Characterization and removability of priority pollutants in an oil-spilled site using composted *Cassava sludge*

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Abstract

We investigated characteristics of crude oil-contaminated soils of a town within an oil-exploration zone of southeastern Nigeria in 2006. Target sampling technique was used in collecting soil samples, which were later prepared for various laboratory analyses. *Cassava sludge* was obtained from wastewater disposal pit and composted using Aerated Pile method. Five temporal treatments, namely 30, 60, 90, 150 and 180 days were observed when 0.5 kg composed *Cassava sludge* was applied on 5-kg soil set up in a completely randomized design. Results showed differences in chemical composition of sludge and its compost. There were significant (P = 0.05) variation in the removability of priority pollutants using composted *Cassava sludge*: with greater efficacy at 120 and 180 days for total cadmium and nickel. Further studies should consider varying rates of this sludge and different soils since soils of the area are formed from dissimilar lithologies. [Life Science Journal. 2008; 5(3): 62 – 66] (ISSN: 1097 – 8135).

Keywords: characterization; contaminants; crude oil; degradation; permissible limits; sludge; spillage; traffic, tropical soils

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1 Introduction

Environmental degradation associated with oil exploration is a major problem confronting oil-producing countries. The degree of degradation is dependent upon the composition and quantity of priority pollutants, and on the configuration of the receiving media. In spite of the public outcry over environmental pollution due to oil exploration, more crude oil wastes are being released into soils and water bodies. Heavy metals are released into the soil through oil spillage resulting from oil well blowouts, pipeline leakages, spent drilling mud, effluent water discharges, metals scrap, power construction operations, continuous gas flaring, combustion of oil by electric power generator at flow stations, supporting heavy boat traffic and domestic wastes (Aiyesanmi, 2005).

In soils, petroleum hydrocarbon creates condition which lead to the unavailability of essential plant nutrients such as nitrogen, and the availability of some toxic elements such as arsenic, and lead to plants (Akamigbo and Jidere, 2002; Gill *et al*, 2003). Crude oil had a dispersive effect on sprouting of ginger while it had variable effects on the microbial biomass (Ekpo and Nwankpa, 2006). It weakens soil microbes thereby inhibiting their activity (Manahan, 1994). Also, crude oil pollution influences plant root development (Ekpo, 2002), soil water absorption by plants (Atuanya, 1987), biotoxicity (Atuanya, 1987), soil structure, water stress and nutrients deficiencies (Odjegba and Sadig, 2002; Gil *et al*, 2003) and decline in crop performance (Gaskin *et al*, 2007).

Heavy metals associated with crude oil spillage are naturally found in soils (Ojanuga *et al*, 1996), but monitoring is necessary for understanding metal load (Odu *et al*, 1996) as elevated accumulation has direct consequences to man and ecosystem (Agbozu *et al*, 2007).

Treataility of soils affected by crude oil spillage depends not only on soil characteristics, but on type, avail-

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ability and affordability of remediation techniques (Ram *et al*, 1993). Some scholars investigated soil washing mechanism and modeling of the process (Chu and Cha, 2003; Ye and Young, 2003; Urum *et al*, 2005; Zhou *et al*, 2005) chemical remediation techniques (Khattak and Page, 1992; Mench *et al*, 1994), phyto-remediation techniques (Lee and Chen, 1994; Brooks, 1998) and organic adsorbents (Stewart *et al*, 2003; Sekar *et al*, 2004; Carrasqueros *et al*, 2006; Gueu *et al*, 2007).

Cassava Manihot esculenta (Cantz) is one of the dominant starchy staple crops grown in most countries in the continent of Africa (John *et al*, 2006), especially Nigeria (Nzekwe and Afolami, 2001), where it has currently become a high income generating crop as well as an export crop. The domestic and industrial relevance attached to cassava has resulted in the emergence of varying scales of processing industries including gari processing industries. According to Babawale (2001) gari is a major staple food product from cassava which is consumed by more than 80% of the Nigerian populace. Cassava processing for gari involves peeling, including, grating, dewatering, sieving and frying. Dewatering leaves a lot of wastes including sludge especially if manually performed. These wastes were investigated for use in treating soils polluted by crude oil. Utilization of cassava wastes for remediation of polluted and degraded sites would be sanitizing the environment while enriching fast-fertility declining soils of the study area. In the light of the foregoing, the major objective of this study was to characterize composted *Cassava sludge* while utilizing it as an organo-remediation technique in a crude oil-spilled site.

2 Materials and Methods

2.1 Study area

Obinze is a military settlement lying between the latitudes 5º 10' and 5º 25' North, and the longitudes 6º 45' and 7º 00' East. The town is about 25 kilometers away from the capital city of Owerri southeastern Nigeria. Soils of the area are formed from coastal plain sands of the Oligocene-Miocene geologic era. The mean annual rainfall ranges from 2400 mm to 2500 mm while mean annual temperature range is from 27 ºC – 29 ºC. It has a rainforest vegetation although anthropogenic activities such as military activities, nomadic farming, arable farming, sand mining and constructions have depleted its originality. Sometimes the military base intercepts illegal traffickers in petroleum and petroleum products for handover to law enforcement agencies. There has been consistent leakages of these intercepted petroleum tankers before a recent burst of high capacity type resulting into spillage into surrounding arable farmland. In addition to this, we collected 10 core samples of soils from polluted site for bulk density studies.

2.2 Samples preparation

We collected a 30-kg soil sample from the oil-spilled site and stored it at 4 ºC before its characterization. Soil sample was quartered and subsamples were used for laboratory analysis in terms of oil characteristics.

Cassava sludge was obtained from wastewater disposal pits. Final compost was produced from the above sludge with green wastes (1.2 volume) following the Aerated Pile method (Wilson *et al*, 1980).

Optimum moisture content (OMC) was obtained using undisturbed soil samples as a difference of water contents at – 0.03 MPa determined by pressure plate, and at – 1.5 MPa determined by pressure membrane (Dane and Hopmans, 2002).

2.3 Experimental design

For each pollutant, 5 temporal values of 30, 60, 90, 120 and 180 days and soil sample (5 kg weight) in plastic containers were replicated 3 times in a completely randomized design. In each replicate, 0.5 kg composted sludge (10% soil weight) was applied to ascertain percentage removability of the pollutants.

2.4 Laboratory analysis

Bulk density of soil was determined by core procedure according to Grossman and Reinsch (2002) while particle size distribution was measured by hydrometer method (Gee and Or, 2002). Total carbon (TC) was measured by loss on ignition using C and N Analyzer (Carlo-Erba, Milan. Italy) (Nelson and Sommers, 1996). Total nitrogen (TN) was determined using micro-kjeldahl method (Bremner, 1996). Soil pH was measured potentiometrically using Beckman zeromatic meter in a 1 : 2.5 soil/solution ratio according to the procedure of Hendershot *et al* (1993). Electrical conductivity was determined from the filtrate obtained from the suspension used in pH analysis using a conductivity meter. The total petroleum hydrocarbon (TPH) was determined using Fourier Transform Infra-red spectrometry (FTIR) (QAL/AM/S 16) at wavelengths ranging between 2800 cm to 3200 cm.

Soil samples were digested for Cr, Cd, V and Ni using a mixture of concentrated HCl04 HN03 at a ratio of 2 : 1. and metals were extracted with 0.5 ml HCl (Lacatusu, 2000). The aliquots obtained were measured for Cr, Cd, V and Ni using Atomic Absorption Spectrophotometer (Alpha 4 Model). The analytical procedures were checked by analysis of DOLT-3 Matrix Certified Reference Material with known concentration for heavy metals (Castillo and Calder, 1990).

2.5 Statistical analysis

Soil data on removability was subjected to analysis of variance (ANOVA) using software (SAS Institute, 2001). and means were separated using least significance difference at 5% level of probability.

3 Results

Comparative concentration of specific nutrients in the two forms of cassava wastes (sludge and final compost) are of interest. Distinct variability in TC, TN, exchangeable basic cations, available phosphorus (Av. P) and contaminants are shown in Table 1. Low values of TN and high values of TC were observed in contaminated soils (Table 2), and carbon-nitrogen ratio (17 : 1) was higher than 12 to 14 range characteristic of West African soils (Ahn, 1979). However electrical conductivity did not exceed the critical level of 9400 ds/cm considered harmful to crops (Odu *et al*, 1985). Generally, the values of contaminants were higher than tolerance limits in soils (WHO, 2006). Pronounced changes occurred in the physicochemical properties of soils (Table 3). Composted *Cassava sludge* has varying efficiency in the removal of these contaminants with time (Table 4) with some contaminants (Cd and Ni) being more efficiently removed by the organic waste. The composted *Cassava sludge* reduced the contaminants content of soils but not below permissible limits (WHO, 2006).

4 Discussion

Decrease in TC content in composted C*assava sludge* (138 g/kg in dry weight basis) when compared with uncomposted sludge (342 g/kg dry weight basis) indicates that micro-organisms used some carbon amounts in building their own structures. Again, these micro-organisms might have altered resistant carbon into other forms such as CO_2 which is more bioavailable. These results are consistent with findings of Charest *et al* (2003) which stated that composted *Cassava sludge* did not supply TN greater losses during composting (Bertran *et al*, 2004). Increased exchangeable calcium content of composted sludge enhanced stability of organic fractions against further microbial degradations (Baldock and Skjemstad, 2000). The stabilizing effect of exchangeable calcium could be the reason why calcium humic acid (CaHA) fractions are more humified than mobile humic acids (MHA) (Ve *et al*, 2004). Lower TN value in composted sludge could be attributed to volatilization due to high temperature of the study area as well as activities of proteolytic bacteria in the waste. High exchangeable potassium in composted *Cassava sludge* is traceable to the slash-and-burn farming system which releases a lot of

Table1. Typical chemical characteristics of the *Cassava sludge* and the produced compost (in dry weight basics)

Properties	Sludge	Final compost
TC (g/kg)	342	138
TN (g/kg)	20	13
C/N	17	10
Ca^{2+} (cmol/kg)	9.3	9.8
Mg^{2+} (cmol/kg)	7.8	5.3
K^{+} (cmol/kg)	7.4	18.1
Av. P (mg/kg)	2.2	1.5
Cr (mg/kg)	2.6	0.9
Cd (mg/kg)	3.3	2.4
V (mg/kg)	2.8	1.2
Ni (mg/kg)	7.6	2.3
TPH (mg/kg)	38.6	12.4

Ca^{2+}: exchangeable calcium, Mg^{2+}: exchangeable magnesium, K^{+}: exchangeable potassium, Cr: total chromium, Cd: total cadmium, V: total vanadium, Ni: total nickel.

Table 2. Characteristics of contaminated soils

Property	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)	TC (g/kg)	TN (g/kg)	C/N	OMC (g/kg)	EC (ds/cm)	BD (g/kg)	pH (water)	TPH (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	V (mg/kg)	Ni (mg/kg)
Value	840	50	110	40	2	20	160	58	1.39	4.6	7.8	6.9	15.6	5.5	43.5

Table 3. Characteristics of contaminated soils

Property	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)	TC (g/kg)	TN (g/kg)	C/N (g/kg)	OMC (g/kg)	EC (ds/cm)	BD (g/kg)	pH (water)	TPH (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	V (mg/kg)	Ni (mg/kg)
Value	850	30	120	24	3	8	180	51	1.26	5.1	2.3	2.6	0.9	1.7	15.6

Table 4. Effect of composted sludge on removablity of contaminants at room temperature with time (days)

Pollutant	Time (Days)					$LSD_{0.05}$
(mg/kg)	30	60	90	120	180	
Cr	15	25	35	40	50	1.25
Cd	35	60	65	75	90	0.92
V	20	25	30	35	45	1.08
Ni	25	40	60	80	85	0.96
TPH	1.8	2.5	6.5	7.5	9.0	0.09

potash on which cassava grows. Higher values of contaminants (Cr, V, Ni and TPH) in the sludge is a confirmation of pollution of the untreated sludge. Values of these contaminants are above permissible limits (WHO, 2006), suggesting a high tendency of *Cassava sludge* compost to retain these contaminants. Soils contaminated with crude oil (Table 2) exhibited high C/N ratio (20) compared with decontaminated soils (Table 3) having a C/N ratio of 8 due to increased oxygen content in dewatered sludge (composted sludge), and consequent proliferation of autochthonous and aerobic bacteria which increased mineralization processes. Improved OMC in decontaminated soils is indicative of reduced presence of water-repellent organic constituents. Total Cd and Ni had high removal percentage at 120 and 180 days, suggesting Cr is use of composted cassava sludge in their remediation. Low removal percentage in Cr is suggesting a preponderance of anionic chromium in soils which might have repelled negatively charged surfaces of composted *Cassava sludge*. The implication of this is that the anionic forms of the contaminants become more available in the pedosphere thereby creating greater chances of uptake by crops consumed by humans. Composted *cassava sludge* exhibited least efficiency in the removal of TPH which is attributable to possible precipitation of organic substances contained in the compost by Ca and Mg (Torres *et al*, 2005). To circumvent this, Torres *et al* (2007) recommended addition of zeolite powder to capture exchangeable Ca and Mg. Addition of surfactant-bearing amine group could be helpful in removing TPH since the amine functional group protonated and behaves as a cation and this can attract negatively charged TPH substances.

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