

Comparative effect of Organic Amendments on Heavy Metals Adsorption in Soils and their Chemical properties

O. I. Nwachukwu¹, D. M. Olim², S. M. Afu³, E. A. Akpa^{4*} and P. I. Adie⁵

¹Department of Science and Meteorology, Michael Okpara University of Agriculture
Umudike, Nigeria

^{2, 3, 4 & 5}Department of Soil Science University of Calabar
Calabar, Nigeria

*Corresponding author's email: enyaanari [AT] gmail.com

ABSTRACT---- *Incubation experiment was carried out to evaluate and compare effects of some selected amendments on adsorption of heavy metals in soils and their chemical properties. The experiment was CRD consisting of twelve treatment combinations with three replications. Soil samples were collected from the vicinity of Michael Okpara University of Agriculture and amended with organic amendments at the rate 20 ton/ha and heavy metals at the rate of 60 mg/kg, thoroughly mixed and wetted daily throughout the incubation period of 30 days. 0.05M EDTA solution was used to extract heavy metals. EDTA solution was filtered from soil with Whatman No1 filter paper. The soil was analyzed for chemical properties before and after experiment using standard procedures. Higher amount of heavy metals was extracted from the control soils than the amended soils indicating retention of heavy metals by the amendments. All the amendments were significantly ($P<0.05$) different in adsorption of copper with poultry manure having significantly ($P<0.05$) the highest adsorption capacity while the control had the least. Cocoa pod was significantly ($P<0.05$) higher on adsorption of lead with cow dung and poultry manure not being significantly ($P>0.05$) different from each other. Cow dung had the highest ($P<0.05$) on adsorption of zinc. Heavy metals combined with amendments had significant ($P<0.05$) effect on soil chemical properties. Most chemical properties were significantly ($P<0.05$) higher in soils treated with both amendments and heavy metals than soils treated with only heavy metals. Poultry manure, cocoa pod and cow dung appeared to have greater potential in removing heavy metals from soils.*

Keywords--- Adsorption, amendments, chemical properties, heavy metals, incubation

1. INTRODUCTION

Heavy metals are those elements in the periodic table with atomic number higher than 20 and densities greater than 6 g/cm³ except alkali metals and alkaline earth metals [1]. Heavy metal ions are the highest harmful inorganic contaminants existing in the environment and can be of natural history or result from human activities [2]. They result from a variety of industries such as mining, plating, dyeing, electrochemical, metal processing and battery storage plus human activity [3]. The environmental challenges associated with heavy metals are that they cannot be eliminated easily and most of them have poisonous effects on plants and animals even at low concentration [1]. Heavy metals pollution is a major problem which causes negative effect on soil properties and limitation of productive and ecosystem functions [4]. They can alter soil properties especially soil biological population and properties [4]. The influence of heavy metals on soil properties is mostly manifested through their effect on soil microbial population as well as their activities. The soil microbial population has a crucial function in the process of organic matter decomposition and mineralization which allows recycling of nutrients [5]. Several studies have indicated that accumulation of heavy metals in soils exerts toxic effects on soil micro-organisms and consequently induces disturbances as to the diversity, population size and overall activities of the soil microbial communities [6]. Plants need some heavy metals for their growth but excessive amount of these metals can cause damage to the plants. As these metals cannot be broken down by plants, when concentrations within the plant goes beyond optimal levels, they cause severe damage to the plant both directly and indirectly [7]. Some direct toxic effects caused by high heavy metal concentration include inhibition cytoplasmic enzymes and damage to cell structure due to oxidative stress. An example of indirect toxic effect is replacement of essential nutrient at cation exchange sites of the plants [8].

Soil organic matter is a complex and varied mixture of organic substances. It provides much of the cation exchange and water holding capacities of surface soils [9] (Brady and Weil, 2008). Humus, however, constitutes about 50 to 90 % of the cation-adsorbing power of mineral surface soil and due to its specific surface area and CEC, it plays an important but complicated role in affecting the mobility of heavy metal pollutants in soils [10]. When present as part of the solid

phase, soil organic matter can serve as adsorption medium for heavy metals [11]. Complex reactions involving soil organic matter, and especially its more active components; humic materials (humic and fulvic acids) enhance the adsorption of heavy metals in soil thereby controlling their physicochemical behavior, accumulation, mobility and ability to penetrate the food chain [12]. Organic matters possess biochemical compounds such as glycine, citric, tartaric and gluconic acids that have strong chelating properties to react with heavy metals which result in their sorption and reduced mobility in the environment. Organic amendments are promising bio-adsorbents for removal of heavy metals from waste water and the environment [13;14 and 15].

Soil is a crucial element for all terrestrial ecosystems. It provides the nutrient bearing medium for plant life and abundant plant growth requires soil environment that is free of inhibitory factors. In small quantities, heavy metals are essential to the efficient functioning of the plants but in excess amount they become toxic to all life forms. The capability of soil to adsorb metal ions from aqueous solution has caught the interest of many scholars because it has positive consequences in both agricultural issues like soil fertility and productivity and environmental questions such as remediation and reclamation of polluted land and waste deposition. To avoid acute concentrations of heavy metals in soils and the contamination of food chain, there is need to find out ways of regulating/controlling their solution concentrations by using appropriate organic materials as adsorbents in heavy metal contaminated soils to enhance the productivity of such soils. The study therefore highlights the comparative effects of heavy metal adsorption on soils and their chemical properties.

2. MATERIALS AND METHODS

Location of experiment

The experiment was carried out in the Soil Science Laboratory of Michael Okpara University Agriculture, Umudike (MOUAU), Abia State of Nigeria. The area lies between latitude $5^{\circ} 28'N$ and $5^{\circ} 30'N$ and longitude $7^{\circ} 31'E$ and $7^{\circ} 33'E$ of the equator [16].

Collection and preparation of experimental materials

Cocoa pod was sourced from a cocoa plantation in Okworogung village in Obudu Local Government Area of Cross River State, Nigeria while cow dung and poultry manure were obtained from the animal farm unit of (MOUAU). Poultry manure and cow dung were sun dried, ground and sieved with 2 mm sieve to obtain uniform size fraction. The soil used in the study was collected at the depth of 0-15 cm from arable land within the same University, air dried, ground and sieved with 2mm sieve. The cocoa pods were washed, sun dried, milled and also sieved with 2mm sieve to obtain uniform size fraction as reported by [14].

Experimental design

The experiment was set up in completely randomized design (CRD) consisting of twelve (12) treatments combinations with three (3) replications making a total of 36 experimental units. The treatments involved were copper without amendment (Cu0), copper with cocoa pod (CuCp), copper plus poultry manure (CuPm), copper plus cow dung (CuCd), lead without amendment (Pb0), lead with cocoa pod (PbCp), lead with poultry manure (PbPm), lead plus cow dung (PbCd), zinc without amendment (Zn0), zinc with cocoa pod (ZnCp), zinc with poultry manure (ZnPm) and zinc plus cow dung (ZnCd).

Experimental procedures

One hundred grams of soil each was weighed into a plastic pot, then 1g of single amendment was added to the soils amounting to application rate of 20 tons per hectare and thoroughly mixed except for the control which had no amendment. The amended soils were then contaminated with heavy metals at a rate equivalent to 60 mg/kg by weighing 0.24 g, 0.09 g and 0.26 g of $CuSO_4 \cdot 5H_2O$, $PbSO_4$ and $ZnSO_4 \cdot 7H_2O$ respectively into the amended soils and the non-amended soils. The metal salts were thoroughly mixed with the soils to homogenize the distribution of the applied heavy metals and allowed to incubate for thirty days. Each soil was wetted daily with 80 ml of distilled water throughout the incubation period at room temperature to mimic natural field condition as stipulated by [17].

Preparation of EDTA Solution

0.05M EDTA solution was prepared by dissolving 18.621 g of ethylene diamine tetra acetic acid in 1000 ml of distilled water. 18.621 g of EDTA was weighed into 1000 ml measuring cylinder, and 500 ml of distilled water added followed by continuous stirring until the EDTA was dissolved. Then distilled water was added and brought to 1000 ml mark. The pH of the solution was determined to be 4.6 using pH meter. The EDTA was obtained from Scharlab S.L.gato perez, Spain

Extraction of heavy metals and determination

To extract the heavy metals from the amended and incubated soils, 5 g of each soil was weighed into 120 ml plastic bottles and 50 ml of 0.05M EDTA solution was added after which the soil/solution mixture was shaken on a

mechanical shaker for 30 minutes. The solution was then filtered out from the soils with Whatman No.1 filter paper. The clear supernatant was then analyzed for heavy metal concentration.

Laboratory Analysis

Soil samples were air-dried, crushed and sieved with 2 mm sieve and analyzed in the laboratory using standard routine methods. Particle size distribution was determined using Bouyoucous hydrometer method. Soil pH was determined using the procedure reported by [18]. Organic carbon was determined by Walkley-Black wet oxidation method described by [19]. Total nitrogen was determined by the salicylic thisulphate digestion method followed by distillation using the modified micro-kjeldhal method as outlined by [18] while available phosphorus was determined using Bray P-1 described by [20]. Exchangeable bases were determined by leaching the soil samples with 1ml neutral NH₄OAc as the extractant solution. Calcium (Ca) and Mg were determined by the EDTA complexometric titration method while K and Na were determined by flame photometry. Exchangeable acidity was determined by titration method described by [19]. Heavy metals (lead, zinc and copper) in amendments were determined using perchloric acid digestion method as outlined by [18] while extracted heavy metal solutions were read using atomic adsorption spectrophotometer. ECEC was obtained by the summation method of [21] which is the summation of E_b and E_a and base saturation obtained by expressing the exchangeable bases as a percentage of the ECEC.

Data analysis

All the data obtained from both experiments were subjected to analysis of variance (ANOVA) using Genstat discovery edition 3 [22]. Significant treatments means were separated using Fisher's Least Significant Difference (LSD) at 5 % level of probability.

3. RESULTS AND DISCUSSION

Heavy metal level in the amendments

Heavy metal levels in the amendments presented in Table 1 shows that lead and zinc were the least and the most concentrated respectively in the amendments. Poultry manure had the highest level of the three metals across while cocoa pod had the least. The concentration levels of the heavy metals were below the maximum permissible limit for organic fertilizer materials [23], maximum permissible limit in soils [24], pollutant concentration limit for land applied bio-solid [25] and concentration of metals in livestock feeds and animal manures in England and Wale reported by [26]. The difference between metal levels in the amendments used and animal manures reported by [26] may be most likely due to differences in feed composition /supplement of the animal feeds.

Table 1: Copper, Lead and Zinc level 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
Maximum permissible limit of heavy metals (mg/kg) in organic fertilizer materials, land applied bio-solid, soils and animal manures			
A	200	120	600
B	1500	300	2800
C	100	100	300
D1	80	<100	400
D ₂	50	<20	180

Source: A = [24]; B= [25]; C= [23], D₁= [26] for poultry manure; D₂= [26] for cow dung.

Extracted heavy metals after incubation

The amount of heavy metals extracted after thirty days of incubation of heavy metal contaminated and amended soils are presented in Table 2 which shows that the amount of metals extracted was higher in the control soils than the soils with amendments proving the efficacy of amendments in binding of heavy metals. The higher the extracted value of heavy metals the lower the adsorption or retention of the metal by the amendment and vice versa. The amount of copper extracted was smaller in all the soils than lead and zinc which may be due to smaller ionic radius and lesser degree of hydration in the shell of copper that allowed for intimate contact with the humic component of the organic materials. In a related experiment, [27] found out that cocoa pod can be efficiently used as low cost alternative for removing heavy metals from aqueous solutions while [28] proved that agricultural materials can effectively bind metals in soil in short term.

All the treatments were significantly (P<0.05) different in their effect on extraction of copper with poultry manure having the highest adsorption capacity followed by cow dung while the control had the least. The treatments were also

significantly ($P < 0.05$) different in adsorption of Pb except for cow dung and poultry manure that were not significantly ($P > 0.05$) different. Cocoa pod had significantly ($p < 0.05$) the highest effect on adsorption of lead followed poultry manure and cow dung. The treatments equally showed significantly ($p < 0.05$) different effect on the extraction zinc except poultry manure and cocoa pod that had the same effect on adsorption of the metals with cow dung having significantly ($p < 0.05$) the highest effect on adsorption of zinc.

Table 2: Extracted Copper, Lead and Zinc (mg/kg)

Treatment.	Cu	Pb	Zn
Cd	33.83	41.67	37.17
Pm	30.33	40.50	39.00
Cp	39.17	36.17	38.67
Ctrl	43.00	57.67	43.50
LSD(0.05)	2.821	1.383	1.201

Cd= cow dung, Pm= poultry manure, Cp = cocoa pod, Ctrl=control.

Chemical properties

Higher pH was observed in soils that received both amendments and heavy metals than soils that received only heavy metals as shown in Table 3. The results agree with the findings of [29], [30] who observed that application of farmyard manure caused an increase in soil pH and [17] who obtained significant effect of amendment on soil pH. Lead combined with poultry manure had the highest significant ($P < 0.05$) effect on pH followed by zinc plus poultry manure that was significantly different ($P < 0.05$) but not different from copper plus poultry manure and zinc mixed with cocoa pod. Lead in combination with cow dung, lead mixed with cocoa pod and zinc combined with cow dung were not significantly different from each other but different from other treatments. Copper plus cocoa pod was significantly ($P < 0.05$) different but not different from zinc without amendment and copper mixed with cow dung in their effect. Copper without amendment and lead with no amendment had the least effect on pH and were not significantly ($P > 0.05$) different from each other but different from other treatments (Table 3). This is line with findings of [31] evaluated the sole effect of heavy metals on soils and stated that the soils with only heavy metals had the least pH. Highest available P value 19.0 mg/kg was obtained in lead plus poultry manure amended soil followed by 17.37 mg/kg in lead combined with cow dung while the least values were recorded in zinc without amendment, copper without amendment, copper plus cocoa pod and copper poultry manure (Table 3). Higher P in lead plus poultry agrees with the study of [32]. (2010). Available P values were higher in virtually all the soils treated with heavy metals and amendments than those treated with only heavy metals. This is consistent with the study of [33], [34] in their study attributed increase in P to the release of organic acid during decomposition which in turn helped in releasing P. Lead plus poultry manure had the highest significant effect on available P and was significantly ($P < 0.05$) different in its effect from the rest of the treatments followed by lead plus cocoa pod, lead plus cow dung, copper plus cow dung, zinc mixed with poultry manure and zinc mixed cow dung that were not significantly ($P < 0.05$) different from each other in their effect. Copper without amendment, zinc without amendment, copper plus cocoa pod and copper mixed poultry manure had the least effect on P and were not significantly different from each other in their effect but different from other treatments (Table 3).

The effects the treatments on total N were similar to those of pH and available P. Lead plus poultry manure, Zinc plus poultry manure, copper mixed poultry manure, copper mixed cow dung and lead without amendment had significantly ($P < 0.05$) higher effect on total N than other treatments but not different from each other while zinc without amendment and copper without amendment had the least significant effect on total N. Highest value of organic carbon (18.0 g/kg) was recorded in lead plus cocoa pod soil and is about two to four times higher than the rest of the soils while the least value of 5.6 g/kg was observed in zinc without amendment soil (Table 3).

Higher value of organic carbon in lead plus cocoa pod soil agrees the report of [35] that cocoa pod husk is made up of 42.04 % carbon. Lead mixed with cocoa pod had the highest effect on organic carbon and was significantly different ($P < 0.05$) from other treatments. Copper combined with cow dung had the second significant effect but not different from lead plus cow dung and copper combined with cocoa pod while copper without amendment, zinc without amendment and lead without amendment had the least organic carbon level and were not significantly ($P > 0.05$) different from each other (Table 3). Most of the exchangeable bases were virtually significantly ($P < 0.05$) higher and different in soils that received both heavy metal and amendment except in some few instances. Copper plus poultry manure had the highest effect on Ca^{2+} and was significantly ($P < 0.05$) different from the remaining treatments (Table 3). [29] and [36] obtained similar observation.

Soils that received both heavy metals and organic amendments had significantly ($P < 0.05$) higher values of H^+ than soils applied with only heavy metals. This situation showed the contribution of organic matter to acidity through dissociation of H^+ from the humic components of organic amendments. Zinc treated with poultry manure was significantly ($P < 0.05$) higher

in its effect on H⁺ content than other treatments followed by copper plus poultry manure. Copper added with cow dung had the third effect on H⁺ and was significantly (P<0.05) different followed by copper without amendment, lead with cow dung, zinc plus with cocoa pod and zinc cow dung that were not significantly different from each other but different from the rest of the treatments. Lead added with cocoa pod, zinc without amendment and lead without amendment had the least effect on H⁺ and were also significantly (P<0.05) different in their effect. Aluminum was significantly (P<0.05) higher in most soils without amendments than in those soils treated with amendments which may be due to inherently high content of Al³⁺ in the soils. Copper mixed with cow dung had the least effect and was significantly different from others (Table 3).

Zinc added with cocoa pod had the highest significant (P<0.05) effect on ECEC and was significantly different while copper mixed with cocoa pod had the least effect. Lead applied with poultry manure, zinc plus poultry manure, and copper plus poultry manure had the second highest effect and were not significantly (P>0.05) different from each other but from other treatments. [36] reported significant effect of animal manures on ECEC. Similarly, [37] found the effect of organic materials on ECEC and recommended that for improved ECEC organic manures should be applied to soils. Highest and lowest BS values of 83.73 % and 63.85 % were obtained in soils treated with lead plus poultry manure and zinc plus poultry manure respectively. Smaller BS value in zinc plus poultry manure soil than lead plus poultry manure soil may be due to saturation of exchange sites by zinc ions that prevented adsorption of basic cations and left them in solution. Lead applied with poultry manure had the highest significant (P<0.05) effect on BS and was not different from lead without amendment, zinc mixed with cocoa pod and copper mixed with cocoa pod while lead with cocoa pod, lead with cow dung, and zinc without amendment were also not significantly (P>0.05) different from each other in their effect but different from other treatments. The least significant effect was recorded for zinc mixed with poultry manure (Table 3).

Table 3: Effect of heavy metals and organic amendments on soil chemical properties after 30 days of incubation

Trt comb	pH	Avail.P (mg/kg)	Total N. (g/kg)	OC (g/kg)	Exch. Bases			Na ²⁺	Ex. acid. H ⁺	Al ³⁺	ECEC	BS %
					Ca ²⁺	Mg ²⁺	K ⁺					
					← Cmol/kg			→				
SPBEx	4.5	19.8	1.2	6.0	1.5	1.0	0.77	2.00	1.95	1.65	8.87	59.41
Cu0	4.5	15.30	1.23	6.0	2.5	0.9	0.78	2.16	1.67	0.63	8.64	73.37
CuCp	4.9	15.10	1.50	9.0	2.5	0.9	0.97	2.04	1.23	0.36	8.00	80.10
CuPm	5.1	15.37	1.80	7.0	3.7	1.2	0.81	2.10	2.09	1.04	10.94	71.38
CuCd	4.7	17.17	1.70	11.6	2.8	1.5	0.56	2.18	1.83	0.076	8.95	78.67
Pb0	4.5	16.17	1.70	6.6	3.4	1.16	0.91	2.14	0.04	1.67	9.92	82.76
PbCp	5.0	17.33	1.13	18.0	1.8	1.4	0.91	2.82	0.40	1.74	9.03	76.39
PbPm	5.4	19.00	1.83	7.0	2.9	3.4	0.57	2.22	1.20	0.56	10.86	83.73
PbCd	4.93	17.37	1.40	10.6	2.0	1.7	0.95	2.21	1.63	0.48	9.04	76.60
Zn0	4.8	15.33	1.06	5.6	0.8	2.8	0.87	2.11	0.63	1.56	8.78	74.95
ZnCp	5.1	15.70	1.26	7.6	1.2	5.1	0.77	2.78	1.52	0.87	12.25	80.40
ZnPm	5.2	17.14	1.80	8.0	1.7	2.06	0.76	2.76	3.71	0.41	11.40	63.85
ZnCd	5.06	17.06	1.40	8.0	1.7	2.1	0.80	2.68	1.69	1.06	10.07	72.63
LSD(0.05)	0.161	0.317	0.169	2.692	0.165	0.175	0.021	0.178	0.122	0.187	0.422	2.752

SPBXp= Soil properties before experiment. Cu0=Cu without amendment, CuCp=Cu+cocoa pod, CuPm=Cu+poultry manure, CuCd=Cu+cow dung, Pb0=Pb without amendment, PbCp=Pb +cocoa pod, PbPm=Pb+ poultry manure, PbCd=Pb+cow dung, Zn0=Zn without amendment, ZnCp=Zn+cocoapod, ZnPm=Zn+poultrymanure, ZnCd=Zn+cowdung

4. CONCLUSION

The study showed that all the amendments have good potential to be used as low cost adsorbents in remediating the effect of heavy metals in heavy metal contaminated soils and also had significant effect on extraction of heavy metals. All treatments had significant effect on soil chemical properties with the treatment combination of both organic amendments and heavy metals having virtually higher effect than the effect of sole heavy metal. It is therefore recommended that for reduced mobility, bioavailability and solution availability of heavy metals, low cost organic amendments such as cocoa pod, poultry manure and cow dung should be used in metals contaminated soils which will also improve the soil physical and chemical condition for improved productivity.

5. REFERENCES

- [1] Sherene, T. 2010. Mobility and transport of heavy metals in polluted soil environment. *International Journal of Biological Forum*. 2(2),112-121.

- [2] Siegal, F.R. 2002. Environmental geochemistry of potentially toxic heavy metals. Springer-verlag, Heidelberg. Pp 150-161
- [3] Kadirvelu, K., Thamaraiselvi, K. and Namasivayam C. 2001. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from Agricultural solid waste. *Bioresources Technology*. 63-76.
- [4] Friedlova, M. (2010). Influence of heavy metals in soil biological and chemical properties. *Soil and Water Research*. 1:21-27.
- [5] Castaldi, S., Rutigliano F.A., and Virzo De Santo, A. 2004. Suitability of soil microbial parameters as indicators of heavy metal pollution water, soil and air pollution. *Pollution Journal*.158: 21-35.
- [6] Pawlowska, T. and Charvat, I. 2004. Applied Environmental Microbiology. Pp 6643-6649.
- [7] Chibuike, G.U. and Obiora, S.C. 2014. Heavy metal polluted soils: Effect on plant and bioremediation methods. *Applied and environmental soil science*. 2:708 -715.
- [8] Taiz, L. and Zeiger, E. 2002. Plant Physiology, Sinauer associate, Sunderland, Mass, USA. Pp 65-73
- [9] Brady, N.C. and Weil, R.R. (2008). *Nature and properties of soils*, 13th ed. Prentice Hall Ltd, New Jersey. Pp 289-293
- [10] Stevenson, F.J. 1992. *Humus chemistry. Genesis, composition, reaction*. Wiley, intersc. Public. New York: USA. Pp 104-110
- [11] Refaey, Y., Jansen, B.El-Shater, A., El-Haddal, A. and Kalbitz, K. 2014. The role of dissolved organic matter in adsorbing heavy metals in clay-rich soil. *Vadose Zone Journal*. 44-48
- [12] Lo, K.S.L, Yang, W.F. and Clin, Y.C. 1991. Effect of organic matter on the specific adsorption of heavy metals by soil. *Toxicological and Environmental Chemistry*. 34,139-153.
- [13] Meunier, N. Blais, J.F., Laroulandie, J. and Tyagi R.D. (2003). Cocoa shell for heavy metal removal from acidic solutions. *Bioresources Technology*. 90, 255-263.
- [14] Olu-Owolabi, B.I., Oputu, O.U., Adebowale, K.O., Ogunsola, O. and Olajimi, O.O. 2012. Biosorption of Cd²⁺ and Pb²⁺ ions onto mango stone and cocoa pod waste: kinetic and equilibrium studies. *Scientific Research and Essay*.7(15), 1614-1629.
- [15] Ojedokun, A.T. and Bello, O.S. 2016. Sequestering heavy metals from waste water using cow dung. *Water resources and industry*. 13:7-13.
- [16] Adindu, R.U., Igboekwe, M.U., Ughegbu, A.C., Eke, K.T. and Chigbu, T.O. 2013. Characterization of infiltration capacities of the soil of Michael Okpara University of Agriculture, Umudike-Nigeria. *Geosciences*, 3(4), 99-107.
- [17] Abdel-Kader, N. H., Shahin, R.R. and Khater, H. A. 2013. Assessment of heavy metal immobilization in artificially contaminated soil using some local amendments. *Open Journal of Metal*. 3, 68-76
- [18] Udo, E.J., Ibia, R.O., Ogunwale, J.A., Ano, A.O. and Esu, E.I. 2009. *Manual of soil, plant and water analyses*. Sibon books limited. Lagos: Nigeria. Pp 45-78
- [19] Srikanth, P., Sormasekhar, S.A., Kanthi, G.K. and Raghu, B.K. 2013. Analysis of heavy metals by using atomic adsorption spectroscopy from the samples taken around Visakhapatnam. *International Journal of Environmental Ecology, Family and Urban Studies*.3(1):127-132.
- [20] Murphy, J. and Riley, J.P. 1962. Modified simple solution for determination of phosphorus in natural water. *Anal. chmi. Acra*. Vol. 27:31-36.
- [21] International Institute of Tropical Agriculture (IITA), 1979. Method of soil and plant analysis. Manual series of soil and plant analysis. Pp 125-129.
- [22] Genstat (2007). Genstat for Windows, Discovery, 3rd edition. Lawes Agricultural Trust, Rothamsted Experimental Station, UK.
- [23] European Union (2014). Essential safety and quality requirements for organic fertilizing materials. Fertilizer working group meeting. Pp 1-67
- [24] World Health Organization (WHO), 2014. Maximum permissible level limit (MPL) of heavy metals (mg/kg) in irrigation water, soils and vegetable established by World Health Organization(WHO). Pp 27-39
- [25] United State Environmental Protection Agency (USEPA), 1994. Plain English guide to the EPA part 503 bio-solid rule. USEPA office for waste water management. Washington DC. Pp 155-161
- [26] Nicholson, F.A., Chambers, B.J., Williams, J.R. and Unwin, R.J. 1991. Heavy metals content of livestock feeds and animal manure in England and Wales. *Bio- Resource Technology*.70:23-31
- [27] Obike, A.I., Igwe, J.C., Emeruwa, C.N. and Uwakwe, K.J. 2018. Equilibrium and kinetic studies of Cu (II), Cd (II), Pb (II) and Fe (II) adsorption from aqueous solution using cocoa (*Theobroma cacao*) pod husk. *Journal of Applied Science and Environmental Management*. 22(2),182-190
- [28] Nwachukwu, O. I. and Pulford, I.D. 2008. Comparative effectiveness of selected adsorbent materials as potential amendments for remediation of lead copper and zinc contaminated soil. *Soil Use and Management*, 24:199-207.

- [29] Tomado, T. and Mitiku, W. 2017. Effect of combined application of organic and mineral nitrogen and phosphorus fertilizer on soil physic-chemical properties and grain yield of food barley (*Hordium vulgare L*) in Kaffa zone of South Western Ethiopia. *American Journal of Sustainable Agriculture*. 2, 74-79.
- [30] Gupta, G. and Charles, S. (1999). Trace elements in soils fertilized with poultry manure. *Poultry science*.78(12), 1695-1698.
- [31] Dawaki, U. M., Dikko, A. U., Noma, S. S. and Aliyu, U. 2013. Heavy metals and physic-chemical properties of soils in Kano Urban Agricultural Lands. *Nigeria Journal of applied Science*.21(3),239-246
- [32] Adeli, A., Tewolde, A. H., Sistani, K. and Rowe, D. E. 2010. Comparison of broiler litter and commercial fertilizer at equivalent N rate on soil properties. *Soil Science Society of American Journal*.41,2432-2447.
- [33] Ayeni, L. S., Adetunji, M. T. Ojeniyi, S. O. Ewulo, S. B. and Adeyemo, A. J. 2008. Comparative and accumulation of cocoa husk ash and poultry manure on soil and maize nutrient content and yield. *American Journal of Sustainable Agriculture*. 2:92-97.
- [34] Ayeni, L. S. and Adetunji, M. T. 2010. Integrated application of poultry manure and mineral fertilizer on chemical properties, nutrient uptake, yield and growth component of maize. *Natural Science*. 8,60-67.
- [35] Okoya, A. A., Akinyele, A. B., Ofoezie, I. E., Amuda, O.S., Alayande, O.S. and Makinde, O.W. 2014. Adsorption of heavy metal ions onto chitosan grafted cocoa husk char. *African Journal of Pure and Applied Chemistry*. 8(10), 147- 161.
- [36] Bakayoko, S., Soro, D., Nindjin, C., Dao, D., Tschannen, A., Gardin, O. and Assa, A. 2009. Effect of cattle and poultry manures on organic matter content and adsorption complex of a sandy soil under cassava cultivation (*Manihot esculenta, Crantz*). *African Journal of Environmental Science and Technology*. 3(8), 190-197.
- [37] Afu, S.M., Asadu, G.L.A., Ofem, K.I. and Olim, D.M. 2016. Contributions of organic matter fractions to cation exchange capacity of soil organic matter under four different land uses in Southeastern Nigeria. *African Journal of Agricultural Science and Technology*. (AJAST). 4(12), 871-876.