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Evaluation of the Effects of Various Organic Wastes in the Reduction of Heavy Metals in a Polluted Soil Undergoing Bioremediation

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Abstract
Heavy metals are commonly found in soils polluted with contaminants from anthropogenic sources. Bio-sorption is a passive mechanism of heavy metal removal by dead or living biomass and it is a relatively inexpensive means of bio remediating contaminated soils and water. In this study, the role played by three organic wastes in removing heavy metals in a soil contaminated by spent engine oil was assessed. The study investigated the initial concentration of some heavy metals in soil collected from a mechanic workshop in Minna, Niger State, Nigeria. Chicken droppings, cowpea haulms and groundnut haulms were added to the contaminated soil for twelve weeks and concentration of the heavy metals was monitored by taking readings every two weeks. Another soil was left untreated, to serve as control. Contaminated soil was collected from Keteran Gwari mechanic workshop and amended with sterile chicken droppings, cowpea haulm, and groundnut haulm. Another portion of the soil was left untreated to serve as control. This study was carried out for a period of twelve weeks under laboratory conditions. Samples were taken from each treatment at two weeks interval to determine concentration of heavy metal. The result obtained revealed high concentration of lead, chromium, Cadmium, arsenic, zinc, copper and Nickel in the contaminated soil. At the end of the bioremediation, the concentration of heavy metals was still above the acceptable limits (NESREA, 2007; WHO, 2007; WHO, 2011). There was a significant difference in the reduction of lead, chromium, arsenic, zinc and copper ($p<0.05$) between the treated soil and control(untreated)soils. However, there was no statistically significant difference in the reduction of cadmium and nickel ($p>0.05$) The chicken droppings contain Nitrogen (1.16%), Phosphorous (17.44mg/kg) and 12.34% organic carbon, cowpea haulms contains 1.10%,11.20mg/kg and 10.21% nitrogen, phosphorous and organic carbon respectively, while the groundnut haulms had 0.89% nitrogen, 11.92mg/kg phosphorous and 10.41% organic carbon. The content of nitrogen, phosphorous and organic carbon in the organic wastes used to treat contaminated soil in this study; possibly improved the activities of bacteria which lead to increase in their population hence reduced the concentration of heavy metals through a mechanism called biosorption. During biosorption, heavy metal ions directly bind to the organic wastes thereby reduces their concentration in soil. The used of organic waste to stimulate the activities of microorganisms during bioremediation is cost effective, efficient and environmentally friendly, hence can complement the use of expensive inorganic fertilizer and conventional methods that are expensive and also generate toxic byproducts which adversely affect the environment.

Keywords: Heavy Metals, Bio-sortion, Biomass, Bioremediation, Organic Waste, Chicken Droppings, Cowpea Haulms, Ground Nut Haulms

Introduction

Increasing urbanization and industrialization have resulted in the increased use of machineries to carry out various functions, however, automobile engines and power generators are the most used engines for transportation and supply of light and energy. During engine operations, the parts undergo continues wear due to friction between metallic parts, high temperature, pressure and corrosion of metals. However, to minimize wear and tear, lubricating (engine) oil is used to smoothen the operation of such engines (Soukayna *et al*., 2018). The spent engine oil contains a mixture of different compounds derived from the original base oil, its additives, and heavy metals that comes from scraping down due to motion of the pistol and rings as well as the crankshaft inside the engine block. There are high values of heavy metals in the spent engine oil and these metals may be retained in soil in form of oxides, hydroxides and carbonates Egbuchua and Bosah, (2011). The heavy metals found in the spent engine oil include lead, Arsenic, cadmium, chromium, zinc and copper. These heavy metals persist in the environment due to their absolute nature. The heavy metals in the spent engine oil can dissolve in water and move through the soil easily and subsequently get into human body through the food web from plants (Das and Chandran, 2010; Ajao *et al*., 2014; Eniola *et al*.,2014) are of the opinion that when heavy metals get into tissues of human body through the food chain, serious health problems can result. Heavy metals such as zinc, magnesium, copper, chromium, or nickel may have a nutritional benefit to the organism as cofactors, while other metals, such as lead, cadmium, mercury, arsenic, and gold, are not yet identified beneficial to the organism (Spiegel, 2002). Regardless of the nutritional benefit, all metals lead to toxic effects when accumulated in high concentrations in the cell. The toxicity of the metals is dependent upon the concentration, but also the chemical structure, time of exposure, and the source of the metal contamination (Solgi, *et al.*, 2012).

Materials and Methods

Sampling Site

The study area for this research was the metropolitan Minna, the capital of Niger State. Minna is located in the eastern senatorial district of the state at latitude N 09^0 36’ 05” and longitude E 06^0 32’ 24.8” with a landmass of 1664km^{2}and a human population of 3488180 persons (National population commission, 2006). The study site (ketaren Gwari) is located opposite the old secretarial along kpakungu in western part of the town. The occupants of ketaren Gwari are mostly settlers that sell spare parts and electronics. The contaminated soil samples were collected from spots 100 feet away from each other with the following coordinates: 9^o 36’19.97N 6^{o}32’14.49E, 9^{o}36’19 47N 6^{o}32’15.46 E, 9^o 36’20.48N 6^{o}32’15.24E, 9^{o}36’19.09N 6^{o}32’14.58E, 9^{o}36’18.10N 6^{o}32’15.00E, 9^{o}36,19.29N 6^{o}32,16.34E, 9^{o}36’18.49N 6^{o}32,14.28E, 9^{o}36.19.92N 6^{o}32’15.94E, 9^{O}36’21.06N 6^{o}32’15.90E, 9^{o}36’18.81N 632’15.68E.

There is a garden beside the mechanic workshop, this garden receive it water supply from a seasonal stream located between the garden and keteran Gwari mechanic workshop. During the raining season, runoff from the workshop also carries waste into the garden. Heavy metals from the contaminated soil, seep into the water table and contaminate the ground water. These toxins are taken up by plants and accumulate in their tissue which subsequently gets into human body through food web from plants. The toxins can cause various forms of health problems like kidney damage, various kinds of cancer, brain damage, reduced growth and development (Daniel *et al*., 2016).

Collection of samples

Soil: Soil samples collected randomly from several points using a soil auger at a depth of 0-15cm.The samples were pooled together to form a composite sample and transported to the laboratory in for further analyses. Organic wastes: Chicken droppings were collected from poultry house of College of Education, Minna. While the cowpea haulms and groundnut haulms were obtained from a farm near Shango village, Minna. All samples collected were transported in clean plastic bags to the Environmental laboratory in Ahmadu Bello University, Zaria for analysis.

Physicochemical properties of soil

The pH of the soil was determined using a pH meter (HANNAH,18424);total nitrogen, available phosphorous, organic carbon and exchangeable bases were determined using the Kjeldahl digestion method as described by Macgill(2002) while the water holding capacity of the soil was determined using the method of Vidali (2001).The physical properties of the experimental soil (quantity of clay, sand and silt in the soil sample) was determined using hydrometer method by Agarry and Oladipupu, (2012). The soil type was determined by comparing the values of clay, silt, and sand obtained with soil triangular chart (Vidali, 2001).

Determination of heavy metal content of the soil

The initial concentration of heavy metal in contaminated soil was determined using atomic absorption spectrophotometer (AAS). Ten (10) gram of soil was weighed into a 250mL capacity bottle and 100mL of 0.1M hydrochloric acid was added, covered with a lid and shaken for 30 minutes. The supernatant was filtered through a Whatman filter paper number 42. One catalyst tablet for appropriate metal (metal on test) was added to 100mL of soil solution and shaken. More tablets would be added continuously until the mixture changes color. The number of tablets used was noted for each metal. Twenty-five (25) mL of the solution was then poured into sample tube (cuvette) and inserted into the spectrophotometer (model 6405 UV Jenway UK). The READ/ENTER button of the instrument was pressed. The displayed figure was multiplied by the number of tablets used. The reading was recorded in milligram per liter (mg/L). The wavelength for different metals varies therefore the instrument was set at their appropriate wavelength for particular metal (Eghuchua and Bosah, 2011).

Heavy metal remediation experiment

Table 1: Experimental pots and their contents

1	2	3	4
1kg Soil+100g CD+150ml dH_2O	1kg Soil+100g CPH+150ml dH_2O	1kgSoil+100g GNH+150ml dH_2O	1kgSoil+150ml dH_2O
1kg Soil+100g CD+150ml dH_2O	1kg Soil+100g CPH+150ml dH_2O	1kg Soil+100g GNH+150ml dH_2O	1kgSoil+150ml dH_2O
1kg Soil+100g CD+150ml dH_2O	1kg Soil+100g CPH+150ml dH_2O	1kg Soil+100g GNH+150ml dH_2O	1kgSoil+150ml dH_2O

Key: 1.CD=Chicken droppings; 2.CPH=cowpea haulms; 3.GNH=ground nut haulms

One-kilogram (1kg) of air-dried contaminated soil was weighed into four (4) different two (2) liter capacity plastic containers and labeled 1-4. Each organic waste was air dried and grounded using a clean blender. One hundred gram (100g) of each organic waste (sterilized) was added to soils in containers 1, 2 and 3 separately and mix thoroughly. Each treatment was replicated 3 times. Three (3) vessels containing only contaminated soil(control)was labeled 4.One hundred and fifty milliliter(150ml) of sterile distilled water equivalent to 60% predetermined water holding capacity of the soil samples was added and incubated under ambient conditions on the laboratory bench. The content of each vessel was mixed manually once per week to enhance aeration and kept moist during the experimentation period by adding sterile distilled water at half the WHC of the soil. Ten (10) gram subsamples of was taken from each container after 2 weeks of incubation and subsequently at 2 weekly intervals for the determination of residual heavy metal in soil. Each treatment was set up in triplicates and monitored for 12 weeks. Residual heavy metal in soil was determined using the AAS, and the percentage reduction of heavy metal was calculated using the formula below:

$$\frac{\text{Initial concentration} - \text{Final cocentration}}{\text{Initial concentration}} \times 100(\text{Vidali, 200} \qquad (1)$$

Result

Soil physicochemical properties and heavy metal content

Table 2 shows the physicochemical properties of the experimental before bioremediation. The pH of 6.6 was recorded in the contaminated soil, however, the hydrogen ions of the soil sample falls within neutral level. Percentage nitrogen and phosphorous recorded in contaminated soil prior to bioremediation were (0.5% and 11.8mg/kg) respectively. The total organic carbon (TOC) of the contaminated soil was 8.23%, while water holding capacity (WHC) of the contaminated soil was 30%. The particle size composition which determines the textural structure of soil, showed that the experimental soil contained 80% sand, 10% silt and 10% clay, thence confirmed to be sandy loam.

The concentration of heavy metals analyzed was very high above acceptable limit of WHO in soil; lead (295.75mg/kg), cadmium (32.85mg/kg), chromium (38.75mg/kg), nickel (47.00mg/kg), zinc (755.50mg/kg), copper (77.25mg/kg) and arsenic (65.57mg/kg).

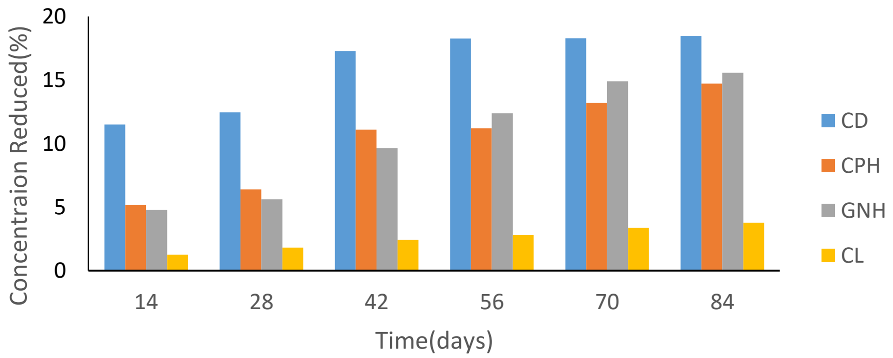
Table 2: Physicochemical properties and heavy metal content of contaminated soil

Parameter	Contaminated soil
pH	6.6
Nitrogen	0.5%
Phosphorous	11.8mg/kg
Organic carbon	10.26mg/kg
Water holding capacity	30%
Lead	295mg/kg
Chromium	38.75mg/kg
Cadmium	32.85mg/kg
Nickel	47.00mg/kg
Arsenic	65.57mg/kg
Zinc	755.50mg/kg
Copper	77.25mg/kg
Sand	80%
Silt	10%
Clay	10%
Soil texture	Sand loamy

Removal of heavy metals in soils amended with organic wastes:

Removal of lead

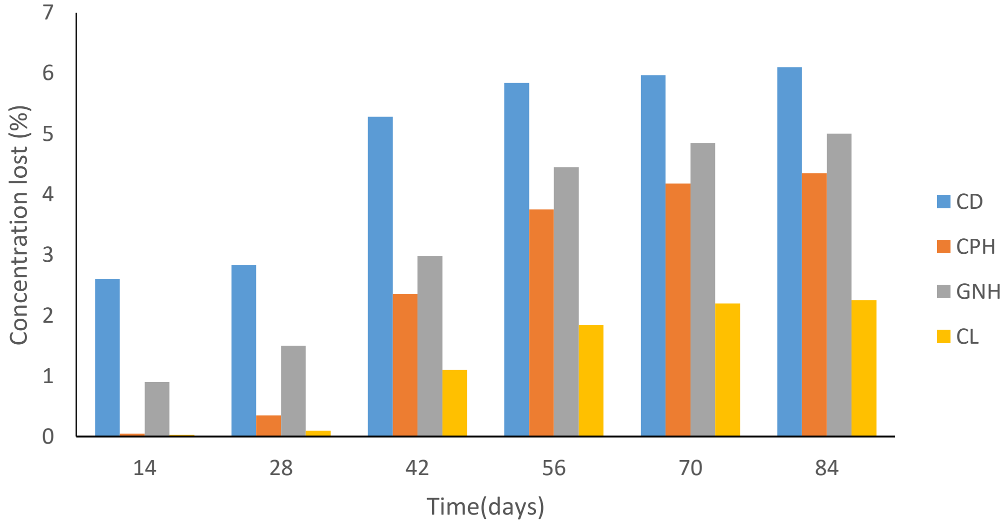
The result of lead reduction in soil during bioremediation is presented in figure1.In this study, the concentration of lead in engine oil contaminated soil was very high 295.75mg/kg, which is much higher than the acceptable limit set by WHO, (2011).The reduction progressed in a steady manner in all the categories until the end of the study period. After 12 weeks, this concentration reduced to54.25mg/kg, 43.25mg/kg and 45.25mg/kg in soil samples treated with chicken droppings, cowpea haulm and groundnut haulm respectively. The findings showed that soil treated with Chicken droppings (CD) recorded the highest reduction rate of lead (18.45%) Cowpea Haulm (CPH) and Groundnut Haulm (GNH) treated soil had 14.72% and 15.57% reduction respectively. In the control pot, lead was reduced by 25.75mg/kg (3.77%) of the initial concentration (fig.1). There was a statistically significant difference ($p<0.05$) in the mean reduction of lead in the treatments when compared to the control.



Key: CD =Chicken Droppings; CPH =Cowpea Haulm; GNH= Groundnut Haulm; CL =Control
Figure 1: Effect of organic wastes on Lead reduction in soil

Removal of Cadmium (mg/kg)

Within the first two weeks of the experiment (Figure 2), except in chicken droppings treated soil, <1% of cadmium was reduced in the soils amended with cowpea haulm, groundnut haulm and control. After twelve weeks of study, the highest loss of cadmium (6.1%) was recorded in the soil amended with chicken droppings. While the CPH and GNH amended soils had14.44% and 18.57% cadmium reduction respectively. The total concentration of cadmium reduced in the control soil after 12 weeks was 2.25% (figure.4). Statistical analysis of the mean of the percentage reduction revealed that there was no statistically significant difference (P>0.05) in the reduction of cadmium between all the treatments and controls.

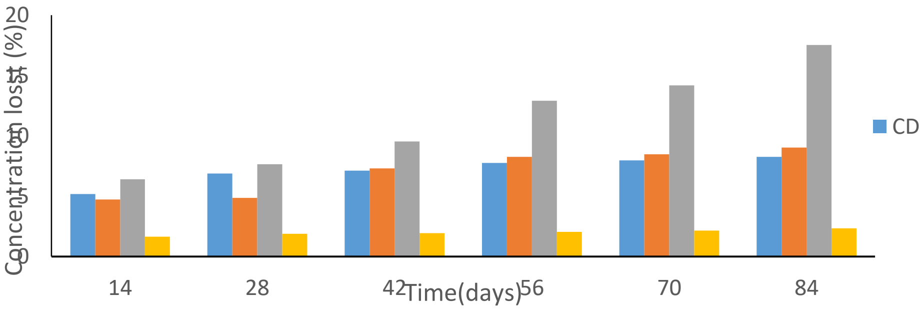


Key: CD =Chicken Droppings; CPH =Cowpea Haulm; GNH = Groundnut Haulm; CL =Control

Figure 2: Effect of organic wastes on Cadmium reduction in soil

Removal of chromium (mg/kg)in soil

The reduction in chromium in soil undergoing bioremediation of soil contaminated with spent engine oil. In this study, a fluctuated pattern in concentration of chromium was observed in the control soil during the study period. However, from day 56of the study to day 84, the reduction in Cr followed a steady pattern became steady. Percentage reduction of chromium in all the treatments was less than 18% with the highest reduction observed in soil treated with GNH 17.54%. The soils amended with CD and CPH had 8.26% and9.03%reduction respectively. Only 0.9 mg/kg (2.32%) of chromium was reduced in the control soil at the end of the experiment. ANOVA of the mean of percentage reduction showed statistically significant difference between the treatments and control at (p<0.05).

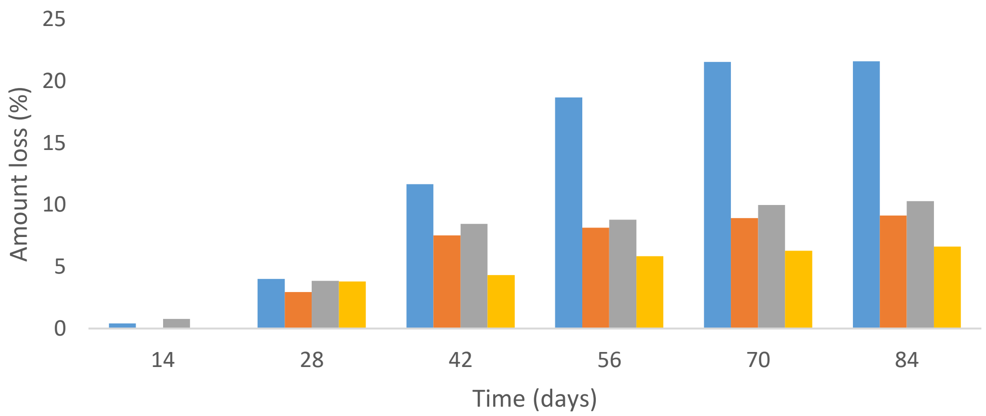


Key: CD =Chicken Droppings; CPH =Cowpea Haulm; GNH = Groundnut Haulm; CL =Control

Figure 3: Effect of organic wastes on Chromium removal in soil

Effect of organic wastes on Arsenic removal (%)

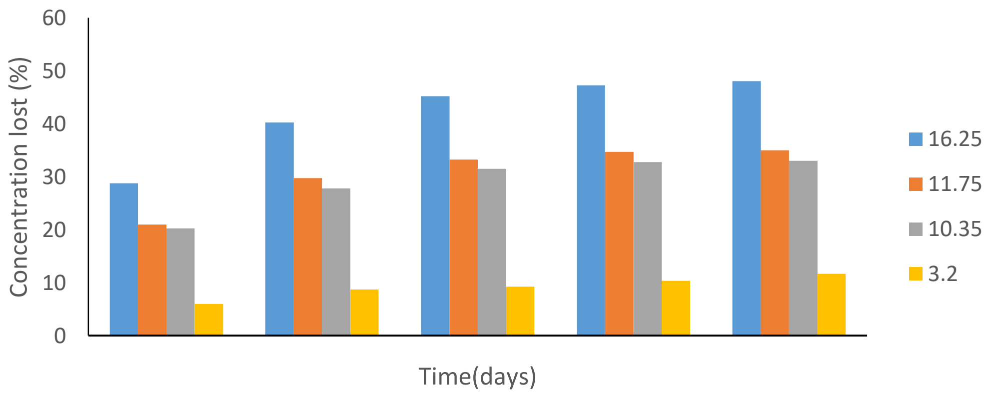
In this study, the initial concentration of arsenic determined in the experimental soil is 65.57mg/kg. Reduction of arsenic in soil during bioremediation ranged between 4.32mg/kg (6.61%) in control soil to 14.11mg/kg (21.58%) in GNH treated soil. Soil amended with CPH and CD had 5.97mg/kg (9.13%) and 6.72mg/kg (10.28%) reduction respectively (figure 6). Statistical analysis using ANOVA revealed that there is no significant difference at ($p>0.05$) in the reduction of arsenic among cowpea haulms and groundnut haulms treated soils and control. However, statistically significant difference ($p<0.05$) was observed in the percentage reduction of Arsenic between soil treated with chicken droppings and control soil (fig4)



Key: CD =Chicken Droppings; CPH =Cowpea Haulm; GNH = Groundnut Haulm; CL =Control
Figure 4: Effect of organic wastes on Arsenic removal in soil(%)

Zinc (mg/kg)

Removal of zinc from soil during remediation is presented figure 5. Zinc concentration in the experimental soil was found to be 755.50mg/kg. The initial concentration of 755.50mg/kg reduced to 633.33mg/kg in the control soil after 12 weeks. Percentage reduction ranged from 5.75% in CD soil to 24.65% in soil treated with GNH. Zinc concentration in CPH treated soil was reduced by 8.56% while control soil showed 16.17% reduction. Analysis of variance revealed that reduction in concentration of zinc among the treatments and control is highly significant at ($p<0.05$).

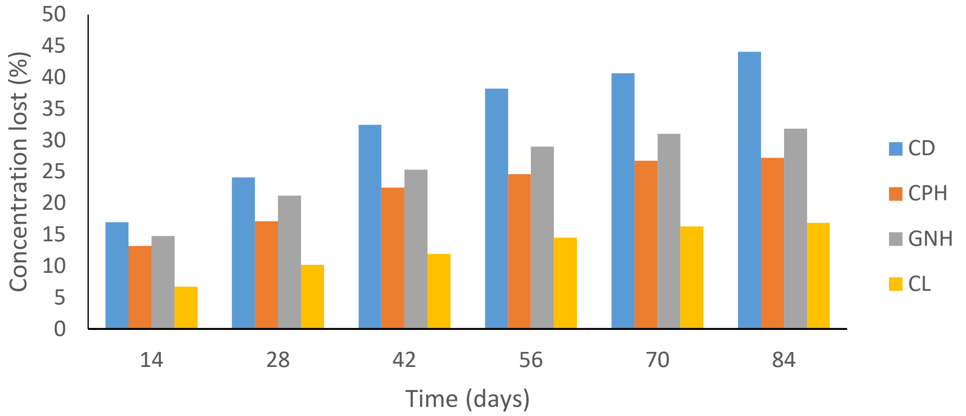


Key: CD =Chicken Droppings; CPH =Cowpea Haulm; GNH = Groundnut Haulm; CL =Control
Figure 5: Effect of organic wastes on Zinc reduction in soil(%)

Copper (%) removal in soil

The initial concentration of Copper in soil was 77.25mg/kg at the first sampling. This eventually reduced to 13.06 mg/kg (16.85%) on the final day of experiment in the control soil. In the soils amended with organic wastes, the percentage reduction observed ranged from 17.00%in CPH treated soil to 44.05%in soil amended with chicken droppings.

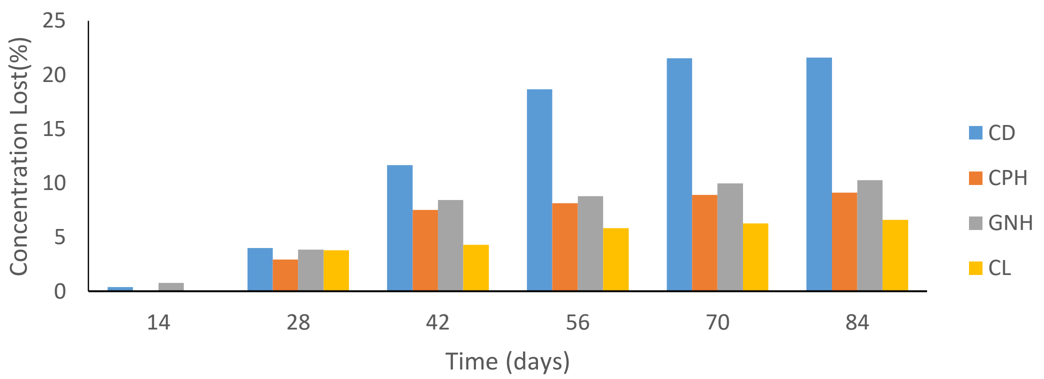
A loss of 31.84% (24.68mg/kg) was observed in GNH treated soil, while a total reduction of 27.21% (21.09mg/kg) was recorded in soil amended with cowpea haulm at the end of the experiment (12 weeks). There was statistically significant difference ($p<0.05$) in the reduction of copper between chicken droppings treated soil and control. There was no statistically significant difference ($p>0.05$) between cowpea haulms, groundnut haulms and control (figure 6).



Key: CD =Chicken Droppings; CPH =Cowpea Haulm; GNH = Groundnut Haulm; CL =Control
Figure 6: Effect of organic wastes on Copper reduction in soil(%)

Nickel mg/kg

Figure 7:Shows the results of nickel reduction in this study. Nickel concentration in soil was 47.00mg/kg at the onset of the experiment, the concentration was reduced by 4.1mg/kg (8.73%) in the control category on the final sampling. In soil stimulated with CD the initial concentration of Nickel was reduced by 15.00mg/kg (31.95%) after 12 weeks. Nickel concentration in soil treated with CPH and GNH had total reduction of 10.08mg/kg (21.47%) and 10.17mg/kg (21.66%) respectively. Statistical analysis of data using ANOVA indicates that was no statistically significant difference at ($P>0.05$) between the control soil and treatment category.



Key: CD =Chicken Droppings; CPH =Cowpea Haulm; GNH = Groundnut Haulm; CL =Control
Figure 7: Effect of organic wastes on Nickel removal in soil(%)

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Discussion

Lubricating oil have slow biodegradation and high bioaccumulation rate, while the heavy metals are slowly degraded completely by microorganisms and transform into less toxic forms of metal ions which accumulate in the environment. Bacteria use metals and metalloids as electron donors or acceptors for energy generation, thereby reduce metal ions through enzymatic activity into less harmful ionic form (Bernard *et al*., 2018).Therefore, preventive measures must be taken to ensure that spent engine oil fill with high concentration of heavy metals does not enter our environment (USEPA, 2004). There are numerous other metals present in spent engine oil such as aluminum, magnesium, iron, silicon, and copper (Wasiu *et al*., 2015). However, only those that are known to be very toxic were considered in this study. They include lead, cadmium, chromium, arsenic, zinc, copper and nickel.

The findings of this study revealed that the concentration of heavy metals in soils contaminated with spent engine oil, are above the maximum allowable limits (WHO, 2007; NESREA2009; WHO, 2011). High concentration of lead in the contaminated soil could be as a result of bioaccumulation over a long period of time (Rauckyte, 2016). The noticeable reduction of lead in the soil treated with organic wastes compared to that of the control could be due to the fact that bacteria have adopted different strategies to cope up with the harmful effects of heavy metals. One of such strategy is biosorption which is binding of metal ions with metal binding proteins present on the cell wall(Saba Shamim,2011).Organic waste also have the ability to absorb heavy metals, as well as stimulate the multiplication of microbial cells, (Sibi, 2014).

This finding is similar to that obtained by Amir *et al*. (2014) who recorded relatively high reduction in the concentration of Zinc, Cadmium, and Barium when they analyzed the bioremediation of soil polluted with engine oil using microwave incinerated Rice Husk Ash. Boricha and Fulekar, (2009) and Chaterjee *et al*. (2012) reported that *Bacillus* species can absorb lead from soil by intracellular lead bioaccumulation, efflux mechanism, precipitation and bio sorption. Adams *et al*. (2014) also revealed that adsorption, ion exchange and precipitation of lead with organic matter can contribute to high adsorption rate in soil. These researchers added that presence of *Bacillus* sp and *Pseudomonas* sp in the sample soil contributed to a significant reduction in lead concentration. The work of Malik, (2003) on the bioremediation of soil contaminated by heavy metal leachate from mechanic workshop, demonstrated the removal of lead by *Pseudomonas marginalis, Plectonema boryanum* and *Desulfosporiosinus*. Sulphate reducing bacteria was used to successfully treat metal leachate by converting metal ions from one oxidation state to another, hence reducing their toxic effect (Adams *et al*., 2014; Ruchita *et al*., 2015; Bernard *et al.*, 2018).

In this study, the concentration of cadmium was reduced greatly in soils treated with different organic wastes. This is similar to the work of Adams *et al*. (2014) who used chicken manure to remedy soil contaminated with different quantities of engine oil and recorded considerable dropped in concentration of cadmium in treated soils compared to the control. Srisvastara *et al*.(2009) stated that the mobility and fate of heavy metals in soil depend on their interactions with natural occurring ligands and adsorbents. They conducted a study on cadmium adsorption on bacteria cell using mineral broth of bacterial culture and reported that citrate and humic acid enhanced cadmium adsorption on *Pseudomonas putida*. Rice husk have the potential to adsorb cadmium and Nickel ions from aqueous solution (Srisvastara *et al*., 2009). Vermi composts are effective absorbent for removal of cadmium Cd (11) metal ions from its aqueous solution (Amit *et al*., 2014). Species of bacteria belonging to the genera, *Bacillus* and *Actinomycetes* can successfully reduce the concentration of cadmium during bioremediation of cadmium contaminated agricultural soils (Amir *et al*., 2014).

Findings of this study revealed that the initial concentration of chromium in soils amended with CD, CPH and GNH was greatly reduced after bioremediation process, this can be attributed to the presence of nutrients like nitrogen and phosphorous in the organic wastes, which enhanced biosorption

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of metal ions to the organic wastes. The organic wastes also have the potential to stimulate growth of bacteria growth, hence increase in rate of removal. This finding is similar to that of Agarry and Ogunleye (2012) in which, 10.4% of chromium (VI) was removed from soil contaminated with spent engine oil during bioremediation Species of *Bacillus*, *Pseudomonas* and *Acinetobacter* have the potential for accumulation of heavy metals associated with spent engine oil (Osubor, 2003; Dike *et al*., 2013). *Pseudomonas maltophilia* and *Bacillus megaterium*have shown the ability to detoxify chromium in contaminated soil (Cheung *et al.,* 2007). The work of SriLakshmi *et al*., 2018 revealed the removal of 31,9,63 and 71%Cu (11), Cd (11), Pb (11) and Cr (11) respectively from waste water using cross flow microfiltration in yeast-based bioaccumulation process.

The findings of this study showed that loss of zinc in the control soil (16.17%) was higher than that recorded in soils treated with chicken droppings and cowpea haulms. The reason may be due to the fact that bacteria absorbs more metal ions at low cell densities in control soil because metal uptake depends on binding sites (Bernard *et al*.,2018). These researchers also revealed that higher concentration of biomass or metal can restricts the access of metal ions to binding sites of bacteria. This agrees with the findings of Mario *et al*. (2002) who recorded high concentration of zinc in soil of mechanic workshop under natural condition when compared with amend soil. A study by Grujie *et al*., 2017revealed that biofilm cell of *Rhodotorula mucilaginosa* can remove up to 91.71%to 95.39% metal ion

The concentration of Arsenic, copper and nickel also reduced in soil after the experimental period, but the percentage reduction was lower in the control compared to the treatment categories. However, higher percentage reduction of arsenic and nickel was recorded in soil treated with GNH, while the highest reduction of copper was recorded in CD soil. The reason may not be far from the fact that the organic wastes have the ability to absorb heavy metals. The findings of this study concur with the result of Sibi, 2014 who carried out a research on the reduction of Arsenic from aqueous solution using dried biomass of microalgae. Various agricultural wastes such as sugarcane bagasse, fruit peels and wheat straw can serve as biosorbent of heavy metals thereby offering an eco-friendly and low-cost solution for the removal of arsenic from contaminated soil (Mohammed *et al*., 2015; Saba, 2018). *Bacillus*, *Pseudomonas* and *Streptomyces* species were used by various researchers to remove heavy metal from contaminated environment due to their metal sequestering properties. ((Chen *et al*., 2005; Abbas *et al*., 2014 and Saba,2018). Bacterial species such as *Micrococcus*, *Thiobacillus*, *Arthrobacter* and *Enterobacter* can also absorb heavy metal from soil (Arti Hansda *et al*., 2015).

Heavy metals are highly toxic, immobile and persist in water and soil, therefore accumulate in the upper inches of soil fast (Pourrut *et al*.,2011 and Tangahu *et al.*,2011).Despite their toxic effect, microorganisms can survive in their presence because they exhibits several mechanisms to reduce or tolerate their toxicity(Spain and Alm,2003;Ma *et al*.,2016 and White *et al*.,2016).Microorganisms have negatively charged functional groups on their cell wall (such as carbonyl, carboxyl, amino, sulfydryl, hydroxyl etc.).These negative charges on cell surface of microbes are responsible for metal adsorption, thence reduction in metal concentration, because of the presence of anionic structures that empower the microbes to bind to metal cations. This process of metal removal by microorganism is term biochemical mechanism(Ma. *et al*.,2016).Another mechanism used by microorganism to survive metal toxicity is the molecular mechanism, this constitute genetic determinants of heavy metal resistance that can be localized either on the chromosomes or extra chromosomal genetic elements(Aneva,2009).

In this study, the most efficiently removed heavy metal was copper. This could be attributed to the fact that component of organic wastes form complex with the heavy metals, remove them from solution and reduce their concentration in media. Copper is less toxic hence easily form complexes with organic wastes and bacterial cell walls (Kumar,et al.,2013;Aljert and Almasri,2018).

In this present study, based on the ability of nutrients in organic wastes to stimulate bacterial growth, we propose groundnut haulms as the best and most effective bio stimulation agent for effective bio sorption of metal ions onto the biomass as well as the bacterial cells. Many organic wastes such as banana peel, rice husks and egg shell serve as biosorbent of heavy metal from contaminated soil (Sibi,2018).However, additional studies are need to untangle the mechanism behind this finding.

Conclusion

Statistical analysis of heavy metal concentration during the bioremediation process showed that there was significant difference between the initial concentration of heavy metals and the residual concentration at the end of the experimental period. However, there was significant difference in the reduction of copper was only observed between CD treated soil and control, but there was no statistical difference between groundnut haulms and cowpea haulms treated soils and control.

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