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BIOREMEDIATION: SYNERGISTIC EFFECTS OF AGRO-WASTES ON THE PHYSICOCHEMICAL PROPERTIES OF CRUDE-OIL POLLUTED SOILS

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ABSTRACT:

This present study examined the physicochemical properties of crude-oil polluted soils remediated with agricultural wastes. Seven kilograms each of composite soil samples contained in 108 plastic buckets were spiked artificially with 300mls of crude-oil. The polluted soils were treated with the dispersants (Agro-wastes) in singled and combined forms, after 14 days soil pollution. Soil samples were collected for soil physicochemical test at 30 days, 60days and 90days soil amelioration using standard laboratory procedures. The results show that the soil amended with the agro-wastes increases the soil pH from acidic to alkaline with a range (7.0-8.6) compared to the low pH (5.3-5.6) obtained in the controls. Significant reduction in the organic carbon content in amended soils was observed, with a high significant reduction in soil treated with 10% GnH14P + MaC14P compared to the high value obtained in the crude-oil control soil. The level of soil nitrogen was significantly increased in amended soils while; the controls had the lowest nitrogen level. The phosphorus level in the amended soils was significantly high while, the highest phosphorus value was obtained in soil amended with 10% CasP14P + EFBOP14P and MaC14P + EFBOP14P compared to the low values in the controls. However, the potassium, calcium, magnesium, hydrocarbon ions, and sodium of the soils were significantly affected by the application of the agro-wastes. It was concluded that the application of these agro-wastes at high concentrations, especially the combined agro-wastes influences the improvement of the soil physicochemical properties for optimum growth and plants productivity.

Keywords: Amendment, Crude-oil, Polluted, Agro-wastes, Soils

1. INTRODUCTION

Soil is a complex matter made up of mineral elements, organic matter, water and air. This component determines to a large extent the soil structure, porosity and texture. Soil physicochemical properties have great priority over the soil quality (Agbor *et al*., 2023). The degradation of the soil quality by pollutants/ contaminants affects the soil texture adversely and could render the soil unproductive depending on the nature of the pollutants. However,

most pollutants like crude oil spills reduces the soil water retention capacity, thereby blocking the soil air-pores, which coherently lowers soil aeration with increased bulk density of the soil which could affect plant growth and productivity. Crude oil pollution has been reported over the years to affect soil health Agbor *et al*., (2023) and Hunt, (1997). The abundance and activities of soil microorganisms is highly affected especially the non-hydrocarbon degraders. Soil microorganisms help in the bioavailability of the essential nutrients to plants. The optimal growth rate of microorganisms and hydrocarbon biodegradation can be sustained by ensuring that adequate concentrations of nutrients and oxygen are present and that the pH is between 6 and 9. Most bacteria have a limited tolerance for acidic conditions while fungi are more resistant to acidic conditions. Soil type can also determine the bacteria or fungi that can enhanced the degradation of petroleum hydrocarbons in an alkaline or acidic conditions (Vanloocke *et al*. 1975). An increase in soil pH tends to decrease the availability of calcium, magnesium, sodium, potassium, ammonia, nitrogen and phosphorus, while a decrease in soil pH results in decreasing availability of nitrate and chloride (Sharpeley, 1991., Agbor et al., 2020). Adjustment of soil pH by neutralizing soil acidity to increase the pH involves a technique known as liming (Baker, 1994), while the pH of marine environment is uniform, steady, and slightly alkaline. Dibble and Bartha (1979) found that, bacterial degradation of hydrocarbons was minimal in a naturally acidic soil (pH 3.7). Stimulation of hydrocarbon biodegradation increased with rising soil pH in response to liming up to the highest value (pH 7.8) tested.
Nutrient supplementation has been successful in hydrocarbon degradation in hydrocarbon-contaminated soil and groundwater where nitrogen and phosphorus levels have been shown to be limiting (Compeau *et al*. 1991). Atlas (1981) reported that when a major oil spill occurred in marine and freshwater environments, the supply of carbon was significantly increased and availability of nitrogen and phosphorus generally become the limiting factor for oil degradation. In marine environments, it was found to be more pronounced due to low levels of nitrogen and phosphorus in sea water (Floodgate, 1994). Freshwater wetlands are typically considered to be nutrient-deficient due to heavy demands of nutrients by the plants (Mitsch *et al.* 1993., Morgan and Atlas, 1989), therefore, additions of nutrients were necessary to enhance the biodegradation oil pollutants (Choi *et al*., 2002; and Kim *et al.* 2005). Several authors have reported that addition of nutrients can strongly stimulate oil biodegradation in contaminated soils (Verstracete *et al*. 1976; Dibble and Bartha, 1979). They also reported the negative effects of high NPK levels on the biodegradation of hydrocarbons (Ondot *et al*. 1998) especially on aromatics (Carmicheal *et al*. 1997). Okolo *et al*. (2005) reported that biodegradation can be enhanced in the presence of poultry manure alone. Hunt (1976) also found that fertilizer application to sub-arctic soil enhanced microbial hydrocarbon degradation. This present study examined the physicochemical properties of crude oil polluted soils amended with some agro-wastes.

2. MATERIAL AND METHODS

Study location
The research was carried out in the Environmental Biotechnology unit in the Department of Genetics & Biotechnology, University of Calabar.
Experimental laboratory
Physicochemical analysis of the soil was carried out at Soil Science Laboratory, Faculty of Agriculture, University of Calabar, Calabar.
Source of agro-wastes and production of the dispersants
The crude oil (Bonny light) was obtained from the Nigerian Agip Oil Company (NAOC), Port Harcourt, Rivers State, Nigeria, while the 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. The collected agro-wastes (GH, MC, EFBOP, CP) were sun-dried for 10 days, then pulverized into powder using electric blender (Model 4250, Braun, Germany). The powdered substances were sieved to pass through 2 mm sieve. They were labeled and stored in containers.

Site of soil collection

Soil samples for this study were obtained from the Biological Science Experimental Farm, 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.

Soil sample collection

Top soils (0-25cm depth) were randomly collected from four points, using a Dutch auger, then bulked to form a composite soil sample and six kilograms (6kg) each of the composite soil samples were weighed and transferred into hundred and fifty (150) labeled plastic buckets (PB) with drainage holes at the base. The plastic buckets were arranged in triplicate in a completely randomized design (CRD).

Artificial pollution and soil treatment

The soil contained in each PB, except the pristine control groups were polluted with 0.3 liters of crude oil. The PB containing the polluted soils were mixed thoroughly and allowed to stand for 14 days (these were allowed indigenous microorganisms to become acclimatized with the new soil condition). After the 14 days the amendments were applied in combined and single forms using the following concentrations pristine soil (+ve control, 0% amendment), crude oil soil (-ve control, 0% amendment), 3% amendments, 7% amendment and 10% amendments (As previously adopted by procedures of Agbor et al., 2023). Soil samples were collected for physicochemical analysis at 30, 60 and 90 days

Physicochemical analysis of the soil

Soil samples were taken to Soil Science Laboratory for physicochemical analysis of the soil. The soil samples were air-dried for three days, powdered, and then sieved through a 2 mm mesh sieve. The following parameters were analyzed: moisture content, particle size, pH, organic carbon, nitrogen, phosphorus, potassium, calcium, magnesium, hydrogen, aluminum, effective cation exchange capacity (ECEC) and base saturation (BS) (As previously adopted by procedures of Agbor et al., 2013). The different physicochemical parameters were determined, prior to zero day and at the end of bioremediation studies, to determine what changes, had taken place during the period of biodegradation.

Statistical Analysis

Data collected were subjected to three-way ANOVA using SPSS software. Significant means were separated using LSD at 5% probability level.

3. RESULTS AND DISCUSSION

Chemical composition of the agro-wastes

The result obtained for the chemical composition of the different agro-wastes shows that $GnH_{14}P+MaC_{14}P$ had significant increase ($P<0.05$) in nitrogen content than other agro-wastes followed by $GnH_{14}P+EFBOP_{14}P$ with mean of 42.07%. This was followed by $MaC_{14}P+ EFBOP_{14}P$, $CasP_{14}P$ and $GnH_{14}P$. The phosphorus and potassium contents in the agro-wastes showed insignificant difference (P>0.05) in the average values obtained. The calcium content in $GnH_{14}P+EFBOP_{14}P$ was higher (P<0.05) than the calcium content in other agro-wastes with no variation in the mean values. It was observed that the magnesium content in $GnH_{14}P$, $MaC_{14}P$, $CasP_{14}P$ and $EFBOP_{14}P$ was higher in mean values, followed by the magnesium content in $GnH_{14}P+EFBOP_{14}P$. This was also followed by the magnesium content in $GnH_{14}P+$ $CasP_{14}P$ (6.94%). The pH value obtained from $CasP_{14}P+MaC_{14}P$ was higher than other agro-wastes. These were followed by the pH value obtained from $GnH_{14}P+$ $CasP_{14}P$, also followed by the pH value of $MaC_{14}P+$ $EFBOP_{14}P$ (Table 1).

Table 1: Chemical composition of agro-wastes

Parameters	**Nitrogen (%)**	**Phosphorus (%)**	**Potassium (%)**	**Calcium (%)**	**Magnesium (%)**	**pH**
$GnH_{14}P$	$40.91^{c}\pm4.18$	$1.28^{a}\pm0.13$	$0.30^{a}\pm0.04$	$0.20^{b}\pm0.02$	$8.08^{a}\pm0.73$	$5.49^{d}\pm0.57$
$MaC_{14}P$	$38.65^{e}\pm4.27$	$1.50^{a}\pm0.13$	$0.34^{a}\pm0.04$	$0.22^{b}\pm0.02$	$7.92^{a}\pm0.81$	$5.24^{d}\pm0.58$
$GnH_{14}P+MaC_{14}P$	$44.16^{a}\pm4.19$	$1.27^{a}\pm0.12$	$0.34^{a}\pm0.04$	$0.23^{b}\pm0.02$	$6.86^{c}\pm0.75$	$4.80^{e}\pm0.55$
$CasP_{14}P$	$40.91^{c}\pm4.18$	$1.48^{a}\pm0.12$	$0.33^{a}\pm0.03$	$0.24^{b}\pm0.02$	$8.09^{a}\pm0.77$	$5.33^{d}\pm0.57$
$EFBOP_{14}P$	$38.62^{e}\pm4.01$	$1.38^{a}\pm0.12$	$0.32^{a}\pm0.03$	$0.25^{b}\pm0.02$	$7.99^{a}\pm0.71$	$5.37^{d}\pm0.55$
$CasP_{14}P+EFBOP_{14}P$	$39.60^{d}\pm4.25$	$1.30^{a}\pm0.12$	$0.28^{a}\pm0.03$	$0.22^{b}\pm0.02$	$6.80^{c}\pm0.74$	$4.94^{e}\pm0.59$
$GnH_{14}P+EFBOP_{14}P$	$42.07^{b}\pm4.21$	$1.45^{a}\pm0.12$	$0.35^{a}\pm0.03$	$0.24^{b}\pm0.02$	$7.09^{b}\pm0.72$	$5.55^{d}\pm0.61$
$CasP_{14}P+MaC_{14}P$	$39.29^{d}\pm4.25$	$1.24^{a}\pm0.12$	$0.28^{a}\pm0.04$	$0.39^{a}\pm0.17$	$6.00^{e}\pm0.76$	$7.29^{a}\pm0.64$
$MaC_{14}P+EFBOP_{14}P$	$40.81^{c}\pm4.14$	$1.34^{a}\pm0.12$	$0.31^{a}\pm0.03$	$0.21^{b}\pm0.02$	$6.69^{d}\pm0.73$	$5.89^{c}\pm0.57$
$GnH_{14P}+CasP_{14}P$	$39.33^{d}\pm4.23$	$1.39^{a}\pm0.12$	$0.31^{a}\pm0.03$	$0.22^{b}\pm0.02$	$6.94^{c}\pm0.74$	$7.00^{b}\pm0.62$
LSD	0.48	NS	NS	0.02	0.12	0.22

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

Soil physicochemical properties remediated with Agro-wastes

The pH of the soil amended with 10% $MaC_{14}P+EFBOP_{14}$ had the highest pH value, followed by soils amended with varying agro-wastes amendment levels (3%, 6% and 10%) with no variation in the mean values obtained. The soil amended with the agro-wastes had higher pH values than the pristine soils (PS). The values obtained for the PS of the soil were more than the mean values obtained for the crude-oil polluted control soils. These results imply that pollution of soil with reduces the pH values in the soil samples and the addition of amendments in polluted soil increases the pH values of the soils from acidic to alkaline (Table 2). The results for the pH at different duration of soil examination showed that soil amended with $CasP_{14}P+$ $MaC_{14}P$ at 90 days, soil amended with $MaC_{14}P+EFBOP_{14}P$ at 60 days and 90 days and soil amended with $EFBOP_{14}P$ had significantly high pH values of 7.06±0.36, 7.08±0.35 7.12±0.37 and 7.13±0.38 respectively, with no variation in mean values obtained (Figure 1). These were followed by soils amended with $MaC_{14}P$, $EFBOP_{14}P$, $GnH_{14}P$+ $CasP_{14}P$ at 60 days and 90 days, $GnH_{14}P$+ $MaC_{14}P$, $CasP_{14}P$+ $EFBOP_{14}P$, $GnH_{14}P$+ $EFBOP_{14}P$ at 90 days, $CasP_{14}P$+ $MaC_{14}P$ at 60 days and $MaC_{14}P$ + $EFBOP_{14}P$ at 30 days with no variation in mean values obtained

Polluted soil amended with 10% of $GnH_{14}P$+$MaC_{14}P$ had significantly reduced ($P<0.05$) OC content, followed by other amended soils at 3%, 6% and 10% pollution levels, with no variation in mean values (Table 2). The statistics also revealed that the OC contents in the amended soil were reduced compared to the crude oil-polluted soil (without amendments) which had high OC content. The results obtained for the effect of the duration on the reduction of the OC content of the soils showed that all the amended soils except the $CasP_{14}P$ at 30 days had the highest OC content (Figure 2). Table 2 showed that the soil amended with $MaC_{14}P$, $GnH_{14}P$, $GnH_{14}P$+ $CasP_{14}P$ and $EFBOP_{14}P$+ $MaC_{14}P$ had significantly reduced ($P<0.05$) OC content

The total nitrogen content in soils amended with 6%, 10% of $MaC_{14}P$ and $GnH_{14}P$+$MaC_{14}P$, 3%, 6% and 10% of $CasP_{14}P$, $EFBOP_{14}P$, $CasP_{14}P$+$EFBOP_{14}P$, $GnH_{14}P$+ $EFBOP_{14}P$, $CasP_{14}P$+ $MaC_{14}P$, $MaC_{14}P$+ $EFBOP_{14}P$ and $GnH_{14}P$+ $CasP_{14}P$ was the highest with no variation in the mean values, as compared with the low value recorded in the pristine soil (PS) (Table 2). The PS and soils amended with 10% of $GnH_{14}P$ and soil amended with 3% of $GnH_{14}P$+$MaC_{14}P$ had no variation in the mean values. Figure 3 shows that soil amended with $GnH_{14}P$, $MaC_{14}P$ and $GnH_{14}P$+$MaC_{14}P$ at 30 days had reduced nitrogen content compared to other amended soils at 30, 60 and 90 days, with no variation in the mean values.

Phosphorus is an important compound in the soil, it non- availability could affect the normal growth of plants. The soils amended with 10% of $GnH_{14}P$+$MaC_{14}P$, $EFBOP_{14}P$, $CasP_{14}P$+ $EFBOP_{14}P$, $CasP_{14}P$+ $MaC_{14}P$, $MaC_{14}P$+ $EFBOP_{14}P$ had the highest phosphorus content, with no variation in the mean values. These were followed by soils amended with 3%, 6% and 10% of $GnH_{14}P$, $MaC_{14}P$ and $GnH_{14}P$+ $CasP_{14}P$, 3%, 6% of $GnH_{14}P$+$MaC_{14}P$, $CasP_{14}P$+ $EFBOP_{14}P$, $CasP_{14}P$+ $MaC_{14}P$ and $MaC_{14}P$+ $EFBOP_{14}P$ and 6% 10% of $GnH_{14}P$+ $EFBOP_{14}P$ with no variation in the mean values (Table 2). The results obtained showed that the amended soil had high available phosphorus than the pristine and crude oil control soils.

The results for phosphorus content at different duration showed that the available phosphorus in the amended soils with $MaC_{14}P$, $EFBOP_{14}P$ and $MaC_{14}P$+ $EFBOP_{14}P$ at 90 days, $GnH_{14}P$+$MaC_{14}P$, $CasP_{14}P$+ $EFBOP_{14}P$, $CasP_{14}P$+ $MaC_{14}P$ at 60 days and 90 days had significantly higher ($P<0.05$) than other amended soils and durations (Figure 4). These results imply that the combined agro-wastes were effective in increasing the phosphorus content of the soils.

The results for the potassium and sodium levels in the amended, polluted and pristine control soils had no variation in the mean values obtained. The soils amended with 6% and 10% of $GnH_{14}P$+ $EFBOP_{14}P$, $MaC_{14}P$+ $EFBOP_{14}P$ and $GnH_{14}P$+ $CasP_{14}P$ and 10% of $CasP_{14}P$+ $MaC_{14}P$ had more Ca and Mg than other amended soils (Table 2). The soils amended with the agro-wastes significantly increased ($P<0.05$) in Ca content, compared to the values obtained for the pristine crude-oil control soils. These results imply that the pollution of soils with crude oil could reduce the Ca content of the soils.

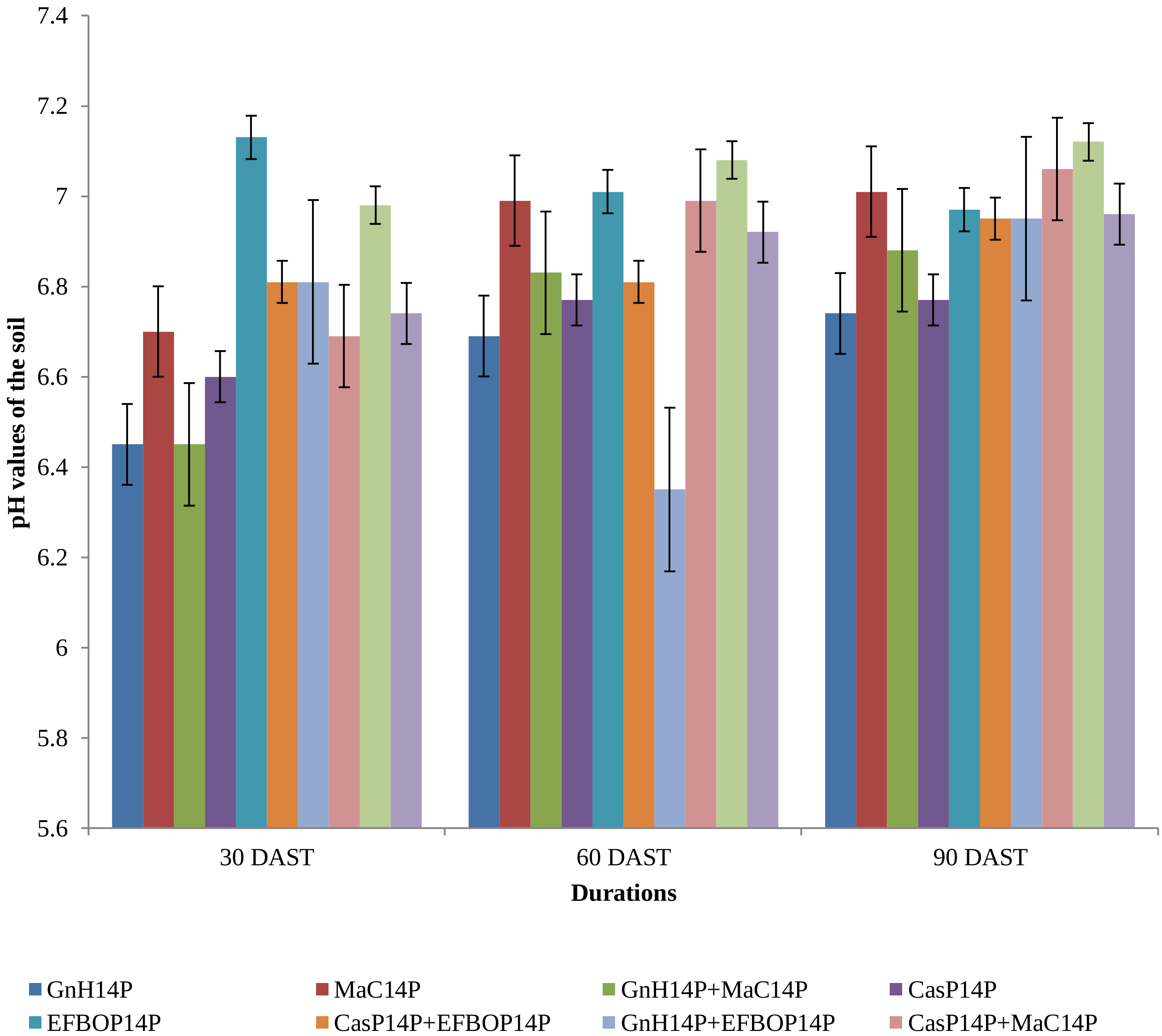

FIG. 1: pH value of polluted soils amended with agro-wastes

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

Table 2: Effect of amendment levels on the physicochemical profile of crude oil polluted soils

Parameters	Trt. levels	pH	Org. C (%)	Total Nitrogen (Cmolkg-1)	Avail. P(Cmolkg-1)	Ca (Cmolkg-1)	Mg (Cmolkg-1)	K (Cmolkg-1)	Na (Cmolkg-1)	H^+ (Cmolkg-1)
$GnH_{14}P$	PC	5.63^c ±0.04	1.13^e ±0.03	0.29^b ±0.01	30.34^d ±0.33	4.11^g ±0.07	1.52^f ±0.06	0.15^a ±0.01	0.08^a ±0.10	1.28^a ±0.03
	CO	5.32^d ±0.04	4.17^a ±0.07	0.16^e ±0.01	21.0^e± 0.54	3.39^h ±0.10	0.94^g ±0.05	0.11^a ±0.00	0.10^a ±0.00	0.86^b ±0.03

	C									
	3 %	7.02^{b} ±0.09	2.49^{c} ±0.13	0.25^{d} ±0.02	40.99^{b} ±1.10	4.77^{f} ±0.04	2.10^{e} ±0.06	0.10^{a} ±0.01	0.08^{a} ±0.01	0.71^{b} ±0.06
	6 %	7.38^{b} ±0.06	2.32^{c} ±0.11	0.27^{c} ±0.02	44.23^{b} ±0.89	5.20^{e} ±0.11	2.22^{e} ±0.06	0.09^{a} ±0.01	0.09^{a} ±0.01	0.66^{b} ±0.05
	10 %	7.77^{b} ±0.11	2.03^{c} ±0.13	0.29^{b} ±0.02	47.60^{b} ±0.92	5.42^{d} ±0.07	2.09^{e} ±0.07	0.07^{a} ±0.00	0.08^{a} ±0.01	0.33^{e} ±0.03
MaC$_{14}$P	3 %	7.24^{b} ±0.09	2.29^{c} ±0.11	0.29^{b} ±0.03	39.23^{b} ±2.02	5.22^{e} ±0.14	2.22^{e} ±0.08	0.11^{a} ±0.00	0.09^{a} ±0.01	0.40^{e} ±0.06
	6 %	8.03^{b} ±0.08	1.99^{c} ±0.14	0.32^{a} ±0.03	44.56^{b} ±2.43	5.84^{c} ±0.06	2.22^{e} ±0.11	0.09^{a} ±0.01	0.09^{a} ±0.01	0.36^{e} ±0.05
	10 %	8.28^{b} ±0.09	1.86^{c} ±0.13	0.35^{a} ±0.02	47.63^{b} ±2.07	5.89^{c} ±0.05	2.48^{d} ±0.15	0.07^{a} ±0.00	0.08^{a} ±0.00	0.30^{e} ±0.04
GnH$_{14}$P+ MaC$_{14}$P	3 %	7.01^{b} ±0.13	2.13^{c} ±0.12	0.29^{b} ±0.03	44.41^{b} ±1.05	5.09^{e} ±0.16	2.21^{e} ±0.08	0.09^{a} ±0.01	0.07^{a} ±0.01	0.58^{c} ±0.08
	6 %	7.52^{b} ±0.17	1.90^{c} ±0.14	0.33^{a} ±0.03	50.81^{b} ±1.06	5.42^{d} ±0.14	2.46^{d} ±0.10	0.07^{a} ±0.01	0.09^{a} ±0.01	0.43^{e} ±0.05
	10 %	8.11^{b} ±0.08	1.74^{d} ±0.11	0.37^{a} ±0.02	55.33^{a} ±1.57	5.77^{c} ±0.10	2.56^{d} ±0.06	0.06^{a} ±0.01	0.09^{a} ±0.01	0.33^{e} ±0.05
CasP$_{14}$P	3 %	7.16^{b} ±0.08	2.89^{c} ±0.17	0.34^{a} ±0.01	34.92^{c} ±1.14	4.76^{f} ±0.06	2.36^{d} ±0.08	0.11^{a} ±0.01	0.09^{a} ±0.00	0.79^{b} ±0.05
	6 %	7.54^{b} ±0.05	2.67^{c} ±0.15	0.37^{a} ±0.01	40.03^{b} ±1.50	5.10^{e} ±0.04	2.61^{d} ±0.09	0.10^{a} ±0.01	0.09^{a} ±0.01	0.63^{b} ±0.05
	10 %	7.94^{b} ±0.06	2.47^{c} ±0.16	0.38^{a} ±0.01	47.86^{b} ±2.10	5.91^{b} ±0.07	2.91^{b} ±0.05	0.08^{a} ±0.01	0.10^{a} ±0.01	0.49^{d} ±0.06

Table 2 continues

Parameters	Trt. levels	pH	Org. C (%)	Total Nitrogen (Cmolkg^{-1})	Avail. P(Cmolkg^{-1})	Ca (Cmolkg^{-1})	Mg (Cmolkg^{-1})	K (Cmolkg^{-1})	Na (Cmolkg^{-1})	H^{+} (Cmolkg^{-1})
EFBOP$_{14}$P	3 %	7.84^{b} ±0.06	2.90^{c} ±0.15	0.36^{a} ±0.01	37.88^{b} ±1.13	5.36^{d} ±0.13	2.47^{d} ±0.17	0.12^{a} ±0.10	0.09^{a} ±0.01	0.38^{e} ±0.03
	6 %	8.02^{b} ±0.76	2.42^{c} ±0.12	0.38^{a} ±0.01	43.57^{b} ±1.62	5.80^{c} ±0.08	2.96^{b} ±0.04	0.10^{a} ±0.01	0.10^{a} ±0.01	0.29^{e} ±0.04
	10 %	8.34^{b} ±0.11	2.27^{c} ±0.13	0.40^{a} ±0.02	52.71^{a} ±2.34	6.12^{a} ±0.05	3.12^{a} ±0.05	0.09^{a} ±0.00	0.10^{a} ±0.01	0.22^{e} ±0.03
CasP$_{14}$P+ EFBOP$_{14}$P	3 %	7.28^{b} ±0.15	2.69^{c} ±0.11	0.38^{a} ±0.01	42.06^{b} ±2.13	5.10^{e} ±0.16	2.11^{e} ±0.08	0.12^{a} ±0.01	0.10^{a} ±0.01	0.63^{b} ±0.04
	6 %	7.87^{b} ±0.06	2.31^{c} ±0.19	0.39^{a} ±0.01	49.13^{b} ±2.16	5.41^{d} ±0.16	2.43^{d} ±0.06	0.10^{a} ±0.00	0.10^{a} ±0.00	0.40^{e} ±0.03
	10 %	8.20^{b} ±0.07	2.10^{c} ±0.16	0.42^{a} ±0.01	54.98^{a} ±2.23	6.09^{a} ±0.07	2.69^{d} ±0.19	0.09^{a} ±0.01	0.20^{a} ±0.02	0.29^{e} ±0.04
GnH$_{14}$P+ EFBOP$_{14}$P	3 %	7.43^{b} ±0.08	2.54^{c} ±0.12	0.31^{a} ±0.01	34.60^{c} ±1.18	5.86^{c} ±01.0	2.13^{e} ±0.08	0.10^{a} ±0.01	0.10^{a} ±0.01	0.58^{c} ±0.04
	6	7.88^{b}	2.28^{c}	0.35^{a}	40.68^{b}	6.06^{a}	2.63^{d}	0.10^{a}	0.10^{a}	0.40^{e}

	%	±0.07	±0.16	±0.01	±0.84	±0.09	±0.10	±0.00	±0.00	±0.06
	10 %	7.24^{b} ±0.48	2.21^{c} ±0.18	0.40^{a} ±0.02	47.47^{b} ±0.76	6.20^{a} ±0.10	2.78^{d} ±0.07	0.08^{a} ±0.00	0.10^{a} ±0.01	0.30^{e} ±0.06
$CasP_{14}P$+ $MaC_{14}P$	3 %	7.41^{b} ±0.12	2.61^{c} ±0.09	0.32^{a} ±0.01	44.26^{b} ±1.51	5.48^{d} ±0.06	2.40^{d} ±0.10	0.15^{a} ±0.01	0.09^{a} ±0.00	0.69^{b} ±0.07
	6 %	7.81^{b} ±0.07	2.24^{c} ±0.09	0.36^{a} ±0.01	49.69^{b} ±1.11	5.64^{c} ±0.02	2.64^{d} ±0.12	0.13^{a} ±0.00	0.09^{a} ±0.01	0.49^{d} ±0.05
	10 %	8.40^{b} ±0.11	2.07^{c} ±0.11	0.39^{a} ±0.01	54.52^{a} ±1.41	6.09^{a} ±0.07	2.98^{b} ±0.04	0.11^{a} ±0.01	0.10^{a} ±0.01	0.34^{e} ±0.03

Table 2: continues

Parameters	Trt. levels	pH	Org. C (%)	Total Nitrogen ($mgkg^{-1}$)	Avail. P ($mgkg^{-1}$)	Ca ($Cmolkg^{-}1$)	Mg ($Cmolkg^{-}1$)	K ($Cmolkg^{-}1$)	Na ($Cmolkg^{-}1$)	H^{+} ($Cmolkg^{-}1$)
$MaC_{14}P$+ $EFBOP_{14}P$	3 %	7.63^{b} ±0.06	2.41^{c} ±0.14	0.35^{a} ±0.01	44.76^{b} ±1.23	5.70^{c} ±0.05	2.42^{d} ±0.05	0.11^{a} ±0.00	0.10^{a} ±0.01	0.81^{b} ±0.06
	6 %	8.13^{b} ±0.08	2.08^{c} ±0.14	0.40^{a} ±0.01	48.97^{b} ±1.67	6.04^{a} ±0.03	2.92^{b} ±0.06	0.10^{a} ±0.00	0.10^{a} ±0.00	0.58^{c} ±0.05
	10 %	8.58^{a} ±0.05	1.89^{c} ±0.14	0.41^{a} ±0.01	52.89^{a} ±1.23	6.11^{a} ±0.13	2.90^{b} ±0.13	0.09^{a} ±0.01	0.10^{a} ±0.01	0.24^{e} ±0.05
GnH_{14P}+ $CasP_{14}P$	3 %	7.50^{b} ±0.07	2.58^{c} ±0.17	0.33^{a} ±0.02	37.34^{b} ±0.95	5.84^{c} ±0.10	2.37^{c} ±0.07	0.12^{a} ±0.01	0.09^{a} ±0.00	0.58^{c} ±0.07
	6 %	7.89^{b} ±0.09	2.41^{c} ±0.12	0.39^{a} ±0.02	42.78^{b} ±1.52	6.07^{a} ±0.13	2.64^{d} ±0.08	0.10^{a} ±0.01	0.11^{a} ±0.00	0.38^{e} ±0.06
	10 %	8.04^{b} ±0.08	2.16^{c} ±0.14	0.40^{a} ±0.02	45.83^{b} ±1.65	6.28^{a} ±0.11	2.90^{a} ±0.05	0.08^{a} ±0.00	0.11^{a} ±0.01	0.27^{e} ±0.03
LSD		0.14	0.09	0.01	1.62	0.08	0.09	NS	NS	0.03

Mean with the same superscript along the vertical arrays showed no significant difference (P>0.05)

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
PC Pristine control
COC Crude oil control

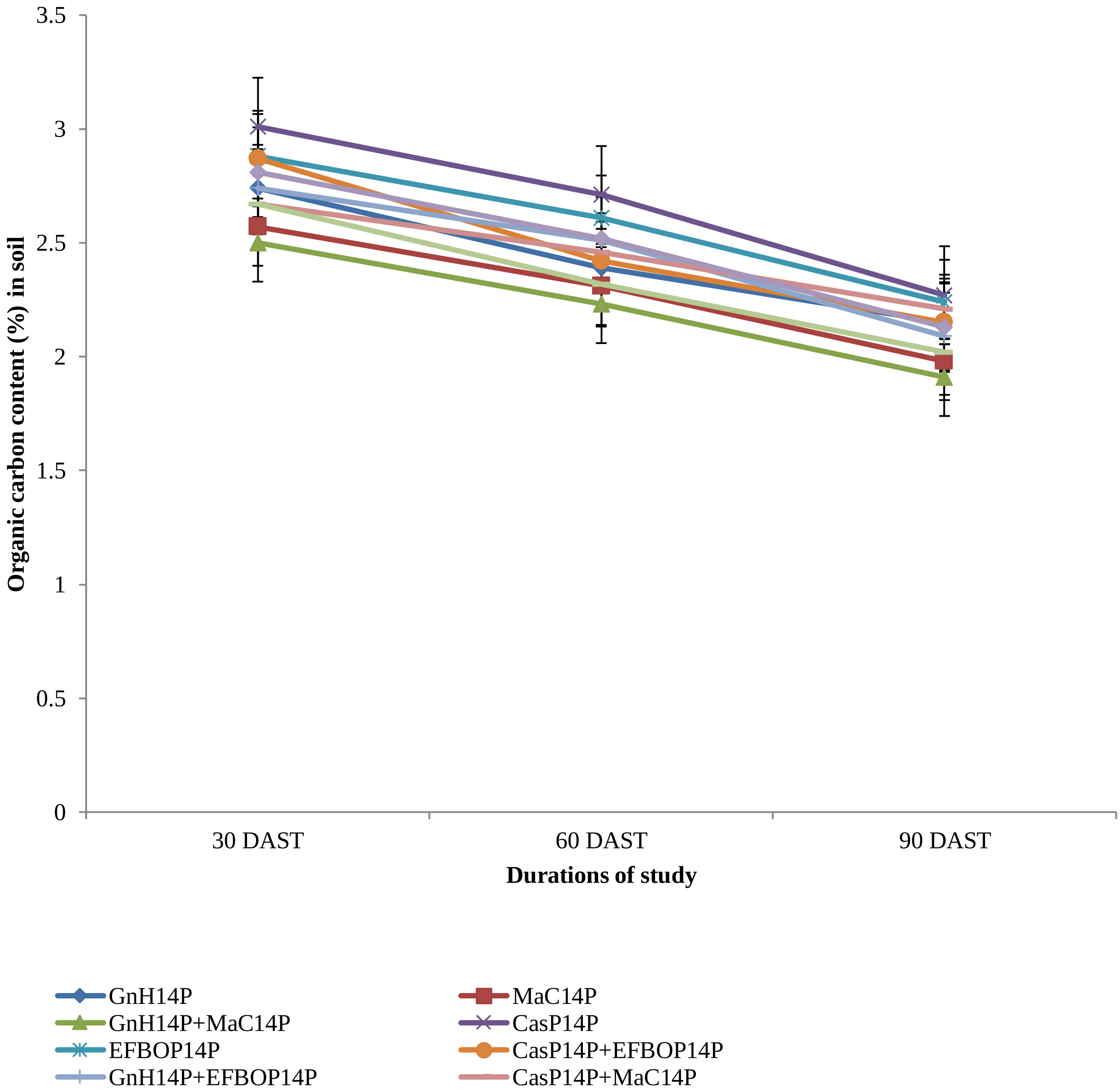

FIG. 2: Organic carbon content of soil amended with agro-wastes

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

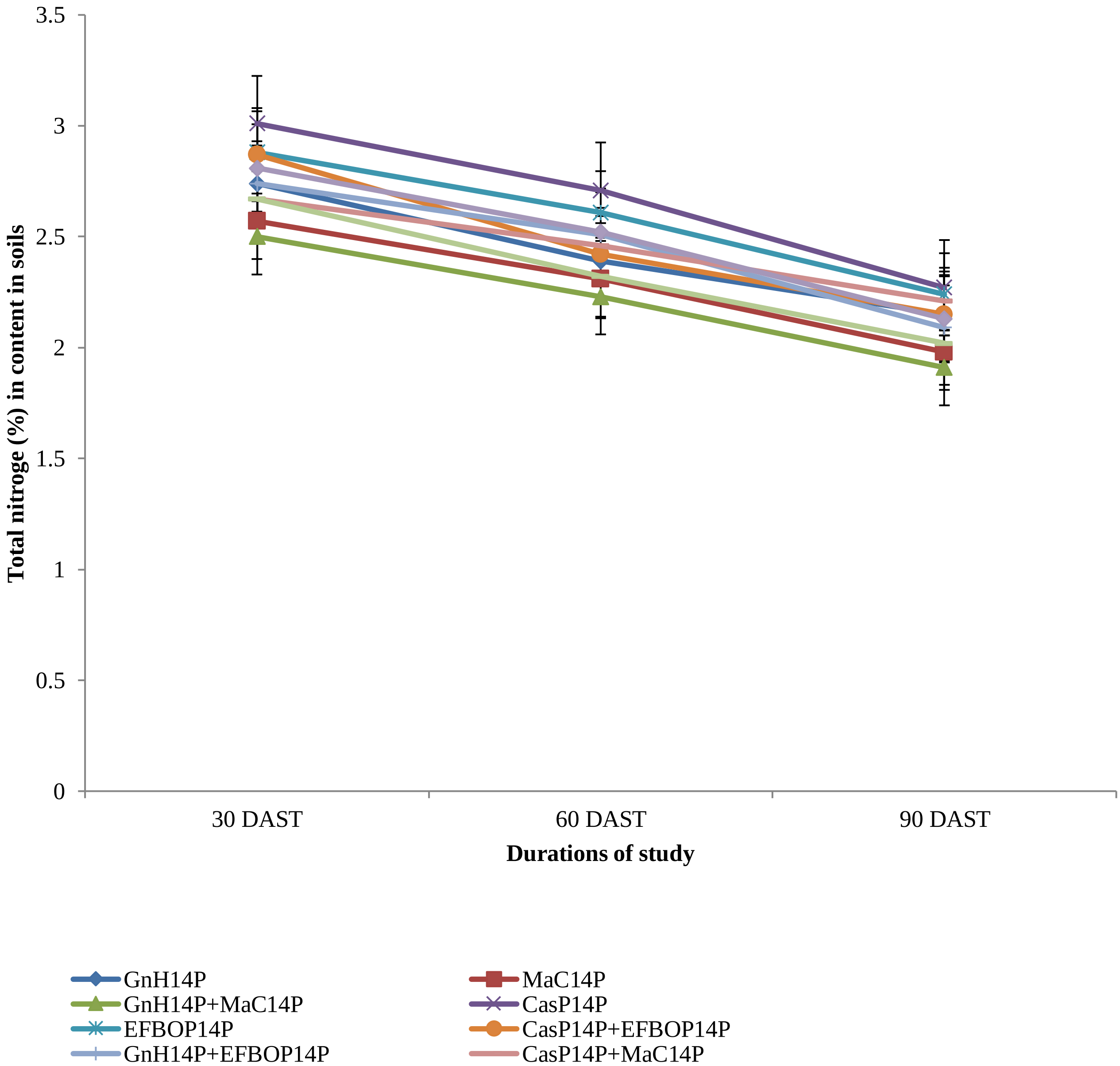

FIG. 3: Total nitrogen content of crude oil-polluted soils amended with agro-wastes

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

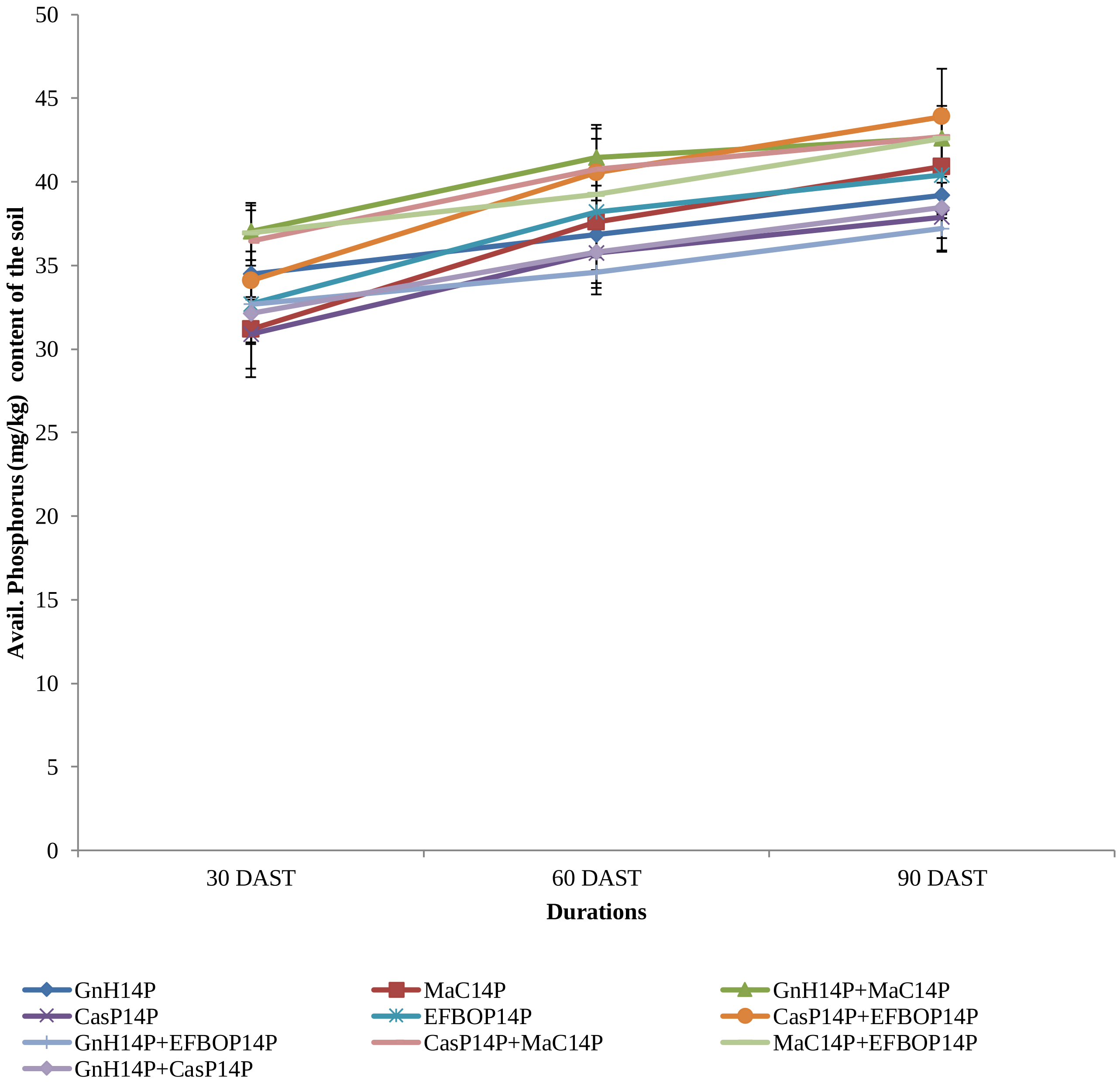

FIG. 4: Available phosphorus content in soil amended with different agro-wastes

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

4. DISCUSSION

Stimulated degradation of crude-oil is at present being encouraged because it ensures rapid remediation of the ecosystems (Ijah and Antai, 2003). Leahy and Colwell (1990) stated that pH is a predominant factor in estimating the rate of crude-oil biodegradation in polluted soil. pH is the product of acidity and alkalinity of a solution. Soil nutrients are more available to plants when the soil is alkaline. The result as presented on Table 2 shows that the un-amended soil samples were generally within the acidic range (5.20-5.90) while, the amendment of the soil with the agro-wastes significantly ($p > 0.05$) increases the soil pH from acidity to an alkaline state, which implies that the amendment possesses a strong buffering capacity. Alkalization of the soil was observed in all the amended soils used during the experiment. However, the strong alkalinity of the soil was mostly observed in soils amended with high concentrations of the wastes. The highest pH value was obtained from soils amended with $MaC_{14}P$ + $EFBOP_{14}P$ at 10% treatment level with a pH of 8.58. Morgan and Atlas (1989), Antai et al., (2023) and Mentzer and Ebere (1996) opine that hydrocarbon degradation in the environment is mostly favored at an optimum pH range of 6.5 and 8.0. Significantly, low pH values partially inhabit the degradation of hydrocarbon products in the soil ecosystem. Hamondi-Belarbi (2018) ascertained that soil amelioration with Carrot peel wastes increased the soil pH and thus, increased the degradation of hydrocarbon products in the soil. Eneje *et al*. (2012) observed that *Calapogonium mucunoides* improved soil fertility indices of the polluted soil as indicated by its effects on soil reactivity (pH) and exchangeable cations; the effect was highest when combined with poultry manure. Interestingly, this study has explored the potentials of these agro-wastes in changing an ecologically acidic soil into an alkaline soil.

Petroleum hydrocarbon soil bio-stimulation with organic manures improved the soil structure, soil moisture, soil aeration and nutrient availability for optimum degradation of hydrocarbon products. The two most essential elements that ensure food production and security globally is the availability of nitrogen. The sustainability of the ever growing population is dependent on plants productivity which is enhanced by phosphorus and nitrogen. The decomposition of the agro-wastes ensures the availability of the phosphorus in form of phosphate in soil. The addition of nutrients increases the phosphorus and nitrogen content of the soil. The increased level of phosphorus and nitrogen stimulates the growth of microbial communities in the polluted soils, especially the hydrocarbon degraders for optimum biodegradation of the hydrocarbon products (Meena et al., 2014). These study show that the phosphorus content of $MaC_{14}P$+$CasP_{14}P$, $GnH_{14}P$+$MaC_{14}P$ and $EFBOP_{14}P$+$MaC_{14}P$ treated soils was significantly higher ($p < 0.05$) than other agro-wastes amended soils. The amended soils except the $GnH_{14}P$ amended soils had higher nitrogen content. Since petroleum hydrocarbon degradation is a natural process limited by temperature, pH and lack of nutrients such as N and P, a higher rate of total hydrocarbon reduction was observed with high organic wastes addition. Therefore, supplementary N and P (and also the C: N ratio) can affect the rate of total hydrocarbon bioremediation. The degradation of crude oil-polluted soil was highly enhanced through the amendment having high nitrogen and phosphorus content which are essentially needed for stimulating petroleum hydrocarbon degraders to degrade the hydrocarbons. This study also shows that there were significant increased ($p < 0.05$) in the total nitrogen and phosphorus contents of the treated soils. This study indicated that crude-oil spills in soil create an imbalance in the carbon-nitrogen ratio compared to the pristine control soil. This could be as a result of the composition of crude-oil which is made up of carbon and hydrogen. This invariably causes a nitrogen deficiency in an oil-soaked soil, which causes a reduction in the proliferation of bacteria and fungi which would have utilized the carbons as their energy source.

However, it was also observed that the exchangeable acidity of the soil reduces in the amended soil, while the exchangeable cations such as magnesium, calcium, potassium and sodium significantly increased ($p < 0.05$) with a base saturation range of 97-99% against the pristine and crude oil polluted soil with a base saturation range of 19-61%. Biodegradation of petroleum hydrocarbons occur rapidly in all the amended soils with a progressive decrease in organic carbon content. High reduction in the organic carbon was observed in soil amended with $MaC_{14}P$, $GnH_{14}P$+ $MaC_{14}P$, $GnH_{14}P$ +$CasP_{14}P$ and $EFBOP_{14}P$. It was observed that the organic carbon of other agro-wastes amended soil was significantly reduced ($p < 0.05$) as compared to pristine control soil. It can thus be said that these agro-wastes possess the potentials enhancing microbial population of the soils for remediating crude oil-polluted soil. Jidere and Akamigbo (2009) observed that poultry droppings and cassava peels possessed strong bioremediation potentials in the reduction of organic carbon in the soil. Adesodun and Mbagwu (2008) applied first-order kinetics in biodegradation of petroleum hydrocarbons. Thus it can be said that these wastes are good remediating agents with the ability of stimulating the fertility of the soil for growing of crops. Nkereuwew *et al*. (2010) observed that the amendment of the soil with high treatment levels of organomineral fertilizer (OMF) significantly reduces the total hydrocarbon content of the soils with increased bacterial and fungal counts of the soils. The success of bioremediation would not be effectively achieved if the remediating agent is unable to restore the contaminated ecosystem for proper growing of crops.

5. CONCLUSION

The loss in biodiversity of many economically important plant species, due to the resultant effects of hydrocarbon pollution, has drastically reduced the agricultural productivity of many oil-producing communities. The mitigation of these problems through an appropriate remediation measures would reduce the effect of the hydrocarbon pollutant in the soil. This research has highlighted the potential use of agro-wastes such as groundnut husks, maize cobs, empty fruit bunch of oil palm and cassava peels in enhancing the degradation of the hydrocarbon polluted soils. The application of these methods of remediation would help in ensuring sustainable development in hydrocarbon producing communities affected by crude-oil spills.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interest regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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