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# Adsorption kinetics of Copper, Lead and Zinc by Cow Dung, Poultry Manure and Cocoa (Theobroma Cacao) Pod

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**ABSTRACT:** *This study highlights the effect of cow dung, cocoa pod and poultry manure in the removal of heavy metals from solution and their applicability to Langmuir and Freundlich models was studied in the Soil Science Laboratory of Michael Okpara University of Agriculture, Umudike in Abia State, Ngeria. The amendments used in the study were locally sourced, sundried, ground and sieved with 2mm sieve. The salts of the three heavy metals were separately used to prepare heavy metal solutions of 100 mg/L. Batch study was carried out at room temperature on a mechanical shaker using 120 ml plastic bottles at different time intervals of 15, 30 and 60minutes. After shaking, the amendments and heavy metal solutions were separated using whatman No 1 filter paper, stored in the refrigerator and analyzed for heavy metals concentration. The amount of heavy metals adsorbed was calculated. The results revealed that high adsorption occur at low equilibrium concentrations in all the amendments with decreasing levels of adsorption with increasing equilibrium with cow dung and cocoa pod having higher adsorption capacity than poultry manure. Coefficient of determination (R2) showed that the experimental data fit in to both Langmuir and Freundlich models. For reduced heavy metal uptake by plants and subsequent contamination of the food chain, cow dung, cocoa pod and poultry manure should be used as amendments in heavy metal contaminated soils.*

**Keywords:** *Amendments, heavy metals, Langmuir and Freundlich models, adsorption, equilibrium concentrations.*

## I. INTRODUCTION

Adsorption kinetics is the measure of the adsorption uptake with respect to time at a constant pressure or concentration and is employed to measure the diffusion of adsorbate in the pores. Adsorption isotherms are set of mathematical models that describe the distribution of the adsorbate species between liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of the adsorbent, the type of coverage and possibility of interaction between the adsorbate species (Kumar *et al.,* 2010). An adsorption isotherm is a graph of the equilibrium surface excess or amount of a compound adsorbed (eg., in units of mmol $L^{-1}$ or mg/$kg^{-1}$) designated by q, plotted against the equilibrium solution concentration of the compound (eg., units of mmol $L^{-1}$ or mg $L^{-1}$), designated by Ceq at a fixed temperature (thus the term isotherm), pressure and solution chemistry (eg.,pH and ionic strength) (Essington, 2005).Langmuir and Freundlich models are the most commonly used theoretical models to generate adsorption isotherms. Some heavy metals are being subjected to bioaccumulation and may pose risk to human health when transferred to food chain. Lead, copper and zinc are metals that tend to accumulate in the environment causing numerous diseases to organisms (Inglezakis*etal.*, 2003).The environmental problems with heavy metals are that they as elements are not destroyable and most of them have toxic effects on living organisms when exceeding a certain concentration (Sherene, 2010). Batch experiments are effective methods of assessing metal binding and desorption kinetics at the laboratory level (Temminghoff*et al.,* 1997), because through them, a wide range of possible field situation scenarios can be simulated by modifying the factors which affect metal sorption. Sorption of metals, either from single (non-competitive), or multi-metal (competitive) solutions is very important in determining metal stability within the soil, metal uptake by plants and the capacity of amendments to immobilize the contaminants (Markiewiez-patkowska*et al.,* 2005).

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Adsorption is a major process responsible for accumulation of heavy metals and some of them are toxic even if their concentration is very low. The study of adsorption processes is of utmost importance for the understanding of how heavy metals are transferred from a liquid mobile phase to the surface of solid phase (Bradl, 2004).In most soil environment adsorption is the dominating speciation process and thus the largest fraction of heavy metal in a soil is associated with the solid phase of that soil (Sherene, 2010).Studies by Meunier*et al.,* (2003) identified cocoa pod as a promising bio-sorbent for metal removal from highly acidic solutions. Agricultural waste materials are considered to be economical and ecofriendly for heavy metal remediation due to their unique chemical composition, availability in abundance, renewability, low cost and greater efficiency(Adekola*et al.,*2016*)*. Some organic materials have the capacity to immobilize toxic metals from soil solution making them temporarily unavailable for plant uptake and subsequent accumulation in the plant. This study tried to evaluate the potential of cow dung, poultry manure and cocoa pod as adsorbents in removing heavy metals from solution and the applicability of Langmuir and Freundlich isotherms using these amendments.

## II. MATERIAL AND METHODS

### 2.1. Collection and preparation of amendments

Poultry manure and cow dung were obtained from the animal farm unit of Michael Okpara University Agriculture Umudike, Abia State Nigeria while cocoa pod was sourced from a cocoa plantation in Okworogung village in Obudu Local Government Area of Cross River State, Nigeria. Poultry manure and cow dung were sun dried, ground and sieved with 2mm sieve to obtain uniform size fraction. The cocoa pods were washed, sun dried, milled and also sieved with 2mm sieve to obtain uniform size fraction as reported by Olu-Owolabiet al., (2012).

### 2.2 Location of experiment

The experiment was conducted in the Soil Science Laboratory of Michael Okpara University Agriculture, Umudike, Abia State of Nigeria.The area lies between latitude 50 281N and 50 301 N and longitude 70 311E and 70 331 E of the equator (Adindu, et al., 2013).

### 2.3 Determination of heavy metals

The filtrates from the batch study were read using atomic adsorption spectrophotometer whileheavy metal in amendment was determined using perchloric acid digestion method as outlined by Udo et al., (2009).

### 2.4 Preparation of heavy metal solutions

Metal salts used to prepare heavy metal solutions were copper sulphatepentahydrate, (CuSO4.5H2O), zinc sulphateheptahydrate (ZnSO4.7H2O) and lead sulphate (PbSO4) presented in Table 1. Metal solutions were prepared at the concentration of 100 mg/L. To prepare concentration of 100 mg/L of each metal, 0.4g, 0.14g and 0.43g of CuSO4.5H2O, PbSO4 and ZnSO4.7H2O were respectively dissolved individually in each one liter of distilled water as reported by Noppadol and Pongsakorn, (2014).

**Table 1: Metal salts used in the study**

| Molecular name | Chemical formula | Molar mass | % metal content | Weight of salt used (g) |
|---|---|---|---|---|
| Copper sulphatepentahydrate | $CuSO_4.5H_2O$ | 249.68 | 25.44 | 0.4 |
| Zinc sulphateheptahydrate | $ZnSO_4.7H_2O$ | 287.56 | 23.0 | 0.43 |
| Lead sulphate | $PbSO_4$ | 303.25 | 68.3 | 0.147 |

### 2.5 Batch sorption

Batch sorption was conducted at room temperature. Two grams of each amendment was weighed into 120 ml plastic bottles to which 50 ml of individual heavy metal solution was separately added. The plastic bottles were then shaken on a mechanical shaker at different time intervals of 15, 30 and 60 minutes as reported by Nwachukwu and Muoneke, (2009). After the shaking, the content of each bottle was filtered out using Whatman No.1 filter paper and stored in the refrigerator until it was analyzed for heavy metal concentration. The amount of heavy metals adsorbed by each amendment was calculated with the following formula by Essington (2005)

$$q = \frac{V1(Cin-Ceq)}{MS} \quad \text{(Equation1)}$$

Where;

q = amount of heavy metal adsorbed per unit weight of amendment (mg/g)

Cin= initial concentration of heavy metal solution (mg/L)

Ceq= equilibrium concentration of solution (mg/L)

MS = mass of amendment (g)

V1 = volume of solution used ( L)

### 2.6 Isotherm models used

Langmuir and Freundlich isotherm models were employed in this study to generate adsorption data. Langmuir isotherm (Langmuir, 1918) is the most commonly used model to generate adsorption isotherm and is presented below as reported by Nappadol and Pongsakorn (2014)

$$Qe = \frac{\alpha\beta Ceq}{1+\alpha Ceq} \quad \text{(Equation2)}$$

Where;

Qe = amount of adsorbed heavy metal per weight of amendment at equilibrium (mg/g).

Ceq = equilibrium concentration of solution (mg/L)

α = Langmuir constant related to bonding energy between the adsorbed ions and the adsorbent (mg/L)

β = maximum adsorption capacity (mg/g)

The linearized form of Langmuir model was used to generate β and α.The linearized form of Langmuir model is presented below;

$$1/qe=1/\beta+ 1/ \alpha\beta(1/Ceq) \quad \text{(Equation 3)}$$

Where 1/β= intercept

1/ αβ = slope

β = 1/intercept

α = 1/β x slope

The intercept and the slope used to obtain β and α were gotten from the linear plot of 1/qe against 1/Ceq.

Freundlich isotherm model (Freundlich, 1907) is the most frequently used model to describe the adsorption of organic and inorganic compounds in solution (Olu-Owolabi et al., 2012) and is presented below as reported by Nappadol and Pongsakorn (2014);

$Qe = Kf\ (Ceq)\ 1/n$ ------------------------------------------------------------------------------- (Equation 4)

Where:

Qe = amount of adsorbed heavy metal per weight of amendment at equilibrium (mg/g).

Kf= maximum adsorption capacity (mg/g)

Ceq =equilibrium concentration of solution (mg/L)

1/n = maximum adsorption intensity (dimensionless).

Linearized form of Freundlich model was also used to obtain Kf and 1/n and is given below;

$\text{Log } Qe = \log Kf + 1/n \log Ceq$ ------------------------------------------------------------- (Equation 5)

Where 1/n = slope, n = 1/slope

LogKf = intercept, kf = antilog of intercept.

The intercept and slope used to obtain Kf and 1/n were gotten from the linear plot of log Qe against log Ceq.

## III. RESULTS AND DISCUSION

### 3.1 Heavy metal composition of the amendments

Heavy metal levels in the amendments are presented in Table 2. The amendments were significantly ($P<0.05$) different in copper content with poultry manure having significantly ($P<0.05$) the highest amount of copper. Lead level was significantly ($P<0.05$) higher in cocoa pod and cow dung than in poultry manure. Zinc level in the amendment was also significantly ($P<0.05$) different with cocoa pod having significantly ($P<0.05$) the highest level of zinc.

**Table 2:Copper, lead and Zinc composition of the amendments used in the study**

| Amenments | Cu (mg/kg) | Pb (mg/kg) | Zn (mg/kg) |
|---|---|---|---|
| Cocoa pod | 16.52 | 0.03 | 22.55 |
| Poultry manure | 18.48 | 0.02 | 26.16 |
| Cow dung | 18.16 | 0.03 | 21.88 |
| LSD(0.05) | 0.015 | 0.00076 | 0.013 |

### 3.2 Adsorption isotherms

Figures 1 to 9 shows the applicability of Langmuir and Freundlich models to metals sorption using cocoa pod, poultry manure and cow dung. Sorption of the three decreased with increase in equilibrium concentration in the adsorbents. Adsorption was initially high in all the amendments at low equilibrium concentration and initial time of shaking then decreased with increase in equilibrium concentration except for adsorption of zinc by poultry manure where adsorption first increased with increase in equilibrium concentration and decreased afterword with increase equilibrium concentration (Fig. 8).

The nature of the isotherm curves are contrary to those reported by Okoya*et al.*(2014) for adsorption of $Pb^{2+}$ and $Cr^{6+}$ using cocoa husk char and Nwachukwu and Pulford (2008) in sorption of Pb,Cu and Zn by bone meal, coir, compost, green waste compost, peat and wood bark but in line with those obtained by Alumaa*et al.*(2014) using Estonian soils in Estonia. The difference in the shape of isotherms may be attributed to the different adsorbents used as affinity of adsorption varies with materials. The isotherms of the three metals in all the amendments have H-shape with fitted lines not starting/passing through low concentrations or origin. Tan, (1998) called H-type isotherm curve as high affinity curve and represents adsorption reactions when the solute has high affinity for solid. The isotherms showed that cow dung has the highest capacity in adsorbing metals followed by cocoa pod while poultry manure has the least.

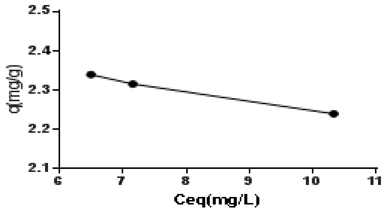

Fig 1: Adsorption isotherm for adsorption of Cu by cow dung

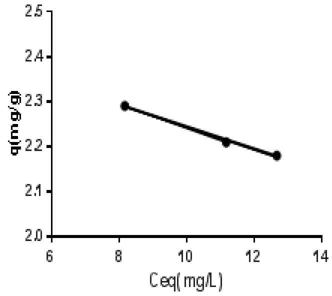

Fig 3: Adsorption isotherm for adsorption of Cu by cocoa pod

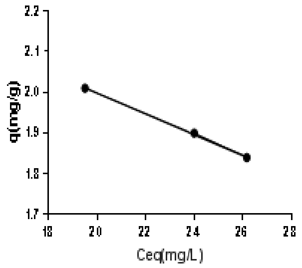

Fig. 2: Adsorption isotherm for adsorption of Cu by poultry manure

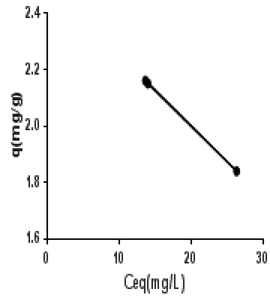

Fig 4: Adsorption isotherm for adsorption of Pb by cow dung

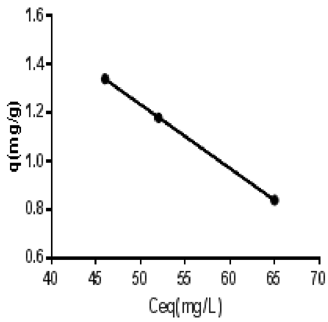

Fig 5: Adsorption isotherm for adsorption of Pb by poultry manure

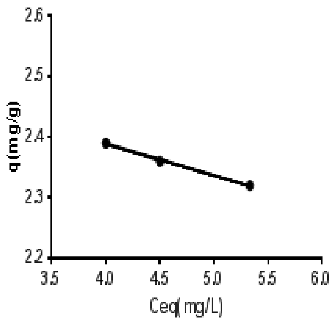

Fig 7: Adsorption isotherm for adsorption of Zn by Cow dung

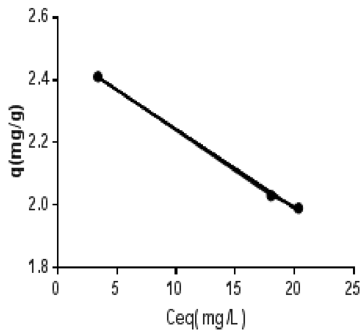

Fig 6: Adsorption isotherm for adsorption of Pb by Cocoa pod

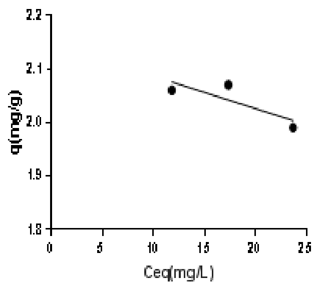

Fig 8: Adsorption isotherm for adsorption of Zn by poultry manure

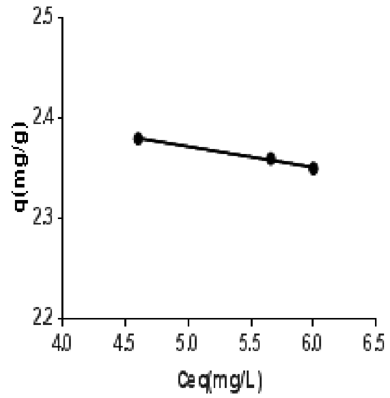


**Fig 9: Adsorption isotherm for adsorption of Zn by cocoa pod**

### 3.3 Langmuir and Freundlich Constants

Langmuir and Freundlich isotherm data with their coefficient of determination ($R^2$ ) presented in Table 3 showed that the experimental data fit both Langmuir and Freundlich isotherms except for Zn poultry manure that has $R^2$ of 0.001 for both Langmuir and Freundlich isotherms which is in agreement with the finding of Nwachukwu and Pulford (2008) who found their data fitted to Langmuir isotherm for Pb and Zn with $R^2 > 0.95$.

The maximum adsorption capacity (β) of Langmuir shows good adsorbing capacities of cow dung and cocoa pod than poultry manure for the three heavy metals. While the $K_f$ value of Freundlich which is also the maximum adsorption capacity is higher (263.572mg/g) for sorption of Pb by poultry manure than those of cow dung and cocoa pod probably suggesting that Pb has greater affinity for poultry manure than Zn and Cu. This is in agreement with the findings of Okoya *et al.* (2014) who stated that higher $K_f$ values exhibited by sorption of $Pb^{2+}$ and $Cr^{6+}$ suggest that $Pb^{2+}$ has greater sorption tendency towards the adsorbent (cocoa husk char) than $Cr^{6+}$.Okoya*et al*. (2014) reported highest $K_f$ value of 1500mg/g for sorption of Pb by cocoa pod husk char while Adekola *et al.,* (2016) reported $K_f$ value of 4.22mg/g for sorption of Pb by African wild mango shell.

**Table 3: Langmuir and Freundlich constants for adsorption of Cu, Pb and Zn by cocoa pod, poultry manure and cow dung.**

| Metals | Adsorbents | Langmuir Isotherm | | | Freundlich Isotherm | | |
|---|---|---|---|---|---|---|---|
| | | α(L/mg) | β(mg/g) | $R^2$ | $k_F$(mg/g) | 1/n | $R^2$ |
| Cu | Cd | -4.09 | 2.086 | 0.997 | 2.794 | -0.0947 | 0.999 |
| | Pm | -0.197 | 1.489 | 0.985 | 4.837 | -0.295 | 0.994 |
| | Cp | -0.996 | 2.009 | 0.998 | 2.899 | -0.1124 | 0.999 |
| Pb | Cd | -0.273 | 1.584 | 0.999 | 4.105 | -0.245 | 0.999 |
| | Pm | -0.032 | 0.443 | 0.949 | 263.572 | -1.373 | 0.982 |
| | Cp | -1.511 | 1.939 | 0.994 | 2.741 | -0.105 | 0.999 |
| Zn | Cd | -2.313 | 2.132 | 0.999 | 2.758 | -0.103 | 0.999 |
| | Pm | 3.567 | 2.246 | 0.001 | 2.363 | -0.0207 | 0.001 |
| | Cp | -4.398 | 2.262 | 0.978 | 2.553 | -0.0459 | 0.985 |

Cd=cow dung, Cp=cocoa pod,Pm=poultry manure

The differences in $K_f$ values may be due to differences in volume of heavy metal solution and adsorbent used by the two scholars. Higher value of $K_f$, result to greater adsorption intensity (Vaishnav *et al*., 2012). A comparison of maximum adsorption capacity (β) values of adsorbents used in this study with those of other studies presented in Table 4 shows difference in values reported in cocoa pod by Olu-owolabi *et al.*(2012) and the cocoa pod used in this study for adsorption of lead. This may be attributed to the difference in method of preparation of the adsorbents and the concentration of heavy metal solutions used. The cocoa pod used by Olu-owolabi*et al.* (2012) was ground to powder and mixed with potassium bromide (KBr) which may have increased the surface area and concomitantly the rate of adsorption.

Langmuir parameter α in Table 3 shows weak interaction or bonding energy between the metals and the adsorbents except for the interaction between Zn and poultry manure. The Freundlich values of 1/n are all less than 1 and negative as shown in Table 3 is an indication of favorable adsorption. This confirmed the report of Adekola *et al.*(2016) and Okoya *et al*. (2014) who stated that values of 1/n less than 1 indicates favorable sorption of heavy metals. Similarly, Al-sultani and Al-seroury (2012) opined that the smaller the values of 1/n the better sorption mechanism and formation of relatively stronger bond between adsorb ate and adsorbent. The findings of this study is in line with those of Adekola *et al.*, (2016) and Okoya *et al.,* (2014) on adsorption of $Pb^{2+}$ and $Cd^{2+}$ by African wild mango shell and adsorption of $Pb^{2+}$ and $Cr^{6+}$ by cocoa husk char respectively. Formation of stronger bond between adsorbents and adsorbates in soils has positive implication in nutrients status of soils as it reduces excessive concentration of nutrient elements in soil solution preventing their loss through leaching as it is commonly observed in areas of high rainfall thereby enhancing their slow and steady release for plant utilization.

**Table 4: Comparison of β (Maximum sorption capacity) reported in literature with that of this study.**

| Adsorbent | ( β)(mg/g) | | | References |
|---|---|---|---|---|
| | Cu | Pb | Zn | |
| Cocoa pod husk | 4.69 | 4.83 | | Obikeet *al.*,(2018) |
| Cocoa husk carbon | | 263.16 | | Okoyaet *al.*,(2014) |
| Cocoa pod | | 5.31 | | OluOwolabiet *al.*,(2012) |
| Cow dung | 2.086 | 1.584 | 2.132 | This study |
| Poultry manure | 2.086 | 1.584 | 2.132 | This study |
| Cocoa pod | 2.009 | 1.939 | 2.262 | This study |

## IV. CONCLUSION

The study revealed that the amendments have greater capacity in immobilizing the heavy metals as evident in the H shape type of isotherm in all the amendments. H shape isotherm implies a formation of stronger bond between the amendments and the heavy metals. It was observed that cow dung and cocoa pod have higher capacity in adsorbing heavy metals than poultry manure. Coefficient of determination showed that the experimental data fit in to both Langmuir and Freundlich models. It is therefore recommended that for reduced mobility and uptake by plants of heavy metals, which can lead to contamination of the food chain organic amendments such as cow dung, cocoa pod and poultry manure should be incorporated into heavy metal contaminated soils.

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