Heavy Metal Degradation in Crude Oil Ameliorated Soils

Agbor R.B.[1], Antai S.P[2]

[1]*Department of Genetics and Biotechnology, University of Calabar, Calabar, Cross River State-Nigeria*
[2]*Department of Microbiology, University of Calabar, Calabar, Cross River State-Nigeria*

***Abstract:* - Heavy metal degradation in crude oil ameliorated soils was studied. Composite soil from three points were obtained and six kilogramme weighed into 150 plastic buckets and each spiked with 300ml of crude oil, allowed for 14 days and then treated with agro-wastes in single and combined forms. The treatment lasted for 90days, after which samples were collected and analysed for heavy metal presence. The result of the study revealed that there were significant reductions in the heavy metal content of the soil ameliorated with varying concentrations of the agro-wastes.The soils amended with high level of the agro-waste tend toenhance the reduction of the heavy metal content than the low concentrations of the agro-waste wastes. The reduction in heavy metal content could be attributed to the bio-active and enzymatic properties of the wastes. It was concluded that the combined amendments are more proficient in the enhancement process.**

***Keywords:* Degradation, soils, heavy metals, agro-wastes**

I. INTRODUCTION

The growth in the world's economy through industrialization via oil processing companies is vital and a down-tool to the ecology. The economy of Nigeria is sustained by its giant strive in maintaining the oil sectors. Oily sludge generated during and after the refining process hasposed a lot of ecological damage to the flora and fauna present in the ecotype. The extinction of some important flora and fauna had been observed. The spills of hydrocarbons in an environment contribute a great mass of heavy metals which are beneficial at a considerable level (Low) and harmful at a high level. Heavy metals (trace metals) are a large group of trace elements which are of great industrial and biological importance. Heavy metals are found naturally in soils as natural components but anthropogenic activities have resultantly increased the quantity of heavy metals in the environment. Soil contamination by heavy metals is consequently the most critical environmental problems as it poses significant impacts to the human health as well as the ecosystems. The contaminants are able to infiltrate deep into the layer of underground waters and pollute the groundwater as well as the surface water. Heavy metals in the soil subsequently enter the human food web through plants and they constitute risk to the ecosystem as they tend to bioaccumulate and can be transferred from one food chain to another. Heavy metals are discovered in various food chains where the results are usually detrimental to microorganisms, plants, animals and humans alike. Remediation in relation to a contaminated site means the management of the site in order to prevent damage to human health or the environment and restoring all or part of the site to a useful purpose. Bioremediation can beeffective only where environmental conditions permit microbial growth and activity, itsapplication often involves the manipulation of environmental parameters to allow microbialgrowth and degradation to proceed at a faster rate (Vidali, 2001).Ikhajigbe et al., (2013) observed significant reduction in heavy metal concentrations at pH of 5, this imply that the adjustment of the pH could influences the reduction of heavy metal content in hydrocarbon polluted soils.

II. MATERIALS AND METHODS

The Nigerian light crude oil was obtained from NAOC(Nigerian Agip Oil Company), located in Port Harcourt, Rivers State, Nigeria, the agro-wastes such as groundnut husks (GH), maize cobs (MC), empty fruit bunch of oil palm (EFBOP) and cassava peels (CP) were collected from local farmers and processing industries in Cross River State, Nigeria.

Production of dispersant from the agricultural wastes

The collected agro-wastes (GH, MC, EFBOP, and CP) were sun-dried for 10 days and blend to powder using electric blender (Model 4250, Braun, Germany). The dispersants were sieved to pass through 2 mm sieve. They were labelled and stored in containers.

Soil samples for bioremediation studies

Site of soil collection

Sandy-loam soils were obtained from theExperimental site ofFaculty of Biological Sciences, University of Calabar, Calabar. The site was used with the intention of using agricultural soil that probably had in the past been under cultivation or grazing and had not been exposed to intentional petroleum hydrocarbon contamination.

Experimental design

The experiment was conducted using 3x10x5 factorial experimental units in a completely randomized design (CRD).

Factor 1: The duration (3 levels).
Factor 2: The agro-wastes (In single and combined forms)

Factor 3: The concentration of the agro-wastes. Pristine control (unpolluted (positive), 0%), crude oil control (polluted (negative), 0%), 3.33% and 6.66% and 10% of the amendments (5 levels).

Soil sample collection

Top soils (0-25cm depth) were evenly obtained from three (3) points, using a Dutch auger, then homogenized to form composite soil sample, six kilograms (6kg) of the soil samples was weighed and transferred into each of the hundred and fifty (150) labelled plastic buckets (PB) with drainage holes at the sides and based. The arrangement of the PB was in triplicate using completely randomized design (CRD).Artificial pollution was done by introducing 300ml (0.3 litres) of crude oil into PB containing the soils, except the pristine soils samples that served as the positive control. The PB containing the polluted soils were mixed thoroughly and allowed to stand for 14 days (these was to allow indigenous microorganisms to become acclimatized with the new soil condition)

Bio-stimulation study

Application of treatment

The polluted soils were treated with the various agro-wastes in single and combined form as follows:

Groundnut husks 2014 powder ($GnH_{14}P$) consist of the following treatment groups, pristine soil (+ve control, 0% $GnH_{14}P$), crude oil soil (-ve control, 0% $GnH_{14}P$), 3% $GnH_{14}P$, 7% $GnH_{14}P$ and 10% $GnH_{14}P$

Maize cob 2014 powder ($MaC_{14}P$) consist of the following groups, pristine soil (+ve control, 0% $MaC_{14}P$), crude oil soil (-ve control, 0% $MaC_{14}P$), 3% $MaC_{14}P$, 7% $MaC_{14}P$ and 10% $MaC_{14}P$

Cassava peels 2014 powder ($CasP_{14}P$) consist of the following treatment groups, pristine soil (+ve control, 0% $CasP_{14}P$), crude oil soil (-ve control, 0% $CasP_{14}P$), 3% $CasP_{14}P$, 7% $CasP_{14}P$ and 10% $CasP_{14}P$

Empty fruit bunch of oil palm 2014 powder ($EFBOP_{14}P$) consist of the following treatment groups, pristine soil (+ve control, 0% $EFBOP_{14}P$), crude oil soil (-ve control, 0% $EFBOP_{14}P$), 3% $EFBOP_{14}P$, 7% $EFBOP_{14}P$ and 10% $EFBOP_{14}P$

Groundnut husks 2014 powder ($GnH_{14}P$) + maize cobs 2014 powder ($MaC_{14}P$) consist of the following treatment groups, pristine soil (+ve control, 0% $GnH_{14}P$+$MaC_{14}P$), crude oil soil (-ve control, 0% $GnH_{14}P$ + $MaC_{14}P$), 3% $GnH_{14}P$ + $MaC_{14}P$, 7% $GnH_{14}P$ + $MaC_{14}P$ and 10% $GnH_{14}P$ + $MaC_{14}P$.

Groundnut husks 2014 powder ($GnH_{14}P$) + empty fruit bunch of oil palm 2014 powder ($EFBOP_{14}P$) consist of the following treatment groups, pristine soil (+ve control, 0% $GnH_{14}P$+ $EFBOP_{14}P$), crude oil soil (-ve control, 0% $GnH_{14}P$+ $EFBOP_{14}P$), 3% $GnH_{14}P$+ $EFBOP_{14}P$, 7% $GnH_{14}P$+ $EFBOP_{14}P$ and 10% $GnH_{14}P$+ $EFBOP_{14}P$.

Groundnut husks 2014 powder ($GnH_{14}P$) + cassava peels 2014 powder ($CasP_{14}P$) consist of the following treatment groups, pristine soil (+ve control, 0% $GnH_{14}P$ + $CasP_{14}P$), crude oil soil (-ve control, 0% $GnH_{14}P$ + $CasP_{14}P$), 3% $GnH_{14}P$ + $CasP_{14}P$, 7% $GnH_{14}P$ + $CasP_{14}P$ and 10% $GnH_{14}P$ + $CasP_{14}P$.

Maize cob 2014 powder ($MaC_{14}P$) + empty fruit bunch of oil palm 2014 powder ($EFBOP_{14}P$) consist of the following treatment groups, pristine soil (+ve control, 0% $MaC_{14}P$+ $EFBOP_{14}P$), crude oil soil (-ve control, 0% $MaC_{14}P$+ $EFBOP_{14}P$), 3% $MaC_{14}P$+ $EFBOP_{14}P$, 7% $MaC_{14}P$+ $EFBOP_{14}P$ and 10% $MaC_{14}P$+ $EFBOP_{14}P$.

Maize cob 2014 powder ($MaC_{14}P$) + cassava peels 2014 powder ($CasP_{14}P$) consist of the following treatment groups, pristine soil (+ve control, 0% $MaC_{14}P$+ $CasP_{14}P$), crude oil soil (-ve control, 0% $MaC_{14}P$+ $CasP_{14}P$), 3% $MaC_{14}P$+ $CasP_{14}P$, 7% $MaC_{14}P$+ $CasP_{14}P$ and 10% $MaC_{14}P$+ $CasP_{14}P$.

Empty fruit bunch of oil palm 2014 powder ($EFBOP_{14}P$) + cassava peels 2014 powder ($CasP_{14}P$) consist of the following treatment groups, pristine soil (+ve control, 0% $EFBOP_{14}P$ + $CasP_{14}P$), crude oil soil (-ve control, 0% $EFBOP_{14}P$ + $CasP_{14}P$), 3% $EFBOP_{14}P$ + $CasP_{14}P$, 7% $EFBOP_{14}P$ + $CasP_{14}P$ and 10% $EFBOP_{14}P$ + $CasP_{14}P$.

Determination of heavy metal content of the soil

A sample of 0.5g of air-dried ground soil was transferred to 25ml conical flask; 5ml of concentration H_2SO_4 was added followed by 25ml of concentrated HNO_3 acid and 5ml of concentrated HCl. The contents of the tube was heated at 200^0C for 1hr in a fuming hood and then cooled to room temperature. After cooling, 20ml of distilled water was added and the mixture was filtered to complete the digestion. Finally, the mixture was transferred to a 50ml volumetric flask, filled to the mark and let to settle for at least 15 hours. The filtrate will be analyzed for total chromium (Cr), iron (Fe), copper (Cu), lead (Pb), Zinc (Zn), cadmium (Cd), Manganese (Mn) by Atomic Absorption Spectrophotometer Model Analyst 200 Perkin Elmer.

Statistics Analysis

Data collected were subjected to a three way analysis of variance using SPSS while significant means were separated using least significant difference (LSD) test at 5% probability level.

III. RESULTS

Heavy metal accumulation in soil amended with agro-wastes

The presence of heavy metal at considerable and acceptable levels in soil is beneficial to crop growth and productivity. The non-availability of the heavy metal in soil is injurious to plant performance. This research evaluated the heavy metal content of the polluted soils during the remediation study.

Manganese content in the polluted soil amended with agro-wastes

The results obtained showed that the hydrocarbon polluted control soils had higher Mn than the amended soils. These were followed by the soils amended with 3% $MaC_{14}P$, 3% $GnH_{14}P$ + $MaC_{14}P$, 3% $CasP_{14}P$, 3% $CasP_{14}P$ + $MaC_{14}P$ and 3% $GnH_{14}P$+ $CasP_{14}P$ which had no variation in mean values obtained, but more than the soils amended with 6% $CasP_{14}P$, 3% $EFBOP_{14}P$, 3% $CasP_{14}P$ + $EFBOP_{14}P$, 3% $GnH_{14}P$ + $EFBOP_{14}P$, 6% $CasP_{14}P$ + $MaC_{14}P$ and 6% $GnH_{14}P$+ $CasP_{14}P$, which had no variation in the mean values obtained. These were also followed by the mean values obtained for soil amended with 6% $MaC_{14}P$, 6% $GnH_{14}P$ + $MaC_{14}P$, 10% $CasP_{14}P$, 6% $EFBOP_{14}P$, 10% $CasP_{14}P$ + $EFBOP_{14}P$, 6% $GnH_{14}P$ + $EFBOP_{14}P$, 10% $CasP_{14}P$ + $MaC_{14}P$, 3% $MaC_{14}P$+ $EFBOP_{14}P$ and 10% $GnH_{14}P$+ $CasP_{14}P$, with no significant differences ($P>0.05$) in the Mn content in the soils. Reduction in the Mn were observed in soils amended with 6% and 10% of $GnH_{14}P$, with mean values similar to that obtained in the pristine controls (Table 1).

The reduction of the manganese level in the soils due to the duration of the study were examined and the results indicated that the Mn level in the soil amended with $GnH_{14}P$ at 90 days and $MaC_{14}P$+ $EFBOP_{14}P$ at 90 days had mean values of 5.47±1.23 $mgkg^{-1}$ and 5.89±1.21$mgkg^{-1}$ respectively, with no variation. These reduction in Mn level was also followed by soils amended with $MaC_{14}P$, $GnH_{14}P$+ $MaC_{14}P$, $CasP_{14}P$, $EFBOP_{14}P$, $CasP_{14}P$ + $EFBOP_{14}P$, $GnH_{14}P$ + $CasP_{14}P$ at 90 days and $MaC_{14}P$+ $EFBOP_{14}P$, $GnH_{14}P$ at 60 days with mean values of 8.33±1.13 $mgkg^{-1}$, 6.70±1.10 $mgkg^{-1}$, 8.74±1.10 $mgkg^{-1}$, 6.98±1.08 $mgkg^{-1}$, 6.85±1.09 $mgkg^{-1}$, 6.51±1.13 $mgkg^{-1}$, 7.05±1.0 $mgkg^{-1}$, 6.35±1.14 $mgkg^{-1}$, 7.44±1.15 $mgkg^{-1}$and 6.82±1.20 $mgkg^{-1}$ respectively, with no variation in the meanMn levels in the soils (Figure 1).

Table 1: Effects of treatment applications on the heavy metal content of crude oil polluted soils

Parameters	Trt. levels	Manganese (Mn) mg/kg	Nickel (Ni) mg/kg	Zinc (Zn) mg/kg	Copper (Cu) mg/kg	Chromium (Cr) mg/kg	Cobalt (Co) mg/kg	Iron (Fe) mg/kg	Lead (Pb) mg/kg
	PC	2.68^{i}±0.03	3.22^{h}±0.11	3.68^{n}±0.02	1.71^{h}±0.01	0.52^{i}±0.01	0.27^{d}±0.01	643.78^{e}±3.37	0.09^{d}±0.01
	COC	15.59^{a}±0.33	13.97^{a}±0.17	25.45^{a}±0.42	15.58^{a}±0.36	10.66^{a}±0.15	2.66^{a}±0.02	1599.33^{a}±5.21	0.70^{a}±0.06
$GnH_{14}P$	3%	6.42^{e}±0.70	7.93^{d}±0.78	10.63^{e}±1.03	9.67^{b}±0.73	6.31^{e}±0.94	1.29^{b}±0.15	1214.67^{c}±7.10	0.34^{c}±0.06
	6%	5.15^{g}±0.61	6.61^{e}±0.58	9.29^{g}±0.98	7.36^{d}±0.76	5.46^{f}±0.86	1.15^{b}±0.16	1137.89^{c}±8.12	0.28^{c}±0.05
	10%	4.76^{h}±0.55	5.54^{g}±0.42	7.81^{j}±0.91	6.09^{d}±0.77	4.53^{f}±0.79	1.03^{b}±0.15	1085.11^{c}±9.4	0.13^{c}±0.02
$MaC_{14}P$	3%	9.38^{b}±0.47	9.60^{b}±0.88	12.0^{b}±1.30	8.66^{c}±1.38	6.10^{e}±1.12	1.64^{b}±0.16	1058.67^{c}±5.2	0.38^{b}±0.06
	6%	7.43^{d}±0.60	8.39^{d}±0.84	9.62^{g}±1.61	7.08^{d}±1.32	4.89^{f}±0.77	1.54^{b}±0.16	983.44^{c}±6.8	0.28^{c}±0.05
	10%	6.62^{e}±0.65	7.81^{d}±0.80	8.64^{h}±1.40	6.58^{d}±1.29	4.04^{g}±0.72	1.36^{b}±0.14	948.89^{c}±5.70	0.23^{c}±0.05
$GnH_{14}P$+$MaC_{14}P$	3%	9.57^{b}±0.93	7.60^{d}±0.84	7.90^{j}±1.03	6.60^{d}±0.85	5.16^{f}±0.66	1.28^{b}±0.11	1100.89^{c}±5.55	0.37^{b}±0.08
	6%	7.97^{d}±0.73	6.21^{f}±0.63	6.73^{l}±0.86	5.47^{e}±0.73	4.18^{g}±0.71	1.11^{b}±0.13	994^{c}±6.2	0.30^{c}±0.06
	10%	7.06^{d}±0.65	5.64^{g}±0.47	6.20^{m}±0.82	4.97^{e}±0.72	3.49^{h}±0.66	1.04^{b}±0.13	934.89^{c}±5.9	0.25^{c}±0.06
$CasP_{14}P$	3%	9.66^{b}±0.92	9.47^{b}±0.84	11.88^{b}±1.66	8.47^{c}±1.15	6.54^{e}±0.99	1.63^{b}±0.13	1175.33^{c}±5.0	0.32^{c}±0.04
	6%	8.88^{c}±0.91	8.74^{c}±0.83	10.37^{e}±1.44	7.79^{d}±1.07	4.93^{f}±0.75	1.48^{b}±0.13	1077.78^{c}±6.80	0.28^{c}±0.03
	10%	7.59^{d}±0.72	8.23^{d}±0.78	9.62^{g}±1.53	6.91^{d}±1.11	4.01^{g}±0.67	1.35^{b}±0.11	1055.56^{c}±6.7	0.24^{c}±0..03
$EFBOP_{14}P$	3%	8.43^{c}±0.85	8.83^{c}±1.05	12.60^{b}±1.33	8.82^{c}±0.70	5.66^{f}±0.82	1.51^{b}±0.10	1208.56^{c}±6.61	0.30^{c}±0.03
	6%	7.11^{d}±0.68	6.91^{e}±0.85	12.12^{b}±1.45	7.46^{d}±0.64	5.28^{f}±0.81	1.29^{b}±0.06	1110.44^{c}±7.28	0.27^{c}±0.02
	10%	6.29^{e}±0.72	6.36^{f}±0.68	10.98^{d}±1.57	6.39^{d}±0.53	4.73^{f}±0.64	1.19^{b}±0.06	1046.78^{c}±7.19	0.22^{c}±0.02
$CasP_{14}P$+ $EFBOP_{14}P$	3%	8.63^{c}±0.54	8.84^{c}±0.62	11.44^{c}±1.09	6.64^{d}±0.85	5.26^{f}±0.89	1.32^{b}±0.10	1154.11^{c}±6.02	0.23^{c}±0.02
	6%	7.82^{d}±0.64	6.68^{e}±0.58	9.74^{g}±0.97	5.38^{e}±0.64	4.48^{f}±1.03	1.17^{b}±0.08	1042.78^{c}±4.50	0.19^{c}±0.01
	10%	7.18d±0.59	5.60g±0.45	8.63h±0.74	4.69e±0.56	3.81g±0.94	1.06b±0.09	1042.78c±0.45	0.19c±0.01
GnH14P+ EFBOP14P	3%	8.48c±0.68	7.90d±1.32	12.02b±1.20	6.83d±0.57	7.48d±1.09	1.61b±0.11	1014.11c±5.36	0.38b±0.05
	6%	7.67d±0.55	6.87e±1.0	10.63e±1.10	6.10d±0.50	5.08f±0.96	1.43b±0.11	956.7c±4.98	0.33c±0.04
	10%	6.67e±0.72	6.20f±0.86	9.37g±1.14	5.24e±0.48	4.00g±0.86	1.28b±0.09	897.56d±5.44	0.26c±0.02
CasP14P+MaC14P	3%	9.16b±0.55	7.77d±1.13	10.53e±1.15	5.09e±0.63	10.44a±1.08	1.39b±0.11	1084.78c±5.56	0.23c±0.03
	6%	8.00c±0.70	5.93f±0.85	9.16g±1.02	4.06f±0.46	8.06c±0.97	1.03b±0.11	1019.78c±5.16	0.19c±0.03
	10%	7.43d±0.61	5.36g±0.72	7.74j±0.69	3.59g±0.48	6.80e±0.83	0.88c±0.11	974c±6.0	0.17c±0.03
MaC14P+ EFBOP14P	3%	7.09d±0.78	8.90c±1.03	10.09f±1.19	6.06d±0.58	8.00c±0.97	1.42b±0.1	1022.56c±5.23	0.30c±0.03
	6%	6.67e±0.68	7.43d±0.87	8.10i±0.90	5.37e±0.52	6.04e±0.68	1.21b±0.08	996.11c±5.52	0.25c±0.03
	10%	5.74f±0.74	6.07f±0.74	7.13k±0.83	4.76e±0.45	4.24g±0.40	1.11b±0.07	936.89c±5.87	0.20c±0.03
GnH14P+CasP14P	3%	9.51b±0.90	8.10d±0.82	9.46g±1.1	6.44d±0.71	9.30b±0.88	1.58b±0.10	1082.33c±6.80	0.31c±0.04
	6%	8.52c±1.01	6.14f±0.91	8.22i±1.03	6.09d±0.82	7.94c±1.05	1.28b±0.08	1023.33c±6.23	0.27c±0.04
	10%	7.74d±1.00	5.50g±0.72	7.52j±0.95	4.87e±0.74	6.59e±0.97	1.16b±0.08	974.22c±6.78	0.23c±0.03
LSD		0.25	0.19	0.14	0.11	0.07	0.08	28.2	0.02

Mean with the same superscript along the vertical arrays indicate no variations

Legend:

$MaC_{14}P$ Maize cob 2014 powder

$EFBOP_{14}P$ Empty fruit bunch of oil palm 2014 powder

$CasP_{14}P$ Cassava peels 2014 powder

PS Pristine soil

COPS Crude oil-polluted soil

These results showed that the soils with the different amendments at 30 days had significantly higher ($P<0.05$) Mn level than other durations adopted during the study. The results imply that the higher the amendment period the lower the Mn content in the soil provided the soil was amended (Table 2). It was also observed that significant reduction in Mn level was achieved in soil amended with $GnH_{14}P$, followed by soil amended with $MaC_{14}P$+ $EFBOP_{14}P$ (Figure 1).

Nickel content in the amended soils

The results obtained for the Ni level in the soils showed that soil amended with 10% $GnH_{14}P$, 10% $GnH_{14}P$+ $MaC_{14}P$, 10% $CasP_{14}P$+ $MaC_{14}P$ and 10% $CasP_{14}P$+ $EFBOP_{14}P$ had significantly reduced ($P<0.05$) Ni content as follows, 5.54±0.42 $mgkg^{-1}$, 5.64 ±0.47 $mgkg^{-1}$, 5.36±0.72 $mgkg^{-1}$ and 5.60±0.45 $mgkg^{-1}$ respectively, with no variation in the mean values obtained. The reduction in the Ni level was also followed by soils treated with 6% $GnH_{14}P$+ $MaC_{14}P$, 10% $EFBOP_{14}P$, 10% $GnH_{14}P$+ $EFBOP_{14}P$, 6% $CasP_{14}P$+ $MaC_{14}P$, 10% $MaC_{14}P$+ $EFBOP_{14}P$ and 10% $GnH_{14}P$+ $CasP_{14}P$ which had no variation in the mean Ni level in the soils. The soils treated with 6% $GnH_{14}P$, 6% $EFBOP_{14}P$, 6% $CasP_{14}P$+ $EFBOP_{14}P$, and 6% $GnH_{14}P$+ $EFBOP_{14}P$ had significantly higher Ni level in the soils but reduced, compared to soils amended with 3% $GnH_{14}P$, 6%, 10% $MaC_{14}P$, 3% $GnH_{14}P$+ $MaC_{14}P$, 10% $CasP_{14}P$, 3% $GnH_{14}P$+ $EFBOP_{14}P$, 3% $CasP_{14}P$+ $MaC_{14}P$, 6% $MaC_{14}P$+ $EFBOP_{14}P$ and 3% $GnH_{14}P$+ $CasP_{14}P$, with no variation in the mean Ni contents of the soils. The crude oil-polluted soils had the highest Ni level as compared to the pristine control and amended soils. The decreased in the Ni level in the amended soils could be as a result of the efficiency of the agro-wastes to remove or biodegrade the element in the soils.The soils treated with $GnH_{14}P$, $GnH_{14}P$+ $MaC_{14}P$, $CasP_{14}P$+ $MaC_{14}P$ and $GnH_{14}P$+ $CasP_{14}P$ had significantly reduced ($P<0.05$) Ni level than other amendments (Table 2). This study has also revealed that the higher the concentrations of the amendment in soil the higher the reduction in Ni level in soils.

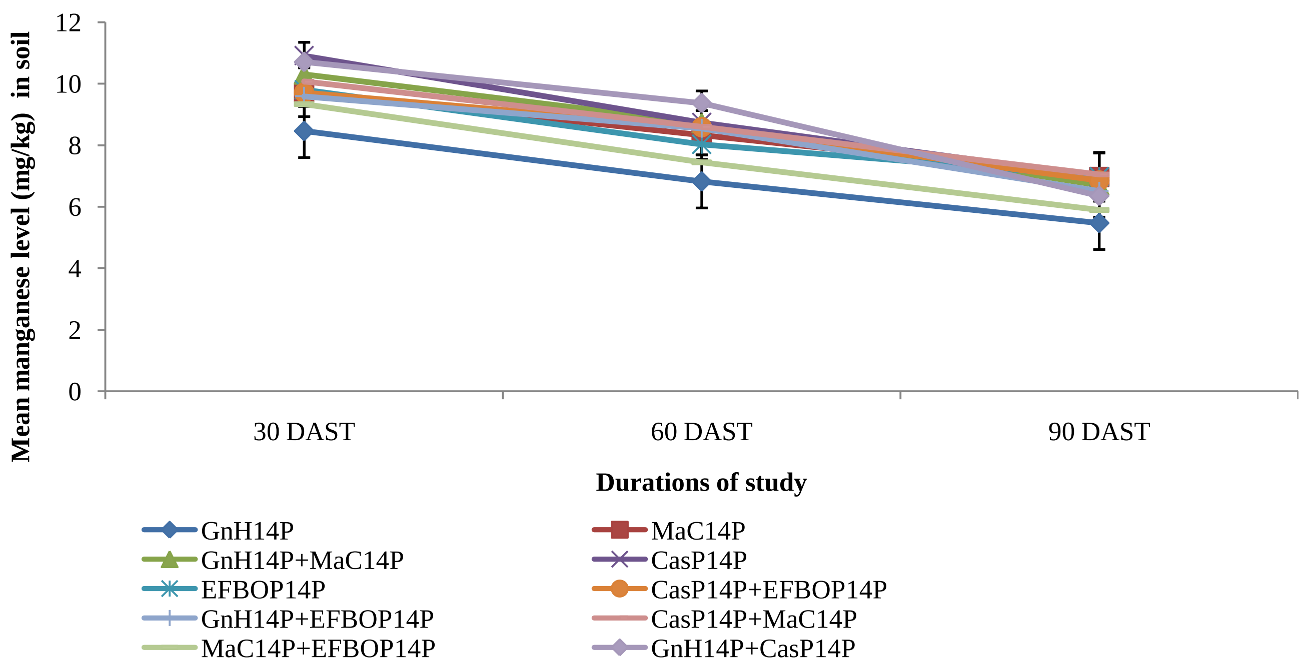

FIG. 1: Manganese content of soil amended with different agro-wastes

Legend:

MaC$_{14}$P Maize cob 2014 powder

EFBOP$_{14}$P Empty fruit bunch of oil palm 2014 powder

CasP$_{14}$P Cassava peels 2014 powder

DAST Days after soil treatment

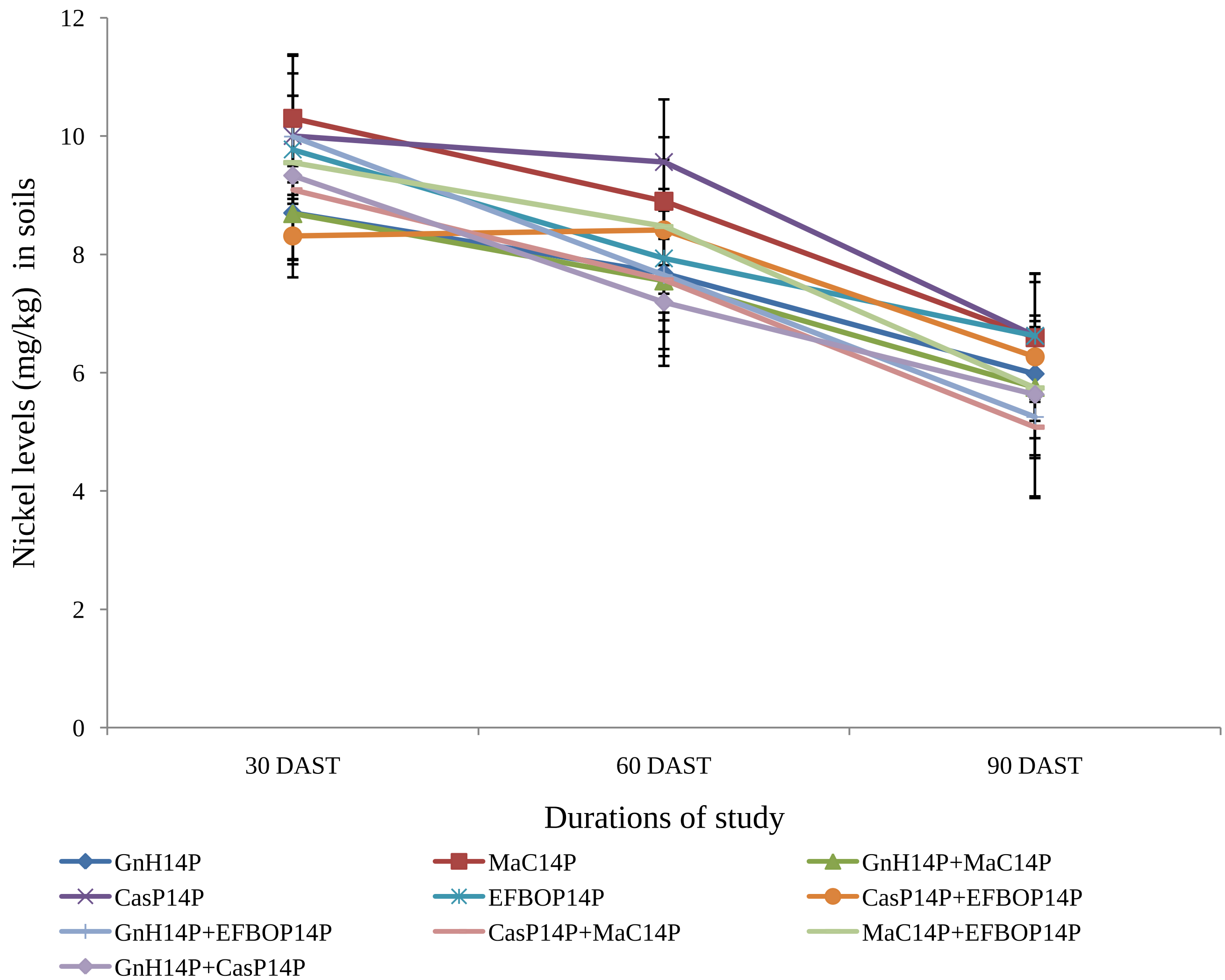

FIG. 2: Nickel content of soil amended with different agro-wastes

Legend:

MaC$_{14}$P Maize cob 2014 powder

EFBOP$_{14}$P Empty fruit bunch of oil palm 2014 powder

CasP$_{14}$P Cassava peels 2014 powder

DAST Days after soil treatment

Figure 2 showed that soils amended with $CasP_{14}P$+ $MaC_{14}P$ and $GnH_{14}P$+ $EFBOP_{14}P$ at 90 days had significantly reduced ($P<0.05$) Ni level, with no variation in the mean values obtained. The significant reduction were followed by soils amended with $GnH_{14}P$ and $GnH_{14}P$+ $CasP_{14}P$ at 90 days which had no variation in the mean values obtained. These were also followed by soils amended with $MaC_{14}P$, $EFBOP_{14}P$, and CasP14P+ $EFBOP_{14}P$ at 90 days with no variation in the mean values obtained. Higher Ni levels were obtained from soils amended with the different agro-wastes at 30 days of the study. These results imply that increased in study periods could result in significant reduction in the Ni contents of the soils.

Availability of zinc in soil enhanced with agro-wastes

The results for Zn content in soils as presented on Table 1 showed that the crude oil-polluted soil had more Zn content than the amended soils and pristine soil. These were followed by soils amended with 3% $MaC_{14}P$, 3% $CasP_{14}P$, 3%, 6% $EFBOP_{14}P$ and 3% $GnH_{14}P$+ $EFBOP_{14}P$ with no variation in mean Zn content, these values were more than the mean values of Zn obtained from soil treated with 3% $CasP_{14}P$+ $EFBOP_{14}P$. Decreased in the Zn content of the soils was obtained from soils amended with 10% $GnH_{14}P$+ $MaC_{14}P$, followed by soil amended with 6% $GnH_{14}P$+ $MaC_{14}P$, also followed by soil amended with 10% $MaC_{14}P$ + $EFBOP_{14}P$. The reduction in the Zn content was also observed from soils amended with 10% $GnH_{14}P$, 3% $GnH_{14}P$+ $MaC_{14}P$, 10% $CasP_{14}P$+ $MaC_{14}P$ and 10% $GnH_{14}P$+ $CasP_{14}P$, with no variation in the mean values obtained.The results as presented on Figure 3 showed that the soil amended with $EFBOP_{14}P$ at 30 days of the study had significantly higher ($P<0.05$) Zn content, followed by soil amended with $CasP_{14}P$ at 30 days treatment duration.These were followed by soil amended with $MaC_{14}P$ at 30 days and soil treated with $GnH_{14}P$+ $EFBOP_{14}P$ at 30 days, with no variation in the mean values obtained

Table 2

Agro-wastes	Iron (mg/kg)	Cobalt (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	Copper (mg/kg)	Chromium (mg/kg)	Nickel (mg/kg)	Manganese (mg/kg)
$GnH_{14}P$	$1136.16^{a}\pm3.59$	$1.28^{c}\pm0.13$	$0.30^{a}\pm0.04$	$11.37^{d}\pm1.17$	$8.08^{a}\pm0.73$	$5.49^{d}\pm0.57$	$7.45^{dc}\pm0.58$	$6.92^{g}\pm0.71$
$MaC_{14}P$	$1040.27^{f}\pm2.74$	$1.50^{a}\pm0.13$	$0.34^{a}\pm0.04$	$11.97^{c}\pm1.19$	$7.92^{b}\pm0.81$	$5.24^{d}\pm0.58$	$8.60^{a}\pm0.59$	$8.34^{c}\pm0.67$
$GnH_{14}P$+$MaC_{14}P$	$1054.58^{e}\pm4.26$	$1.27^{c}\pm0.12$	$0.34^{a}\pm0.04$	$9.99^{f}\pm1.22$	$6.86^{d}\pm0.75$	$4.80^{e}\pm0.55$	$7.33^{d}\pm0.59$	$8.57^{b}\pm0.68$
$CasP_{14}P$	$1110.36^{c}\pm3.84$	$1.48^{a}\pm0.12$	$0.33^{a}\pm0.03$	$12.20^{b}\pm1.20$	$8.09^{a}\pm0.77$	$5.33^{d}\pm0.57$	$8.73^{a}\pm0.58$	$8.88^{a}\pm0.69$
$EFBOP_{14}P$	$1121.78^{b}\pm4.72$	$1.38^{b}\pm0.12$	$0.32^{a}\pm0.03$	$12.97^{a}\pm1.17$	$7.99^{b}\pm0.71$	$5.37^{d}\pm0.55$	$7.86^{b}\pm0.61$	$8.02^{e}\pm0.69$
$CasP_{14}P$+ $EFBOP_{14}P$	$1107.49^{c}\pm2.93$	$1.30^{c}\pm0.12$	$0.28^{a}\pm0.03$	$11.79^{c}\pm0.02$	$6.80^{d}\pm0.74$	$4.94^{e}\pm0.59$	$7.66^{c}\pm0.58$	$8.38^{c}\pm0.66$
$GnH_{14}P$+ $EFBOP_{14}P$	$1022.29^{g}\pm3.98$	$1.45^{a}\pm0.12$	$0.35^{a}\pm0.03$	$12.23^{b}\pm1.15$	$7.09^{c}\pm0.72$	$5.55^{d}\pm0.61$	$7.63^{c}\pm0.64$	$8.22^{d}\pm0.67$
$CasP_{14}P$+$MaC_{14}P$	$1064.33^{d}\pm3.51$	$1.24^{c}\pm0.12$	$0.28^{a}\pm0.04$	$11.51^{d}\pm1.17$	$6.00^{f}\pm0.76$	$7.29^{a}\pm0.64$	$7.25^{d}\pm0.63$	$8.57^{b}\pm0.66$
$MaC_{14}P$+ $EFBOP_{14}P$	$1039.78^{f}\pm3.38$	$1.34^{bc}\pm0.12$	$0.31^{a}\pm0.03$	$10.89^{e}\pm1.19$	$6.69^{e}\pm0.73$	$5.89^{c}\pm0.57$	$7.92^{b}\pm0.61$	$7.55^{f}\pm0.70$
GnH_{14P}+$CasP_{14}P$	$1064.60^{d}\pm3.44$	$1.39^{b}\pm0.12$	$0.31^{a}\pm0.03$	$10.87^{e}\pm1.19$	$6.94^{d}\pm0.74$	$7.00^{b}\pm0.62$	$7.39^{d}\pm0.61$	$8.81^{a}\pm0.70$
LSD	8.90	0.03	NS	0.20	0.08	0.12	0.16	0.07

Comparison of heavy metal content in soil amended with different agro-wastes

Mean with the same superscript along the vertical arrays indicate no variations

Legend:

$MaC_{14}P$ Maize cob 2014 powder

$EFBOP_{14}P$ Empty fruit bunch of oil palm 2014 powder

$CasP_{14}P$ Cassava peels 2014 powder

High significant reduction in Zn was obtained from soils amended with $GnH_{14}P$+ $MaC_{14}P$ at 90 days of treatment duration.These were followed by soils amended with $GnH_{14}P$ at 90 days, $MaC_{14}P$ at 90 days, $GnH_{14}P$+ $MaC_{14}P$ at 60 days, $CasP_{14}P$ at 90 days, $EFBOP_{14}P$ at 90 days, $GnH_{14}P$+ $EFBOP_{14}P$ at 90 days, $CasP_{14}P$+ $MaC_{14}P$ at 90 days, $MaC_{14}P$+ $EFBOP_{14}P$ at 90 days and $GnH_{14}P$+ $CasP_{14}P$ at 90 days, with no variation in the mean values of the Zn present in the soils. These results showed that the soil treated with $MaC_{14}P$ reduced the Zn content of the soils, followed by soil treated with $MaC_{14}P$+ $EFBOP_{14}P$ and $GnH_{14}P$+ $CasP_{14}P$. These results also revealed that the different treatment levels had no variation in the level of Zn present in the soils and the pristine control had significantly reduced ($P<0.05$) Zn content than the treated soils, while the crude oil-polluted control had significantly high Zn content.

Copper content in polluted soil amended with agro-wastes

The results of the copper content in the soil amended with 10% $CasP_{14}P$+ $MaC_{14}P$ significantly reduced the Cu content of the soil than other amendments, while the Cu content in the crude oil-polluted soil was observed to be more than the mean values obtained in the pristine soils. It was also observed that there were significant reductions ($P<0.05$) in the Cu contents of soils amended with 6% $CasP_{14}P$+ $MaC_{14}P$, these were followed by soils amended with 6% and 10% $GnH_{14}P$+ $MaC_{14}P$, 3% $CasP_{14}P$+ $MaC_{14}P$, 6% and 10% $MaC_{14}P$+ $EFBOP_{14}P$ and 10% $GnH_{14}P$+ $CasP_{14}P$ with no variation in the mean values of Cu obtained. This reduction in Cu content was also observed in soils amended with 6%, 10% $GnH_{14}P$ and $MaC_{14}P$, 3% $GnH_{14}P$+ $MaC_{14}P$, 3% $MaC_{14}P$+ $EFBOP_{14}P$ and 3%, 6% $GnH_{14}P$+ $CasP_{14}P$, which had no variation in the mean values obtained. However, the soils treated with 3% $GnH_{14}P$ and 3% $MaC_{14}P$ had more Cu content than other amended soils. The Cu contents of the soils at different durations of study also showed variation in the mean values obtained. It was observed that the soil treated with $MaC_{14}P$ at 30 days had more Cu content compared to other amended soils.

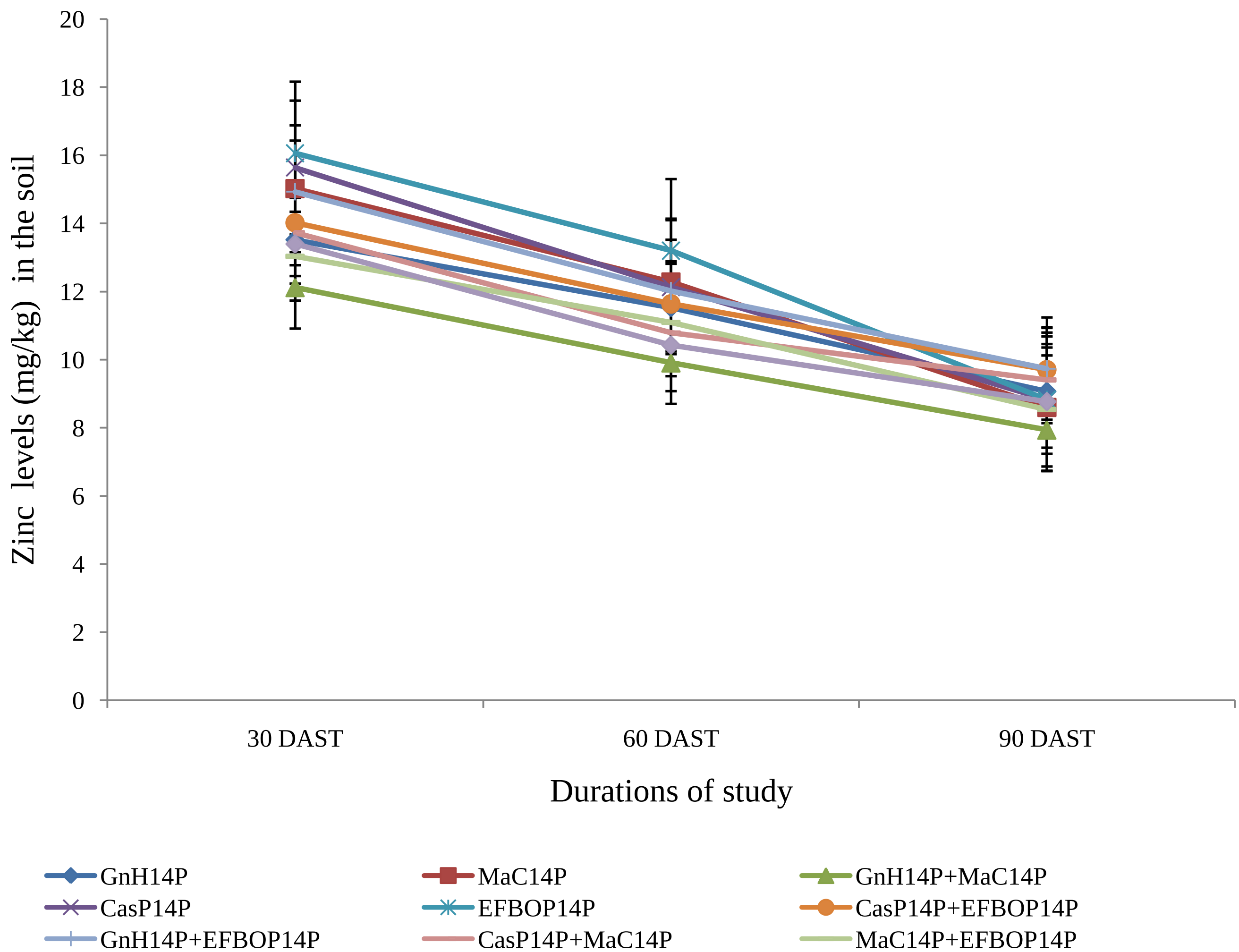

FIG. 3: Zinc content in soils amended with different agro-wastes

Legend:

$MaC_{14}P$ Maize cob 2014 powder

$EFBOP_{14}P$ Empty fruit bunch of oil palm 2014 powder

$CasP_{14}P$ Cassava peels 2014 powder

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These were followed by the soils amended with GnH14P+ $MaC_{14}P$ at 90 days, also followed by soils amended with $GnH_{14}P$ at 30 days of soil treatment. These were also followed by soil treated with $EFBOP_{14}P$ at 30 days, high significant reduction in the Cu content of the soil was obtained in soil amended with $GnH_{14}P$, $MaC_{14}P$, GnH14P+ $MaC_{14}P$, $CasP_{14}P$, $EFBOP_{14}P$, $CasP_{14}P$ + $EFBOP_{14}P$, $GnH_{14}P$+ $EFBOP_{14}P$, $MaC_{14}P$+ $EFBOP_{14}P$, $GnH_{14}P$+ $CasP_{14}P$ at 90 days and

$CasP_{14}P$+ $MaC_{14}P$ at 60 days and 90 days with no variation in the mean values obtained (Figure 4).

The results as presented on Table 2 shows that the soil treated with $CasP_{14}P$+ $MaC_{14}P$ had significantly reduced ($P<0.05$) Cu in the soils than other amended soils. The results obtained indicated that the reduction in the Cu content in the soil was treatment dependent, the higher the treatment levels the greater the reduction in the Cu content of the soils.

Chromium content in polluted soil amended with agro-wastes

The chromium (Cr) content in the soils treated with 10% $GnH_{14}P$+ $MaC_{14}P$ had significantly reduced ($P<0.05$) mean values, followed by the soil treated with 10% $MaC_{14}P$,6% $GnH_{14}P$+ $MaC_{14}P$, 10% $CasP_{14}P$, 10% $CasP_{14}P$+ $EFBOP_{14}P$, 10% $GnH_{14}P$+ $EFBOP_{14}P$ and 10% $MaC_{14}P$ + $EFBOP_{14}P$ which had no variation in the mean values of Cr level in the soils (Table 15). The reduction in Cr level in soil was also observed in soils amended with 6%, 10% $GnH_{14}P$, 6% $MaC_{14}P$, 3% $GnH_{14}P$+ $MaC_{14}P$, 6% $CasP_{14}P$, 3%, 6% and 10% $EFBOP_{14}P$, 3%, 6% $CasP_{14}P$+ $EFBOP_{14}P$ and 6% $GnH_{14}P$+ $EFBOP_{14}P$ which had no variation in the mean values of Cr level in the soils. The reduction in Cr level was also observed in soil amended with 3% $GnH_{14}P$, 3% $MaC_{14}P$, 10% $CasP_{14}P$ + $MaC_{14}P$, 6% $MaC_{14}P$ + $EFBOP_{14}P$ and 10% $GnH_{14}P$ + $CasP_{14}P$ with no variation in the mean values of the Cr content in the soils.The soils amended with 6% $CasP_{14}P$ + $MaC_{14}P$, 3% $MaC_{14}P$ + $EFBOP_{14}P$ and 3%, 6% $GnH_{14}P$ + $CasP_{14}P$ were observed to produce more Cr in the soils, but no variation in the mean values obtained in crude oil-polluted soils.

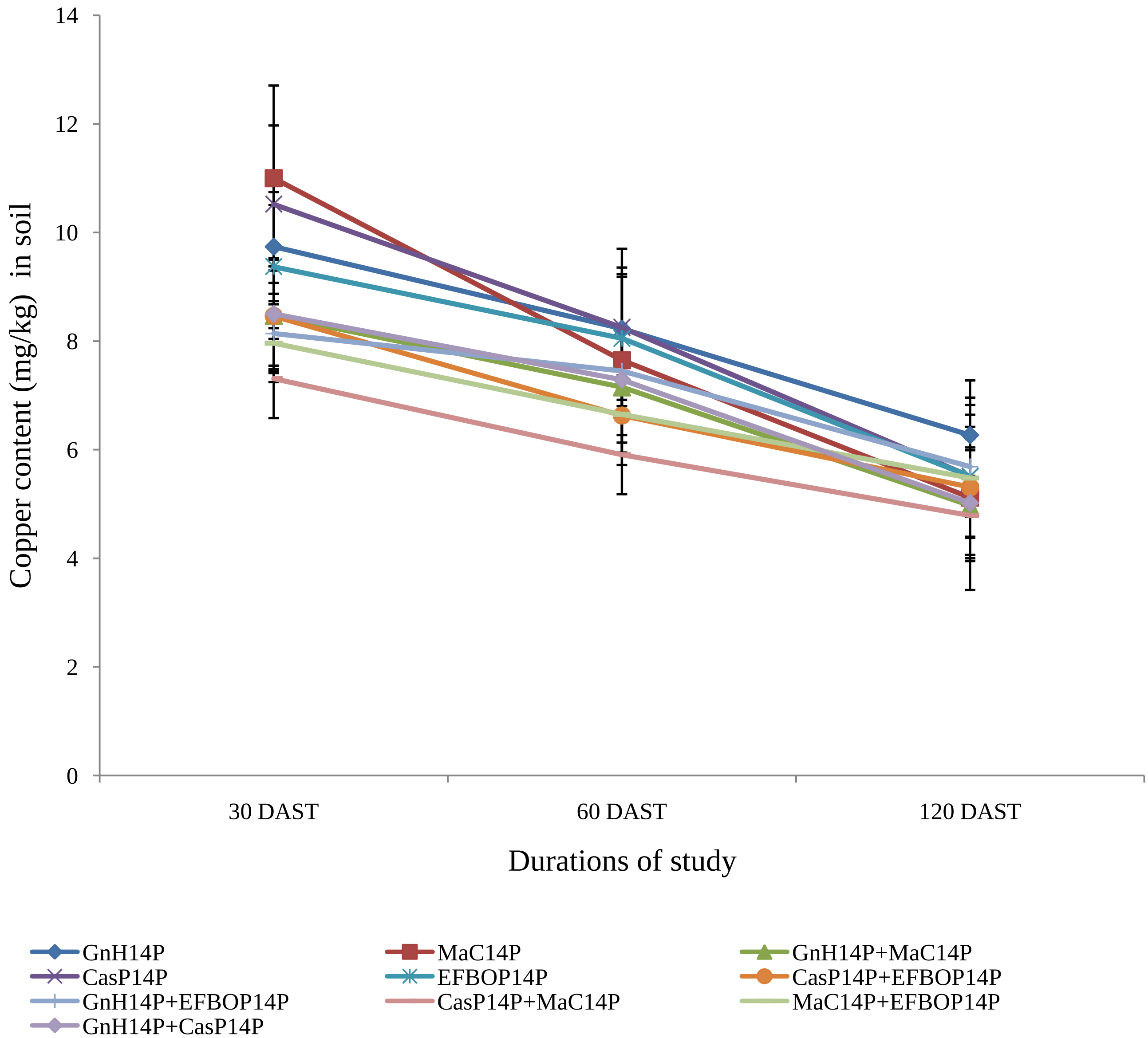

FIG. 4: Copper content of crude oil-polluted soils amended with different agro-wastes

Legend:

$MaC_{14}P$ Maize cob 2014 powder

$EFBOP_{14}P$ Empty fruit bunch of oil palm 2014 powder

$CasP_{14}P$ Cassava peels 2014 powder

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The mean values obtained in pristine soil were observed to be significantly lower than the amended soils (Table 2).

The results obtained as presented on Figure 3 showed that the soils amended with $GnH_{14}P$+ $EFBOP_{14}P$ at 30 days, $CasP_{14}P$ + $MaC_{14}P$ at 30 days and 60 days, $GnH_{14}P$ + $CasP_{14}P$ had higher Cr level in the soils, higher than the mean values obtained in soils amended with $GnH_{14}P$, $MaC_{14}P$, $CasP_{14}P$, $EFBOP_{14}P$, $CasP_{14}P$+ $EFBOP_{14}P$ and MaC14P + $EFBOP_{14}P$ at 30 days of treatment duration. The soils amended with the different agro-wastes at 90 days were observed to produce significantly reduced (P<0.05) mean values, followed by soils amended with the different agro-wastes at 60 days of study. The results as presented on Table 2 showed that the Cr level in soil amended with $GnH_{14}P$ + $MaC_{14}P$ and $CasP_{14}P$+ $EFBOP_{14}P$ had significantly reduced (P<0.05) mean Cr level in the soils. It was also observed that the reduction of Cr level in polluted soils treated with the different agro-wastes was treatment dependent.

Availability of cobalt in the soil enhanced with agro-wastes

The results obtained for cobalt (Co) level, showed that the soil amended with 10% $CasP_{14}P$+$MaC_{14}P$ significantly reduced (P>0.05) the Co level in the soils, followed by soils amended with other agro-wastes at 3%, 6% and 10% with no variation in the mean Co level in the soils. The crude oil-polluted soilhad more the Co level in the soil compared to the mean values obtained in the pristine soil and the agro-wastes amended soils (Table 1).

The results obtained for the cobalt content in the soils due to the different durations adopted showed that the soils amended with $GnH_{14}P$, $GnH_{14}P$+ $MaC_{14}P$, and $CasP_{14}P$+$MaC_{14}P$ at 90 days significantly reduced (P<0.05) the Co level in the soils than other amended soils. These were also followed by soils amended with $MaC_{14}P$, $CasP_{14}P$, $EFBOP_{14}P$, $CasP_{14}P$ +$EFBOP_{14}P$ and $MaC_{14}P$+ $EFBOP_{14}P$ at 90 days which also had significantly reduced (P<0.05) Co level in soils, with no variation in mean values obtained. The results further indicated that the soil amended with the different agro-wastes at 30 days of soil treatment had significantly higher (P<0.05) Co Level than the 60 days and 90 days.The results as presented in Table 2 indicated that the following agro-wastes, $GnH_{14}P$, $GnH_{14}P$+ $MaC_{14}P$, $CasP_{14}P$ +$EFBOP_{14}P$, $CasP_{14}P$+$MaC_{14}P$ used in amending the soils Co level in the soils compared to the soils amended with the different agro-wastes at 60 days of soil treatment, with significantly reduced (P<0.05) Co level in soils. Significantly reduced the Co content of the soils than other soil amendments. The results of the different treatment levels used for the study indicated that 6% and 10% of the agro-wastes amended soils significantly reduces the Co content, followed by soil amended with 3% of the wastes.

Lead content in soil amended with agro-wastes

The results obtained showed that the Pb level in the soil amended with 3%, 6% and 10% of the different agro-wastes significantly reduced (P<0.05) the Pb content in theamended soils, except 3% $MaC_{14}P$, $GnH_{14}P$+ $MaC_{14}P$ and $GnH_{14}P$+$EFBOP_{14}P$ that had more Pb content with no variation in the mean values obtained. It was also observed that the pristine control had reduced Pb content in soils than the crude oil-polluted soils (Table 1).

The results of the study based on the duration showed that soil amended with $MaC_{14}P$, $GnH_{14}P$+ $MaC_{14}P$ and $GnH_{14}P$+$EFBOP_{14}P$ at 30 days had significantly higher (P<0.05) Pb content in the soils than other amended agro-wastes that had reduced Pb content in the soils. Table 2 showed that no variation existed between the Pb content obtained from the different agro-wastes amended soils.

Iron content in soil amended with agro-wastes

The results for the iron (Fe) content in the soil amended with the agro-wastes were significantly reduced at 3%, 6% and 10% treatment levels as compared to the Fe level in the

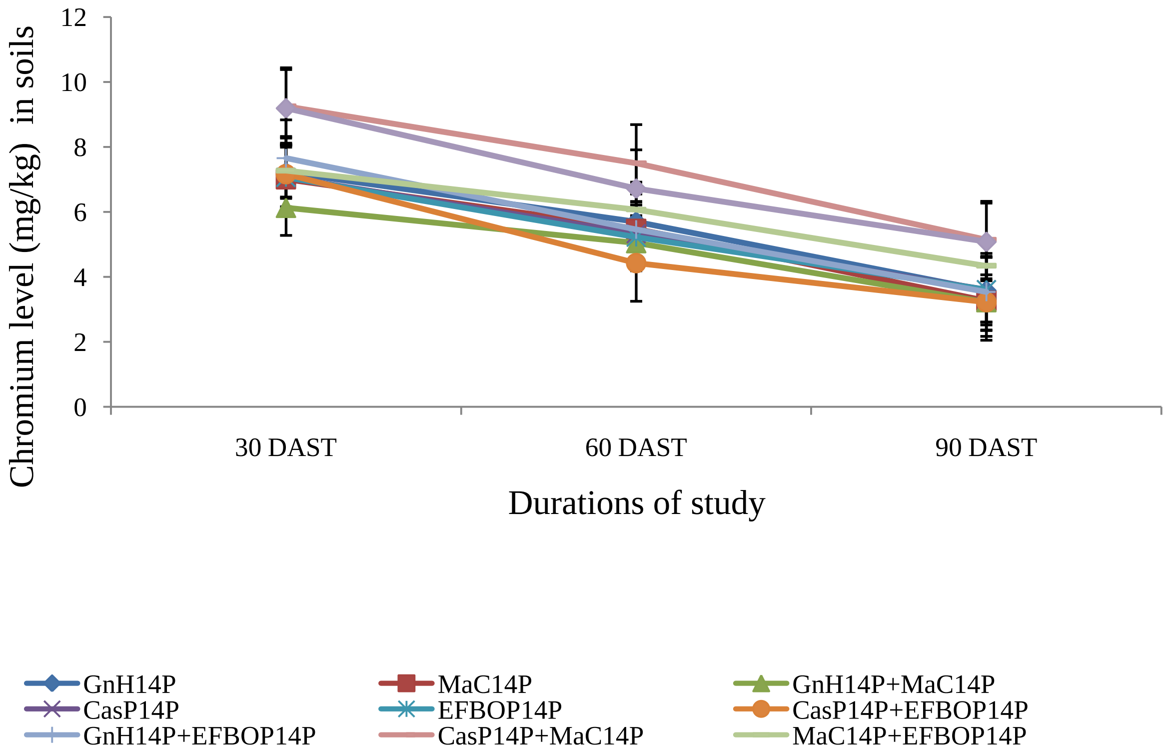

FIG. 5: Chromium content of soils amended with different agro-wastes

Legend:

$MaC_{14}P$ Maize cob 2014 powder

$EFBOP_{14}P$ Empty fruit bunch of oil palm 2014 powder

$CasP_{14}P$ Cassava peels 2014 powder

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pristine control soils, with no significant difference (P>0.05) in the mean values obtained. The crude oil polluted control soil had more Fe contents in the soils. The reduction in the Fe content in the soils enhanced with the agro-wastes could be as a result of the effectiveness of the wastes to increase the proliferation of microbial population in the soils (Table 2). The result also showed that the soil amended with $GnH_{14}P$ had significantly higher (P<0.05) Fe content, followed by soils amended with $EFBOP_{14}P$ with mean value of 1121.78mg/kg, also followed by soils enhanced with $CasP_{14}P$+$EFBOP_{14}P$ and $CasP_{14}P$ with mean values of 1107.49mg/kg and 1110.36mg/kg respectively, with no variation in the Fe content in the soils. The soil amended with $GnH_{14}P$+$EFBOP_{14}P$ had reduced Fe content, followed by soil amended with $MaC_{14}P$ and $MaC_{14}P$+$EFBOP_{14}P$ with no variation in the mean values obtained. The reductions in the Fe content in the soils were treatment dependent, the higher the treatment levels the lower the Fe in the soils.

IV. DISCUSSION

Heavy metals are essential for plant growth and productivity at considerable level but high levels of heavy metal in soil hinder the growth performance of crop planted. The presence of hydrocarbons in the soils increases the heavy metal content of the soils, and thus reduces the microbial population of the soil. The amended of the soil with agro-wastes at different treatment levels significant reduces the heavy metal content of the soil. The reduction of heavy metal content of the soil increases the microbial population of the amended soils.

Reduction of metals can occur through dissimilatory reduction where microorganisms utilize metals as a terminal electron acceptor for anaerobic respiration. For example, oxyanions of chromium (Lovley and Coates 1997,QuiIntana*et al*. 2001) can be used in microbial anaerobic respiration as terminal electron acceptors. In addition, microorganisms may possess reduction mechanisms that are not coupled to respiration, but instead are thought to impart metal resistance. Another mechanism of metal reduction is methylation. Microbial methylation plays an important role in the biogeochemical cycle of metals, because methylated compounds are often volatile. For example, Pb can be biomethylated to dimethyl lead (Pongratz,and Heumann 1999). Microbes may possess reduction mechanisms that are not coupled to respiration, but instead are thought to impart metal resistance. Methylation is another possible mechanism of metal reduction by microbial action. A number of different bacterial species including *Pseudomonas* sp., *Escherichia* sp., *Bacillus* sp., and *Clostridium* sp. have been implicated in the biomethylation of heavy metals (Pongratz,andHeumann 1999). These study isolated and characterized the following microorganism: *Bacillus cereus, Pseudomonas aeruginosa, Proteus mirabilis, Bacillus pumilus*or *Bacillus altitudinis, Proteus penneri, Serratiamarcescens, Providenciarettgeri, Bacillus thuringiensis, Enterobacteriaasburiae*and *Proteus penneri*same as *Proteus vulgaria.* These could be viewed as strong heavy metal removal in soil environment, since similar research reported some of these bacterial species possess strong affinity to degrade heavy metals in the soils. Although many soil microbes carry out a number of transformations of metals, soil microbial activity and functioning can be affected by high concentrations of metals (QuiIntana*et al*., 2001).

The amenability of the soil with agro-wastes at different durations tended to reduces the heavy metal content of the soils. Ikhajiagbe*et al*. (2013) noted that the Heavy metal content of the adjected pH soil was reduce, likewise the THC of the soils. Dike *et al*. (2013) reported that the treatment of the soil with detergent solution reduces the Zn, Ar, Cd, Cr, Pb and Cu content of the soil and recommended that soil washing should be used as an effective mechanism in remediation. The high uptake and sequestration of heavy metals was higher in soils amended with the combined form of the agro-wastes, with more sequestration of the heavy metals in soil amended with $CasP_{14}P+MaC_{14}P$.

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