An Investigation of Presumptive Synergism of Oil Palm Bunch Ash and Sawdust Amendments in Remediation of crude oil Spiked Soil

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ABSTRACT: Presumed synergistic effect of combined amendment of crude oil spiked soil with oil palm bunch ash and sawdust was carried out in a laboratory experiment. Two kilogram (2 kg) of sandy soil was placed in each of five plastic vessels labeled T_A, T_B, T_C, T_D and T_E. T_A was left in its natural state while the others were each polluted with 6.7% v/w of crude oil. T_B was not given any remediation amendment. T_C and T_D were each amended with 13.3% of oil palm bunch ash and sawdust respectively while T_E was amended with 13.3% each of oil palm bunch ash and sawdust. The setups were replicated five times and watered twice weekly. Results showed that soil pH increased from 8.7 ± 0.04 to 10.5 ± 0.06, 5.3 ± 0.01 to 8.5 ± 0.04 and 5.6 ± 0.18 to 11.5 ± 0.15 for T_C, T_D and T_E respectively. Percentage total petroleum hydrocarbon contents reduced by 65% for T_C, T_D and 52% for T_E. Total organic carbon increased from 7.6 ± 0.7 to 8.5 ± 0.5%%, reduced from 4.0 ± 0.1% to 3.7 ± 0.3% and from 4.1 ± 0.1% to 2.2 ± 1.0% T_C, T_D and T_E respectively. Total nitrogen increased from 0.66 ± 0.1 to 0.69 ± 0.0% for T_C, remained nearly the same for T_D and reduced from 0.4 ± 0.0 to 0.2 ± 0.0% for T_E while average phosphorus increased from 0.4 ± 0.0 to 23.0 ± 4.2 mg/kg, 0.3 ± 0.0 to 1.8 ± 0.4 mg/kg and from 0.2 ± 1.0 mg/kg to 52.6 ± 4.6 mg/kg for T_C, T_D and T_E respectively. Conclusively, combined amendment with oil palm bunch ash and sawdust did not induce synergism in soil total petroleum hydrocarbon content reduction. © JASEM

INTRODUCTION

The activities of the oil and gas industry in Nigeria's Niger Delta has brought about widespread environmental pollution in the area. The pollutant of concern affecting the environment of the area is crude oil. Some prominent negative effects of petroleum hydrocarbon on the environment is the alteration of soil properties (Kayode *et al.,* 2009; Barua *et al*., 2011). Studies have shown that soil petroleum hydrocarbon contamination decreases soil moisture content, bulk density, water porosity, water holding capacity, increases soil acidity and decreases phosphorous contents but increases soil total nitrogen content and total organic carbon (Kayode *et al.,* 2009; Barua *et al*., 2011; Marinescu *et al*., 2011; Abosede, (2013). Field assessments of crude oil polluted ecosystems by Okoro *et al.* (2011), Okop and Ekpo (2012) and Oyem and Oyem (2013) reported elevated levels of soil total petroleum hydrocarbon content and total hydrocarbon contents. Studies on the effects of petroleum hydrocarbon on soil or its alteration of soil chemical properties reported negative effects on plants and animals.

The problem of petroleum hydrocarbon environmental pollution in Nigeria's Niger Delta cannot stop now because the oil and gas mining activities still continues. Studies on amendment of petroleum hydrocarbon polluted soil with oil palm bunch material and sawdust reported significant reduction of soil total hydrocarbon content (Amajuoyi and Wemedo, 2015; Tanee and Albert, 2011; Godoy-Faundez *et al*., 2008).

However, there is dearth of report study on combined use of the materials for application in remediation petroleum hydrocarbon polluted soil. Hence, this present work was undertaken to investigate presumed synergism in combined use of the materials for remediation of petroleum hydrocarbon impacted soil. The findings from this study could widen our knowledge on the environmentally beneficial use of the materials for remediation and mitigation of petroleum hydrocarbon polluted soil. This knowledge could be useful for application by the local people for cleanup of small scale and not very severe cases of petroleum hydrocarbon spill especially as the materials are locally available.

MATERIALS AND METHODS

This experiment was carried out at Centre for Ecological Studies, University of Port Harcourt. Top

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soil (sandy soil) was collected within 5 cm depth from a fallow land within the university premises. The soil was air-dried and sieved with 2 mm mesh. Bonny Light Crude Oil was obtained from Shell Petroleum Development Company of Nigeria while oil palm bunches and sawdust were collected from artisanal palm oil mill and wood sawmill. The oil palm bunches were burnt in a furnace to derive its ash i.e. oil palm bunch ash (OPBA). The chemical analysis of sample oil palm ash was carried out and its profile is as shown in Table 1.

Table 1: Chemical Profile of Oil Palm Fruit Bunch Ash used in this Study

S/N	Property	Value
1.	pH	10.59
2.	Conductivity (μs/cm)	103,720.00
3.	Nitrate (ppm)	107.50
4.	Phosphate (ppm)	24.60
5.	Total Organic Carbon (%)	0.20
6.	Chloride (mg/kg)	26,401.90
7.	Cation exchange capacity (meq/100g)	330.70
8.	Sulphate (mg/kg)	110.00
9.	Na^+(mg/kg)	5.03
10.	Ca^{2+}(mg/kg)	0.26
11.	Mg^{2+}(mg/kg)	0.48
12.	Fe^{2+}(mg/kg)	6.34
13.	K^+(mg/kg)	324.93

Two kilogram (2 kg) of the processed soil thoroughly homogenized weighed with digital weighing balance (ohaus scout II SC4010) was randomly placed in each of five (5) plastic buckets (dimensions: 20 cm height by 18 cm diameter: 5000 cm³ volume) with five bottom perforations of 5 mm diameter to avoid waterlogging in the vessels. The buckets of the processed sand were immediately watered with 500 ml of distilled water to simulate natural condition. Each vessel served as a setup and were labeled T_A, T_B, T_C, T_D and T_E. T_A was left without crude oil treatment and so served as double control while T_B, T_C, T_D and T_E were each treated with 6.7% (v/w) crude oil and allowed to stand for 24 hours after treatment for the crude oil to properly infiltrate into the soil. T_B was left so after the crude oil treatment as such, it served as the control while T_C and T_D were further treated by thoroughly mixing the crude oil treated soil with 13.3% (w/w) oil palm bunch ash (OPBA) and 13.3% (w/w) of sawdust respectively. Finally, T_E was prepared by thoroughly mixing 13.3% (w/w) each of OPBA and sawdust with its soil. The details of the setups were as shown below.

T_A - Soil (2 kg): no pollution (**double control**).
T_B - Soil (2 kg) + crude oil (6.7%, v/w): (polluted-no-remediation; **control**).
T_C - Soil (2 kg) + crude oil (6.7%, v/w) + OPBA (13.3%, w/w).
T_D - Soil (2 kg) + crude oil (6.7%, v/w) + sawdust (33.3%, w/w).
T_E - Soil (2 kg) + crude oil (6.7%, v/w) + OPBA (13.3%, w/w) + sawdust (33.3%, w/w).

Each setup was replicated five (5) times. The setups were shaded from direct sunlight and rain and watered with 500 ml of distilled water twice weekly.

Soil samples were collected from each setup for chemical properties analyses. First samples were collected 24 hours after treatment with the crude oil but before amendment with any remediation amendment. Subsequent samplings were carried out at 30 days intervals and the experimental setups were allowed for one hundred and fifty (150) days. Soil pH and conductivity were determined through meter method by means of pH meter (model: Hanna HI 8314) and conductivity meter (model: HACH Ectestr microprocessor series) using slurry of sample soil and distilled water in the ratio of 1:1 (w/v). The meter electrodes were dipped into the slurry and the pH and conductivity displayed by the instruments recorded. Soil total petroleum hydrocarbon (TPH) content was determined through gas chromatography/flame ionization detection (GC/FID) method by means of gas chromatography machine (model: HP 5890 series II) using air-dried soil sample after extraction of its total petroleum hydrocarbon content in dichloromethane as extraction solvent. Total organic carbon (TOC) content was determined by titrimetric method (i.e. Walkley–Black technique) while total organic matter was by calculation using the formula of Combs and Nathan (2011). Rate of reduction of soil total petroleum hydrocarbon content was determined by calculation using the method of Ikhajiagbe and Chijioke-Osuji (2014). Soil total nitrogen and phosphorus contents were determined through spectrophotometry (model: HACH DR/890 colorimeter). Carbon/nitrogen ratio was calculated by

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dividing TOC by total nitrogen while cation exchange capacity was determined in two steps: exchangeable acidity by titration method and exchangeable cations (Ca, Mg, K and Na) by means of spectrophotometry with atomic absorption spectrophotometer (model: GBC avanta).

Mean values and standard deviation of replicates were calculated and used as results. The results obtained were presented in composite column charts in which column represents the mean of five replicates and error bar - the standard deviation.

RESULTS AND DISCUSSION

Petroleum hydrocarbon pollution alters soil physical and chemical properties. However, bioremediation through amendment with some materials has been reported to mitigate the negative effects of the pollution on soil properties. This restores soil properties.

The findings of oil palm bunch ash (OPBA), sawdust and OPBA/sawdust amendments of crude oil polluted soil as remediation treatments is shown in Fig. 1.

There was no change in pH of T_A while crude oil pollution reduced soil pH of T_B to neutral. Oil palm bunch ash amendment (i.e. T_C) turned soil pH highly alkaline while sawdust amendment (i.e. T_D) turned soil slightly alkaline. OPBA/sawdust (i.e. T_E) amendment increased soil pH significantly. The constant pH of T_A is understandable because it was not given neither pollution nor remediation treatments while the reduction in pH of T_B could have resulted due to the crude oil treatment. The results of T_A and T_B contradict the findings of Benka-Coker and Ekundayo (1995); Abii and Nwosu (2009) who reported no significant difference in soil pH of both crude oil polluted and unpolluted sites in Niger Delta, Nigeria. Amendment with OPBA and mixture of OPBA and sawdust increased the pH of T_C and T_E. The increase in soil pH of the setups were due to the OPBA treatment. This observation corresponds with Albert and Tanee (2013) which studied the potential of OPBA for remediation of crude oil polluted soil. The increase in soil pH can be attributed to the OPBA amendment as OPBA sample analysis (i.e. Table 1) showed that it was highly alkaline because of its high cation content.
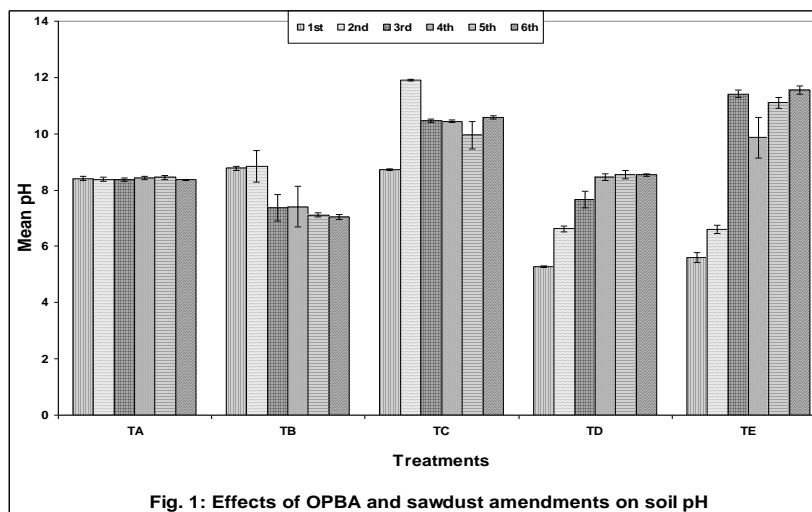

Fig. 1: Effects of OPBA and sawdust amendments on soil pH

Result represent mean of replicates ± standard deviation

Soil conductivity result of treatments were summarized in (Fig. 2). The conductivity of T_A, T_B and T_D were significantly low compared with T_C and T_E (Fig. 2). The high soil conductivity of T_C and T_E could have resulted from amendment of treatments with OPBA. This is acceptable because sample of OPBA had high conductivity due to its high cation content (Table 1). Amendment with sawdust improved nutrients and water adsorption potentials of soil via adding negative charges. This may have resulted in the reduction of soil conductivity.
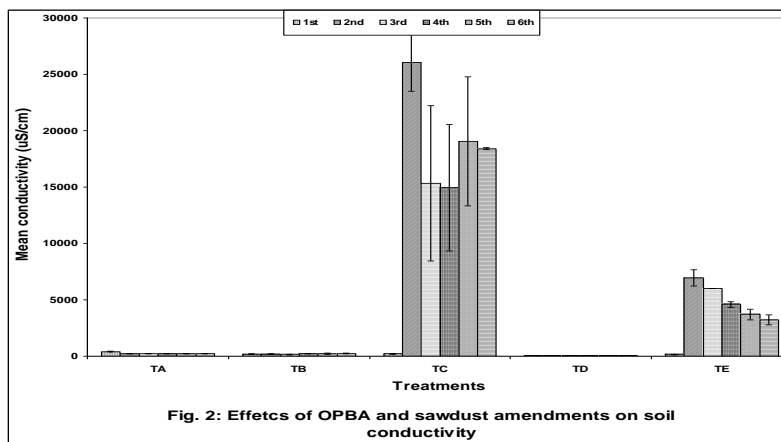
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Fig. 2: Effetcs of OPBA and sawdust amendments on soil conductivity

Result represent mean of replicates ± standard deviation

The effects of OPBA, sawdust and OPBA/sawdust amendments of crude oil polluted soil on total petroleum hydrocarbon (TPH) contents were shown in Fig. 3. Soil TPH content of T_A was negligible as it was not treated with crude oil. Thirty percent (30%) contaminant content reduction was recorded on T_B. This was understandable due to the fact that no remediation treatment was applied to it. Therefore, the mechanism of contaminant removal applicable to this treatment was limited to natural attenuation and this is usually slow and significantly low. Sixty five percent (65%) total petroleum hydrocarbon content reduction was recorded for both T_C and T_D respectively. This higher percentage contaminant loss agrees with Onyelucheya *et al.* (2013); Amajuoyi and Wemedo (2015) which reported similar result as the effect of OPBA amendment on crude oil and diesel oil polluted soils respectively. The observation could have been the result of biostimulation of the OPBA as its characterization by Udoetok (2012) reported high amounts of essential mineral nutrients which are required for metabolism of living organism. Similar high contaminant loss due to sawdust amendments was reported by Boodoosingh *et al.* (2007); Tanee .

and Albert (2011); Atagana (2014) from separate studies of the use of sawdust to enhance degradation petroleum hydrocarbon polluted soil. The high contaminant removal by sawdust was explained by Boodoosingh *et al.* (2007) to result from the fact that sawdust provided alternate carbon source for indigenous oil degrading microorganisms. Therefore, amendment with this material could have stimulated the degradation of the contaminant by indigenous microbes of the soil which led to the high percentage contaminant loss. However, combined treatment with OPBA and sawdust produced 52% contaminant loss. This is a reduction in contaminant loss compared with separate amendments with OPBA and sawdust. This means that there was inhibition of contaminant degradation of the polluted soil in combined amendment with OPBA and sawdust. This is speculated to have resulted from the high alkalinity of the medium due to the impact of OPBA amendment on soil pH. The high alkalinity may have negatively affected the metabolism of the indigenous oil degrading microorganism which are the agents of bioremediation
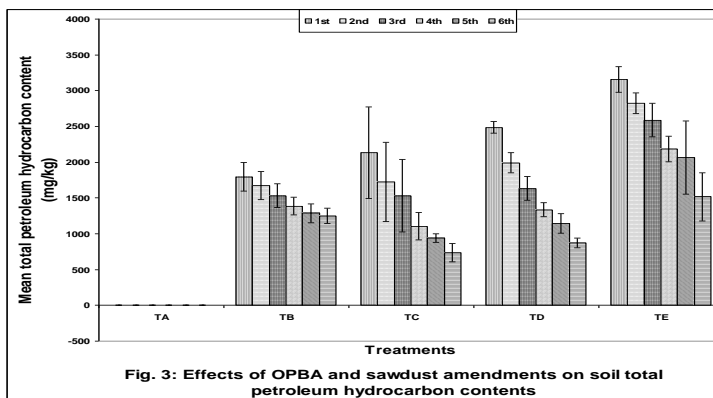

Fig. 3: Effects of OPBA and sawdust amendments on soil total petroleum hydrocarbon contents

Result represent mean of replicates ± standard deviation

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Soil total organic carbon (TOC) and total organic matter contents of T_B and T_C were high compared those of T_A, T_D and T_E (Figs. 4 and 5). The low TOC/TOM of T_A can be explained by the fact that the setup was not treated with the pollutant. However, high TOC result of T_B and T_C agrees the observation of Amajuoyi and Wemedo (2015) and could have resulted from pollution of T_B with crude oil coupled with no remediation treatment given to it while OPBA amendment of T_C could account for its high TOC content. This explanation is supported by the findings of Udoetok (2012) which reported high TOC

from characterization of OPBA. Sawdust amendment of the polluted soil as remediation treatment reduced soil TOC/TOM. This result contradicts the findings of Obasi *et al.* (2013). According to Obasi *et al.* (2013), addition of organic carbon/matter sources such as sawdust can stimulate microbial activity. It therefore can be speculated that such stimulated microbial activity may have taken place in T_D and T_E leading to the observed low total organic carbon and matter obtained in this study.
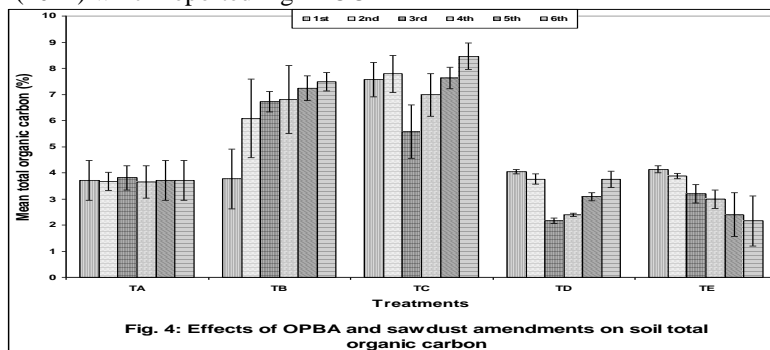

Fig. 4: Effects of OPBA and sawdust amendments on soil total organic carbon

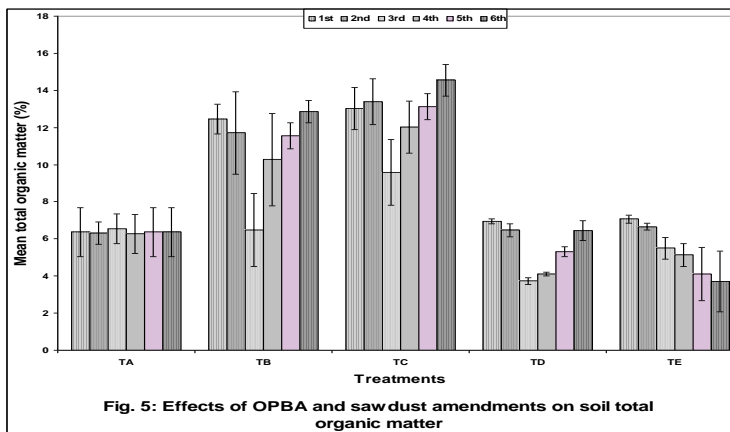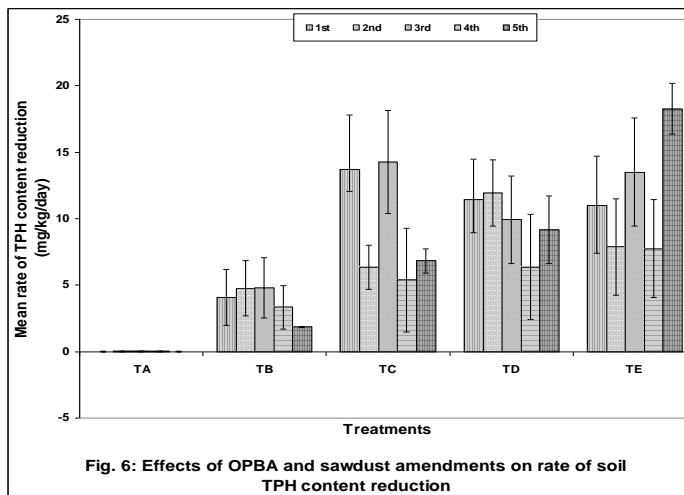Result represent mean of replicates ± standard deviation

Fig. 5: Effects of OPBA and sawdust amendments on soil total organic matter

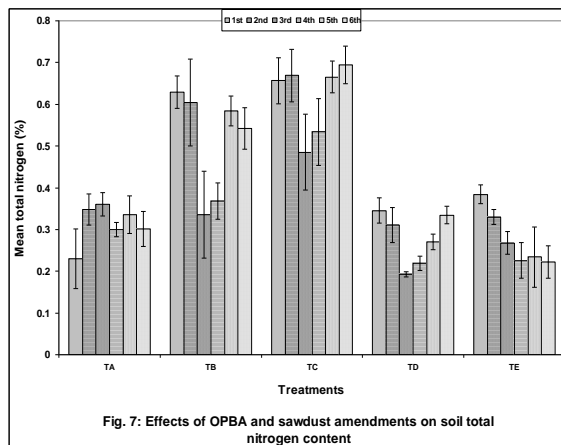Result represent mean of replicates ± standard deviation

Rate of reduction of total petroleum hydrocarbon as influenced by the different pollution remediation amendments is illustrated in Fig 6. Rate of reduction of total petroleum hydrocarbon was least in T_B but higher in T_C and T_D. The observation on T_B agrees with the studies of Amajuoyi and Wemedo (2015). That could have been because of no remediation

amendment was added to stimulate biodegradation of the pollutant while the high rate of TPH reductions of T_C and T_D could have been due to the different amendments of the polluted soil. Combination of OPBA and sawdust (i.e. T_E) did not increase rate of TPH reduction
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Fig. 6: Effects of OPBA and sawdust amendments on rate of soil TPH content reduction
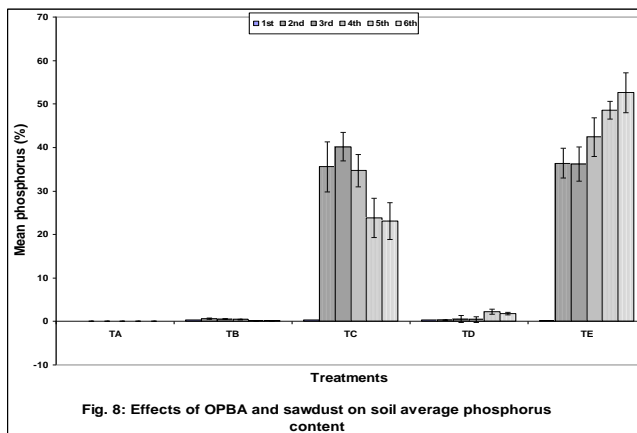
Result represent mean of replicates ± standard deviation and T_C

Fig. 7 showed the effect of OPBA, sawdust and OPBA/sawdust amendments on soil total nitrogen contents of the setups. There were significant difference between soil total nitrogen contents of treatments. Soil total nitrogen contents of T_A was lower than that of T_B which can be explained to be because T_B was treated with crude oil and T_A was not. T_C had higher total nitrogen contents compared with T_D. High soil total nitrogen of T_B and T_C tally with the findings of Eneje and Ebotomei (2011); Albert and Tanee (2013) which reported high soil nitrogen content in crude oil polluted and OPBA amended soils respectively. The observation on T_B suggests that the crude oil is the source of the nutrient while that of T_C was due to OPBA amendments. This is justified by Table 1. OPBA/sawdust (i.e. T_E) produced similar result as sawdust only amendment. Therefore T_E had no synergistic effect on treatment nitrogen content.

Soil phosphorus content of T_A, T_B and T_D were significantly low but high in T_C and T_E (Fig. 8). Crude oil treatment slightly increased average phosphorus content of T_B but significantly increased the average soil phosphorus content of T_C. This can simply be attributed to the OPBA amendment of the treatment. However, soil average phosphorus of T_D was slightly increased. This result implies that amendment with sawdust slightly increased soil average phosphorus content. OPBA/sawdust amendment i.e. T_E significantly increased soil average phosphorus.

Fig. 8: Effects of OPBA and sawdust on soil average phosphorus content

Result represent mean of replicates ± standard deviation

The effect of OPBA and sawdust on soil C/N ratios was summarized in Fig. 9. There were no significant difference between carbon C/N ratios of treatments (Fig. 9). C/N ratio was slightly high at the 1st and 4th samplings for T_A and T_B respectively. OPBA/sawdust amendment (i.e. T_E) had no significant effect on C/N

Fig. 7: Effects of OPBA and sawdust amendments on soil total nitrogen content

Result represent mean of replicates ± standard deviation

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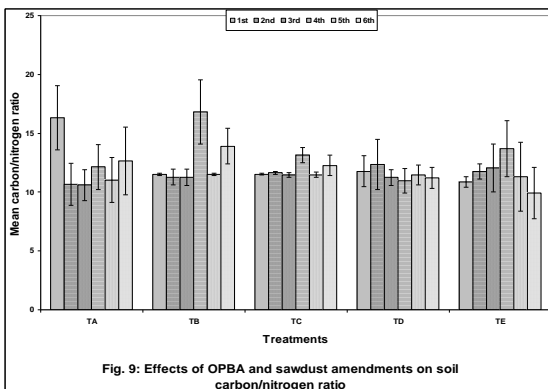ratio compared with their respective separate amendments T_C and T_D.

Fig. 9: Effects of OPBA and sawdust amendments on soil carbon/nitrogen ratio

Result represent mean of replicates ± standard deviation

Soil cation exchange capacity, CEC result as influenced by OPBA, sawdust and OPBA/sawdust amendments was as shown in Fig. 10. Soil cation exchange capacity of T_A was nearly the same at all sampling times. This was almost the case for T_B except at the 3rd sampling. Amendment with OPBA significantly increased CEC of T_C at the 5th and 6th sampling times (Fig. 10). The observed increase in CEC of T_C could be the influence of the OPBA amendment as sample OPBA used in this study showed high cation content (Table 1). However, CEC was reduced in T_D as amendment with sawdust improves nutrients and water adsorption potentials of soil via adding negative charges. CEC of T_E increased with sampling time to its maximum at the 5th and 6th sampling. OPBA/sawdust amendment moderated soil CEC of T_E compared with T_C.
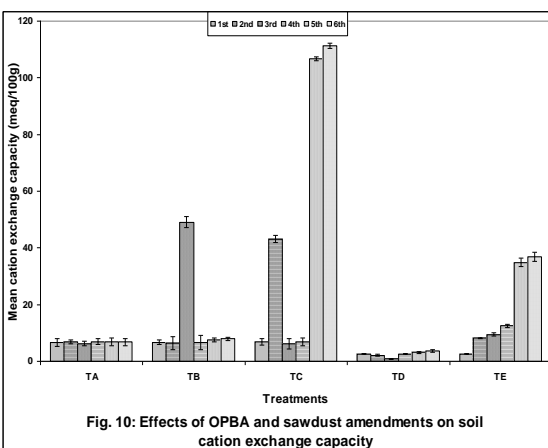

Fig. 10: Effects of OPBA and sawdust amendments on soil cation exchange capacity

Result represent mean of replicates ± standard deviation

Conclusion: Results obtained from the investigation of synergism of crude oil spiked soil by oil palm bunch ash, sawdust, OPBA/sawdust amendments has shown that there was no synergism in soil total petroleum hydrocarbon content reduction. This was justified by the lower percentage soil total petroleum hydrocarbon content loss as observed in OPBA/sawdust amendment compared with each of the separate single amendments with OPBA and sawdust.

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