorbed metals onto soil were obvious. The adsorption isotherms fit the Freundlich and Langmuir equations but the Freundlich gave a better fit. Three adsorption sequences found for the soil were: Zn > Cu > Mn > Pb > Cd > Cr; Cu > Zn > Mn > Pb > Cd > Cr and Cu > Mn > Zn > Pb > Cd > Cr. Neither electronegativity, electrostatics, Misono softness parameter nor hydrolysis properties could explain overtly any of these orders. For individual elements, consideration of the different soil properties such as pH, clay type and contents, Fe and Al oxides as well as organic content of the soil seems necessary to improve prediction of the sequence of adsorption. Desorption of metals follow a similar biphasic pattern of adsorption, characterized by a fast initial reaction (lasting for about 10hrs) followed by a slow reaction steps. However, within the time frame of the experiment (48hrs) desorption was not completely reversible suggesting an evidence of hysteresis.

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