

Evaluation of Cow-Dung Effectiveness for Bioremediation in Petroleum Polluted Loamy Soil Site

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ABSTRACT

The development of local nutrients to enhance remediation of petroleum polluted soil mediums motivated this study. The study therefore, aimed at evaluating effectiveness of cow-dung for bioremediation of petroleum polluted loamy soil environment in the Niger delta area. The study was conducted in two distinct criteria, that is, petroleum polluted loamy soil with no Cow Dung Nutrient (NN) and petroleum polluted loamy soil with cow-dung Nutrient (WN) mediums. The two experimental set-ups were mixed manually to obtain homogeneity of impaction. Average weight measuring 3.2 kg Loamy Soil, Cow-dung 0.5 kg with ranging petroleum volume 50-190 ml for time ranging from 0 to 32 days at intervals of 25 ml petroleum and 4 days exposure time were used in the evaluation study. The evaluation was carried out based on Total Petroleum hydrocarbon (TPH) concentration C_{TPH} as a function of petroleum quantity (v) discharged and exposure time (t). The results obtained showed that total petroleum hydrocarbon concentration (C_{TPH}) increases with increase in the quantity of petroleum discharged at constant exposure time for both NN and WN. Similarly, the TPH concentration (C_{TPH}) decreases with increase in exposure time at constant quantity of petroleum discharged. The TPH concentration (C_{TPH}) shows rapid biodegradability with (WN) than those of (NN) indicating that Cow-dung is a good nutrient for bioremediation of polluted sites. In addition, generalized predictive models for the bio-simulation of TPH concentration (C_{TPH}) as a function of petroleum physical properties, soil conductivity and cow dung mass for NN and WN are developed using Abowei modified Raleigh dimensional approach. The models showed that TPH concentration (C_{TPH}) demonstrated density independency for NN and dependency for WN. The predictive models as developed are:

$$C_{TPH} = \phi_{MNN} [(tK_L \mu_p \sigma_p) / V^{2/3}], \text{ where } \phi_{MNN} = (2.08 V^{2/3} t^{0.4}) / (tK_L \mu_p \sigma_p)$$

$$C_{TPHWN} = \phi_{MWN} [(tM_{cd} K_L \mu_p \sigma_p) / (\rho_p^2 V_p^{7/3})], \text{ where } \phi_{MWN} = \frac{2.08 t^{-0.5} \rho_p^2 V_p^{7/3}}{M_{cd} K_L \mu_p \sigma_p}$$

Keywords: Development; Cow-dung nutrient; Effectiveness; Bioremediation; Petroleum polluted; Loamy soil; Environment

INTRODUCTION

Environmental pollution perturbation problems are obvious due to man-machine interactions in a system development by the application of chemical, physical and biological sciences including social sciences resulting to formation of products for human survival [1-3].

To this end environmental pollution has been discovered to be a major challenge to the development of the society. One of the major environmental pollution is caused by oil spillage due to

the exploration and exploitation of crude oil [4]. The discharge of Petroleum spills into the environment is usually by the action of intentional or unintentional. The consequences resulting in the releasing, spilling, pumping, pouring, emitting, emptying and dumping of Petroleum into the waters or onto lands engineered deleterious effect to aquatic and terrestrial lives. This phenomenon is a key problem in the petroleum rich Niger Delta region of Nigeria [5]. Soil contamination and its adverse effect on the overall ecosystem is one of the major problems we are currently facing today and to combat this environmental problem is the major issue

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of focus in this research. Hence, it is imperative to exploit available technologies for soil restoration; and bioremediation has been recognized as one of the promising alternative [6]. Bioremediation is the use of either naturally occurring or deliberately introduced microorganisms to consume and break down environmental pollutants, in order to clean a polluted site. Bioremediation technologies utilize naturally occurring microorganisms, such as bacteria, fungi, and yeast, to degrade hazardous substances into non-toxic or less toxic substances.

Various researchers have dealt into nutrient applications for bioremediation of petroleum polluted sites, Omogoye and Adewale works on the efficacy of NPK and cow dung combinations on performance influence on soil properties [7]. Their works were limited to non-petroleum polluted site although it gives a prelude to the nutrients effectiveness to curb environmental perturbation problems. The works of Benson et al. is limited to the enhancement of crude oil polluted soil by applying single and combined cow dung and hydrogen peroxide as remediating agents [8]. The results showed that addition of cow dung and hydrogen peroxide enhanced remediation of the polluted soil especially in treatment A and C with significant increase ($P=0.05$) in soil conductivity, pH and nutrients when compared to the un-amended soil. Reduction in total hydrocarbon content of A (79.48%)>C (77.95%)>B (75.75%)>D (46%) with significant increase in hydrocarbon degrading microbes in the amended soil. The amendments have the capacities to enhance remediation of crude oil polluted soil. Also, the combined treatments did not have any advantage over the single treatment options as the use of cow dung single treatment performed best in terms of its remediation potential.

The degree of low biodegradation was observed for a remediation period of 40 days under laboratory conditions. The results obtained revealed a positive correlation coefficient for the various bio stimulants used when compared with the unamended soil. The research study shows that a higher biodegradation rate constant (k) and a low half life time exist for amendments with (cow dung and NPK) and gradually varies with other biostimulants.

Adebola and Iheoma did a research on Impact of bioremediation formulation from Nigeria local resource materials on moisture contents for soils contaminated with petroleum products [9]. The study was on the evaluation of the influence of bioremediation agent (Ecorem) on moisture content of soils contaminated by crude oil and spent engine oil, as a part study on its effect on soil properties. Result showed that Ecorem increased soil moisture content by 11 to 22 folds over the initial 1 to 3.65% of untreated soils, transformed the original soil from non-arable to arable status and did not render the treated soil water logged at close-out. The effect also varies with Ecorem. Soil weight ratio, giving positive correlations with coefficients of up to 0.955 ($P=0.011$); which is a function of petroleum product type.

The study was carried out in a clay and alluvial soil environment in Port-Harcourt Ofoegbu et al. reported on bioremediation of crude oil contaminated soil using organic and inorganic fertilizers [10-12]. The study involves the use of first order kinetics model in the remediation of crude oil contaminated aerable soil at 2, 4 and 6% crude oil spill respectively, this was bio stimulated with inorganic fertilizer (NPK), cow dung and palm kernel husk ash (PKHA) applied singly and in combinations (cow dung and inorganic fertilizer); (cow dung and PKHA) in a 50:50 ratio.

It seems the aspect of the study of bioremediation with respect to petroleum polluted Iterigbeloamy soil environment is lacking. "To this end, this work will focus on the evaluation of cow dung effectiveness on total petroleum hydrocarbon degradability as a function of quantity of petroleum discharged and the exposure time in petroleum polluted Iterigbe loamy soil environment located at Effurun in the Niger Delta area of Nigeria".

MATERIALS AND METHODS

Model development

Dimensional analysis method is exploited in the development of predictive models for the simulation of Total Hydrocarbon concentration (C_{TPH}) dependency as a function of Petroleum quantity and associated physical property variables discharged, impacted soil properties particularly the soil conductivity and exposure time frame with nutrient (NN) and with no Nutrient (NN). The following assumptions here made to arrive at the predictive models, thus:

Assumptions:

- Extent diffusion of petroleum into the soil is constant due to the adoption of manual mixing to obtain homogeneity,
- Temperature is considered constant as the study was carried at ambient condition,
- Mixing velocity is constant as the mixing was done manually,
- Effect of heat capacity is constant and negligible,
- Impacted loamy soil density is considered constant,
- Petroleum sample was obtained from Kolo Creek SPDC Location in Bayelsa State,
- Cow-Dung was obtained Agbarho slaughter Market,
- Plastic bins with appropriate measure dimension were used as a model reactor for the study.

In compliance with these assumptions, predictive models were developed for the simulation of Total Petroleum Hydrocarbons (C_{TPH}) for an impacted loamy soil environment with no nutrient (NN) and with nutrient (WN) and in the subsection below.

Total hydrocarbon concentration (C_{TPH}) with no nutrient (NN)

Dependent on the following at the above specified assumptions. Thus,

Where,

t = Exposure time,

ρ_p = Density of Petroleum,

V_p = Volume of Petroleum Spilled,

K_L = Loamy soil Conductivity,

μ_p = Viscosity of Petroleum,

σ_p = Surface Tension of the Petroleum.

In order to arrive at the desired predictive model, the modified Abowei sighted in Abowei et al. [1,13] dimensional Analysis Technique was applied to ascertain at least approximate variables;

thus:

The considered functional variables were dimensioned appropriately and are defined below:

Time (t)=T

Density (ρ)=kg/m³

Volume (V_p)=m³ (3)

Conductivity (K_L)=T³/kg

Viscosity (μ_p)=kg/m.T

Surface Tension (σ_p)=kg/T²

Now applying dimensions as designated in equation (3) coupled with letters power series gives:

$$C_{TPH} \Rightarrow \phi[(T)^a.(ML^{-3})^b.(L^3)^c.(T^3M^{-1})^d.(ML^{-1}T^{-1})^e.(MT^{-2})^f] \quad (4)$$

Noting that; C_{TPH} ⇒ ML⁻³ and φ=dimensionless Constant (5)

Now equalling with respect to corresponding dimension as in equation (4) gives;

$$T : a + 3d - e - f = 0 \quad (6)$$

$$L : -3b + 3c - e = -3 \quad (7)$$

$$M : b - d + e + f = 1 \quad (8)$$

Equations (6-8) can be solved simultaneously using induction principles as adopted by Abowei and Wami [13], and equation (6) is satisfied if a=1, d=1, e=1 and f=1, and upon substitution into equations (7) and (8) gives a simplified simultaneous equations:

$$-3b + 3c = -2 \quad (9)$$

$$b = 0 \quad (10)$$

And equation (2) is solved to get the c value by substituting b=0;

$$\left. \begin{aligned} 3c &= -2 \\ c &= -2/3 \end{aligned} \right\} \quad (11)$$

Therefore, expecting dimensional values as solved from equations (6-11) results in:

$$\left. \begin{aligned} a &= -1 \\ b &= 0 \\ c &= -2/3 \\ d &= 1 \\ e &= 1 \\ f &= 1 \end{aligned} \right\} \quad (12)$$

Putting these dimensions as in equation (12) into equation (2) gives a basis for the development of a concise predictive Total Petroleum Hydrocarbon concentration (C_{TPH}) for petroleum polluted loamy environment with no nutrient (NN).

$$C_{TPH} = \phi[t.\rho_p V_p^{-2/3} K_L \mu_p \sigma_p] \quad (13)$$

and,

$$C_{TPH} = \phi[(tK_L \mu_p \sigma_p) / V_p^{2/3}] \quad (14)$$

Equation (14) shows that the Total Petroleum Hydrocarbon Concentration (C_{TPH}) is a function of exposure time. Loamy soil

conductivity, Viscosity and surface tension of the petroleum discharged but independent of petroleum density at no nutrient (NN) applications.

Total hydrocarbon concentration (C_{TPH}) with WN

In this case, the quantity of cow-dung (MC) is introduced as a variables parameter into equation (1) to reflect Total Petroleum Hydrocarbon Concentration (C_{TPH}) effect with cow-dung nutrient (WN).

Thus equation (1) can be rearranged dimensionally as:

$$ML^{-3} = \phi_{mva} [t^a \rho^b V_p^c M_{cd}^d K_L^e \mu_p^f \sigma_p^g] \quad (15)$$

In the same vein, by introducing the dimensions in equation (3) into (15) gives that:

$$ML^{-3} = \phi_{mva} T^a (ML^{-3})^b (L^3)^c (M_{cd})^d (T^3 M^{-1})^e (ML^{-1} T^{-1})^f (MT^{-2})^g \quad (16)$$

Equation with respect to corresponding dimensions in equation (16) gives the following simultaneous equations.

$$T : a + 3e - f - 2g = 0 \quad (17)$$

$$L : -3b + 3c - f = -3 \quad (18)$$

$$M : b + d - e + f + g = 1 \quad (19)$$

Conversely, applying induction principles to the simultaneous equations as in (17-19) will provide the desired dimensional variables. Equation (17) is satisfied; if:

$$\left. \begin{aligned} a &= 1 \\ e &= 1 \\ f &= 2 \\ g &= 1 \end{aligned} \right\} \quad (20)$$

Substituting the variables in equation (20) into equation (18) and (19) gives the following simplified pairs of simultaneous equations as stated below:

$$L : -3b + 3c = -1 \quad (21)$$

$$M : b + d = -1 \quad (22)$$

Equation (22) is satisfied if; b=-2 and d=1; and using the value of b into equation (21) gives:

$$\left. \begin{aligned} L &\neq (-3)(-2) + 3c = -1 \\ 6 + 3c &= -1 \\ c &\Rightarrow -2/3 = -2^{1/3} \end{aligned} \right\} \quad (23)$$

Similarly, the expected dimensional values for total petroleum hydrocarbon concentration (C_{TPH}) with nutrient are summarized as:

$$\left. \begin{aligned} a &= 1 \\ b &= -2 \\ c &= -7/2 \\ d &= 1 \\ e &= 1 \\ f &= 2 \\ g &= 1 \end{aligned} \right\} \quad (24)$$

In order to get the Total Petroleum Hydrocarbon Concentration (C_{TPH}) predictive model for polluted loamy soil site with cow dung (WN) the author substituted parameters in equation (24) into (15);

thus:

$$C_{TPHWN} = \phi_{MWN} [t \rho_p^{-2} V_p^{-7/3} M_{cd} K_L \mu_p^2 \sigma_p] \quad (25)$$

Equation (25) with further simplification gives:

$$C_{TPHWN} = \phi_{MWN} [(t M_{cd} K_L \mu_p \sigma_p) / (\rho_p^2 V_p^{7/3})] \quad (26)$$

Where ϕ_{MWN} = dimensionless constant and can be exploited from the experimental work.

Comparison analysis of the two predictive model equations shows that the one with cow-dung nutrient is dependent on the quantity cow-dung and density petroleum. The two models are novel and are generalized for application in any polluted soil medium.

Study location

The study was conducted at the Federal University of Petroleum Resources (FUPRE) Chemical Engineering Department, Effurun (Table 1). The field data soil was shown in the map (Figure 1).

Experimental set-up

Materials: The materials used for the experimental set-up are the following:

1. Loamy Sand Soil.
2. Petroleum.
3. Cow Dung.
4. Acetone Chemical Species.
5. Rags.
6. Hand Gloves.
7. Eye goggles.
8. Nose Mask.
9. Coverall.
10. Shovels PPES
11. Hoes.
12. Machete.
13. Safety Shoes
14. Polythene bags.

Equipment: The following equipment was utilized for the study:

1. Handheld digital pH meter.

Table 1: Study location.

Community	Iteregbi
LGA	Uvwie
State	Delta
Country	Nigeria
Postal/Zip	333110
Latitude	5.520018
Longitude	5.8606612
Climate	Humid Tropical
Temperature	≤ 30°C
Date of Field work	10/07/2018

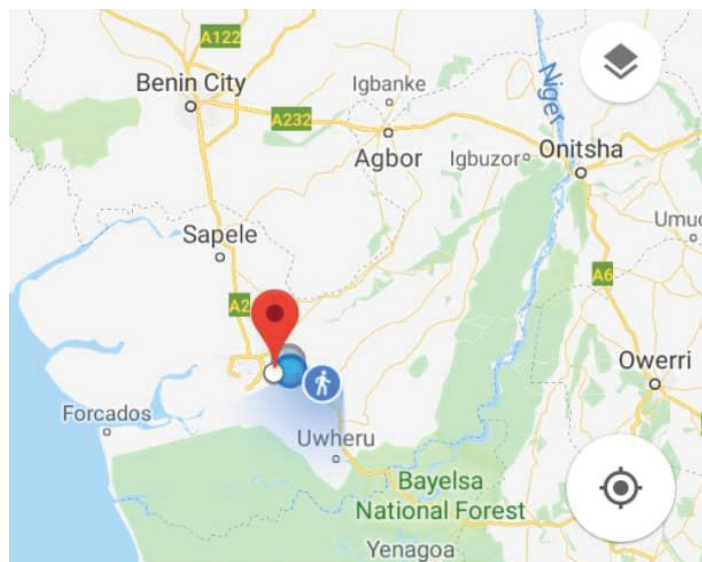


Figure 1: Map showing study location.

2. Handheld digital EC meter.
3. Dry Combustion Chamber.
4. Kjeldahl Facility.
5. Flame Photometric.
6. Atomic Absorption Spectrometric.
7. Lab-science England 721-AUV Spectrophotometer at 480 pm Wavelength.
8. Measuring plastic Buckets.
9. Measuring Cylinder.
10. Weighing Balance.
11. Cole-Parmer Viscometer.
12. Force Tensiometer.
13. Hydrometer.

Preliminary data collection and analysis: Prior to the commencement of the field and experimental work, I strongly adhered to the compliance of personal Protective Equipment (PPES) and monitored by my supervisor. Quantity of loamy soil was collected from the study area as presented in section 3.3 of this report and put into polythene bags. Approximately 70 kg of loamy soil was collected from the study area. Also 100 liters of raw petroleum was obtained from Shell location at Kolo-Creek, Bayelsa State (Figure 2).

Petroleum properties and composition: Petroleum is a mixture of a very large number of compounds. Most of the compounds in petroleum consist of molecules made up of hydrogen and carbon atoms only, we call these type of compounds hydrocarbons. The colour of Petroleum is Black. Its Physical properties vary from locations or oil wells. For the purpose of this research, raw Petroleum was obtained from Kolo Creek Location in Bayelsa State, Nigeria. The Chemical structural formula is summarized as C_nH_{2n} with structure (Figure 3).

Preliminary analysis was conducted to know the physical properties of petroleum and the data was obtained using Cole-Parmer Viscometer, Force Tensiometer and Hydrometer for viscosity, surface tension and density respectively.



Figure 2: Preliminary analysis of soil.

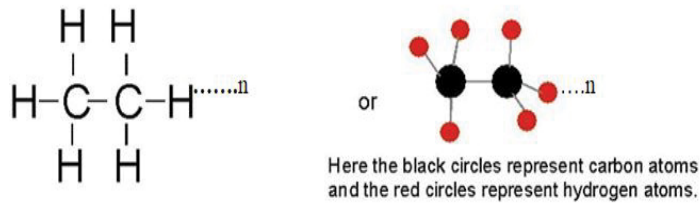


Figure 3: Petroleum structure.

Density (ρ) \Rightarrow 834000 kg/m³

Viscosity (μ) \Rightarrow 10.04 kg/mh

Surface tension (σ) \Rightarrow 0.031 N/M.

Loamy soil composition and properties: Interestingly the loamy soil properties were also determined in order to ensure achievement of study deliverables.

Loam soils generally dark brown in colour contain more nutrients, moisture, and humus, have better drainage and infiltration of water and air, and are easier to till. Other properties includes:

Bulk density 1.33 g/cm³.

Particle size > 63 μ m.

Silt texture composition particle size > 2 μ m.

Clay texture particle size < 2 μ m.

By weight, its mineral composition is about 40-40-20% concentration of sand-silt-clay, respectively. Its textural structure is presented in Figures 4 and 5.

Cow dung composition and properties: The Properties and Composition of Cow Dung is mainly dried from their feeding habit. It is known universally that cow feeds mostly on grasses. It means that the Cow Dung basic elements are made up of carbon, oxygen, nitrogen, and phosphorus. As it goes through the process of photosynthesis, it also contains chlorophyll and cellulose. The two main components of grass are water and lignin.

Cow dung can also be referred as Cattle manure and is basically made up of digested grass and grain. Cow dung is high in organic materials and rich in nutrients. It contains about 3 percent nitrogen, 2 percent phosphorus, and 1 percent potassium (3-2-1 NPK). In addition, cow manure contains high levels of ammonia and potentially dangerous pathogens. Other properties include:

Colour: black.

Chemical composition:

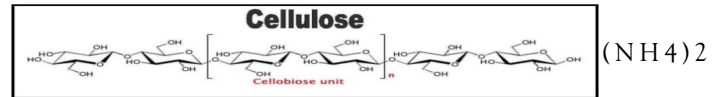
3% Nitrogen,

2% Phosphorus,

1% Potassium (3-2-1 NPK).

In addition, cow manure contains high levels of ammonia and potentially dangerous pathogens. Cow dung contains diverse group of microorganisms such as Acinetobacter, Bacillus, Pseudomonas, Serratia and Alcaligene spp. This makes them suitable for microbial degradation of pollutants.

Cow dung chemical structure: The chemical structure of Cow dung is mainly the combination of Ammonium carbonate hydroxide and cellulose and small proportion of Phosphate, Potassium and calcium. Thus,



CO₃ OH + \Rightarrow Cow Dung

Ammonium Carbonate Hydroxide

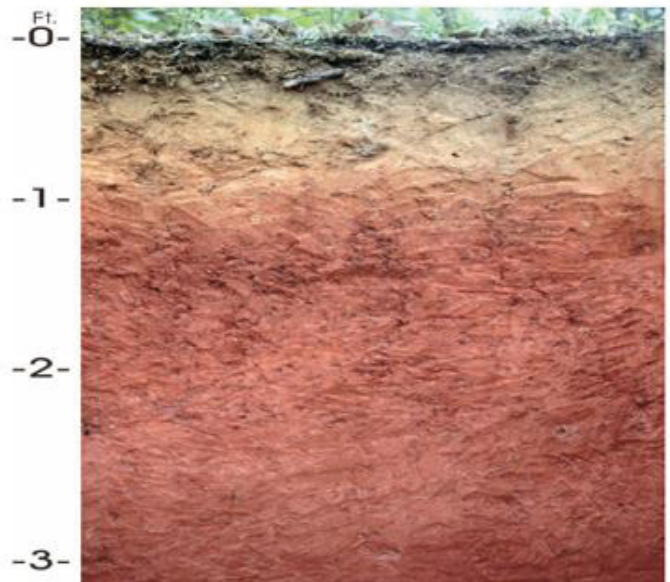


Figure 4: Colour specifications.

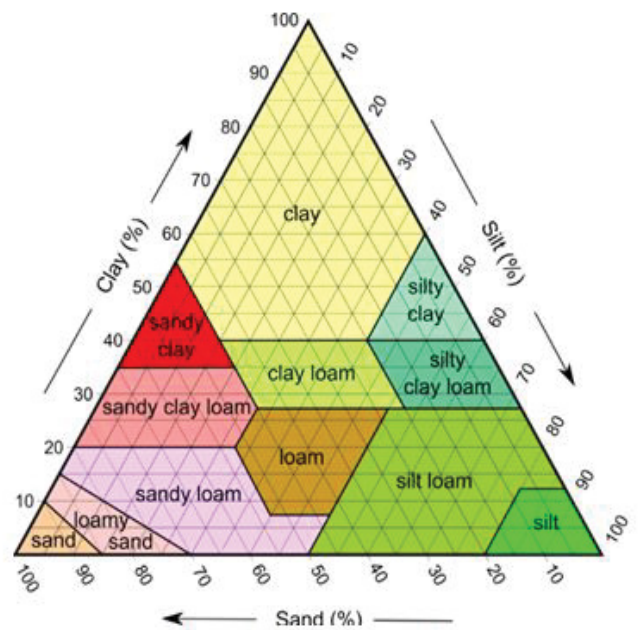


Figure 5: Texture structure.

In line with the above cow dung chemical components are presented in Table 2.

Experimental Procedure

The experimental procedure is shown in Figure 6 and comprise of a graduated laboratory plastic bucket measuring approximately 0.3 m depth and 0.1 m radius. The experimental set-up was in three dimensions. First dimension was a control experimental set-up (CTR) whereby about 3.2 kg of loamy soil was poured into the graduated cylindrical bucket at no petroleum nor cow dung nutrient added throughout the duration of the study period. The aim of the control experimental set-up is to establish possible effect of the original loamy soil physicochemical properties by the addition of the petroleum with no nutrient (NN) and with nutrient (WN). Therefore, the following loamy soil properties were determined for the control experiment in order to benchmark those of the remediated petroleum polluted loamy soil. The soil properties investigated includes:

- pH,
- Electrical conductivity (EC),
- Total organic matter (TOM),
- Total nitrogen,
- Total phosphorus,
- Total potassium.

The second dimension was the mixture of 3.2 kg loamy soil and the varying quantity petroleum with no nutrients poured into eight plastic buckets and duly mixed manually to obtain homogeneity. The second was focused to the provision of Total Petroleum Hydrocarbon Concentration at varying volume and exposure effect.

The third dimension was the mixture at 3.2 kg loamy soil, varying quantity of petroleum and 0.5 kg of cow-dung nutrient poured into eight plastic buckets, duly mixed manually to ensure homogeneity. Thus third provided a basis for the Total Petroleum Hydrocarbon effect for varying petroleum quantity and exposure time with cow - dung nutrient (WN).

Detailed pictorial presentation as evident of research work done sighted in Figure 7. Qualitative quantification of loamy soil and petroleum with no nutrient and with nutrient at various petroleum volume 250-190 ml and exposure time 0 - 32 days at intervals of 20 ml and 4 days respectively is given in Table 3.

The experimental procedure was accomplished coupled with observation and results were deduced and presented in the next section.

RESULTS AND DISCUSSION

The laboratory experiment for total petroleum hydrocarbon

Table 2: Chemical component of cow manure.

Chemical components (%)	Cow Manure
Moisture	75.30
Organic matter	24.20
Total Nitrogen (N)	0.90
Total Phosphorus (P ₂ O ₃)	0.40
Available potassium (K)	0.35
Available calcium (Ca)	0.70

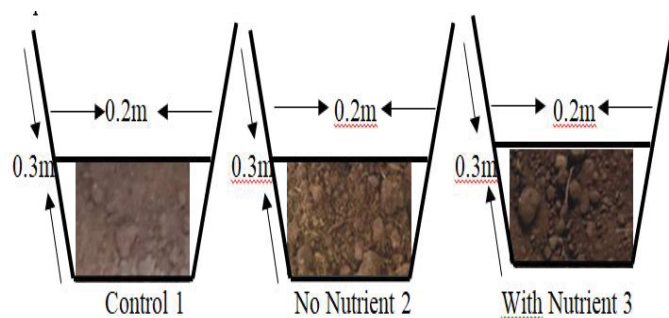


Figure 6: Hypothetical experimental set-up.



Figure 7: Pictorial presentation showing detailed experimental set-ups.

Table 3: Quantification of loamy soil with petroleum at nutrient and with nutrient.

Properties	CTR	NN	WN	Method of Analysis
pH	6.85	8.1	5.72	Handheld digital pH meter
Electrical conductivity (EC) (pS/m)	420	485	739	Handheld digital EC meter
Total organic matter (TOM) (g/kg)	5.19	5.07	118	Dry combustion method
Total organic carbon (TOC) (mg/kg)	34.52	70.18	72.67	Dry combustion method
Total Nitrogen (mg/kg ¹)	400	395	645	Kjeldahl Method
Total Phosphorus (mg/kg ¹)	272	268	341	Flame Photometric
Total Potassium (mg/kg)	207	207	470	Atomic absorption spectrometric
Total Petroleum Hydrocarbon (TPH) (mg/kg)	None Detectable (ND)	To be Investigated	To be Investigated	Atomic absorption spectrometric

concentration (C_{TPH}) was conducted in Luco Scientific Co. LTD - Chemical Laboratory located in Benin, Edo State.

The laboratory experimental work was in four (4) phases

namely:

1. Investigation of physicochemical properties at zero (0) polluted loamy soil-control (CTR), petroleum polluted loamy soil with no cow dung nutrient (NN) and with cow dung (WN) as samples received initially (0-4 days).
2. Investigation of Total Petroleum Hydrocarbon concentration (C_{TPH}) of petroleum polluted loamy soil with no nutrient (NN).
3. Investigation of Total Petroleum Hydrocarbon Concentration (C_{TPH}) of petroleum polluted loamy soil with nutrient (WN).
4. Investigation of physicochemical properties of bio-remediated loamy soil to benchmark the properties at zero (0) polluted loamy soil-control (CTR), petroleum polluted loamy soil with no cow dung nutrient (NN) and with cow dung (WN) as final samples received ending-32 days.

Initial physicochemical properties of loamy soil at control (CTR), NN and WN: Presented in Table 4 are initial Investigation of physicochemical properties at zero (0) polluted loamy soil-control (CTR), petroleum polluted loamy soil with no cow dung nutrient (NN) and with cow dung (WN) as samples received (0-4 days). (Soil Properties in first day of experiment).

Final physicochemical properties of loamy soil at control (CTR), NN and WN: Presented in Table 5 are Investigation of physicochemical properties at zero (0) polluted loamy soil-control (CTR), petroleum polluted loamy soil with no cow dung nutrient (NN) and with cow dung (WN) as samples received ending -32 days. (Soil Properties in 32-day of experiment).

TPH concentration (C_{TPH}) of petroleum polluted loamy soil with no nutrient (NN): Presented in Table 6 are results of Total Petroleum Hydrocarbon concentration (C_{TPH}) of petroleum

polluted loamy soil with no cow dung nutrient (NN) within the study limits of petroleum quantity discharged $V=50$ ml to 190 ml step 20 ml incremental and exposure time of 0 to 32 days step 4 days incremental. The designated letter A1 to A8 is without the addition of the 0.5 kg cow dung nutrient. This analysis is also presented in section 3 of this project where the A values are converted into kg.

TPH concentration (C_{TPH}) of petroleum polluted loamy soil with nutrient (WN): Presented in Table 7 are results of total petroleum hydrocarbon concentration (C_{TPH}) of petroleum polluted loamy soil with cow dung nutrient (NN) within the study limits of petroleum quantity discharged $V=50$ ml to 190 ml step 20 ml incremental and exposure time of 0 to 32 days step 4 days incremental. The designated letter B1 to B8 is with the addition of the 0.5 kg cow dung nutrient and petroleum quantity to the loamy soil of 3.2 kg. This analysis is also presented in section 3 of this project where the A values are converted into kg.

DISCUSSION

In this section, results of the experimental work are discussed in line with the research scope. Therefore, synopsis for discussion includes but not limited to the following:

1. Loamy soil physiochemical properties at the control (CTR) as a function of polluted site with no cow-dung nutrient at the first day of analysis (0-4 days) and the final 32-day.
2. Loamy soil physiochemical properties at the control (CTR) as a function of polluted site with cow dung nutrient at the first day of analysis (0-4 days) and the final 32-day.
3. Total petroleum hydrocarbon concentration (C_{TPH}) effect as a function of petroleum quantity discharged and exposure time with no cow dung nutrient (NN).

Table 4: Initial Physicochemical Properties of Loamy Soil at Control (CTR), NN and WN-50 ml.

Properties	CTR	NN	WN	Method of Analysis
pH	6.85	8.1	5.72	Handheld digital pH meter
Electrical conductivity (EC) (pS/m)	420	485	739	Handheld digital EC meter
Total organic matter (TOM) (g/kg)	5.19	5.07	118	Dry combustion method
Total organic carbon (TOC) (mg/kg)	34.52	70.18	72.67	Dry combustion method
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Total Phosphorus (mg/kg)	272	268	341	Flame Photometric
Total Potassium (mg/kg)	207	207	470	Atomic absorption spectrometric
Total Petroleum Hydrocarbon (TPH) (mg/kg)	None Detectable (ND)	To be Investigated	To be Investigated	Atomic absorption spectrometric

Table 5: Final Physicochemical Properties of Loamy Soil at Control (CTR), NN and WN-50 ml.

Properties	CTR	NN	WN	Method of Analysis
pH	6.85	7.20	6.87	Handheld digital pH meter
Electrical conductivity (EC) (pS/m)	420			Handheld digital EC meter
Total organic matter (TOM) (g/kg)	5.19	5.01	106	Dry combustion method
Total organic carbon (TOC) (mg/kg)	34.52	68.51	72.13	Dry combustion method
Total Nitrogen (mg/kg)	400	214	402	Kjeldahl Method
Total Phosphorus (mg/kg)	272	208	289	Flame Photometric
Total Potassium (mg/kg)	207	207	470	Atomic absorption spectrometric (AAS)
Total Petroleum Hydrocarbon	None Detectable (ND)	Investigated	Investigated	Atomic absorption spectrometric

Table 6: TPH Concentration (C_{TPH}) of petroleum polluted loamy soil with no nutrient (NN).

Time (Days)	TPH	TPH	TPH	TPH	TPH	TPH	TPH	TPH
	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)
	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8
0	51.053	106.842	67.895	89.474	115.789	128.421	135.263	167.895
4	42.105	66.842	77.368	86.842	107.895	101.053	141.579	143.684
8	37.895	58.947	72.105	65.789	91.053	91.579	121.053	130.526
12	26.316	39.474	61.053	64.737	85.263	87.368	99.474	101.053
16	25.789	31.053	56.842	62.632	81.579	83.158	95.789	97.895
20	26.316	30.000	54.211	61.579	80.526	79.474	88.947	95.263
24	23.158	30.000	50.000	60.000	76.842	78.421	83.158	91.579
28	22.632	27.368	48.421	59.474	74.737	77.368	83.579	90.000
32	23.158	26.842	47.895	60.000	74.211	76.316	83.158	90.000

Note: Where $A_1=50$ ml, $A_2=70$ ml, $A_3=90$ ml, $A_4=110$ ml, $A_5=130$ ml, $A_6=150$ ml, $A_7=170$ ml and $A_8=190$ ml

Table 7: TPH Concentration (C_{TPH}) of petroleum polluted loamy soil with nutrient (WN).

Time (Days)	TPH	TPH	TPH	TPH	TPH	TPH	TPH	TPH
	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)
	B_1	B_2	B_3	B_4	B_5	B_6	B_7	B_8
0	127.895	135.263	154.737	162.105	166.842	170.000	174.737	183.158
4	84.211	106.842	130.526	138.421	142.632	155.263	160.526	160.526
8	57.368	76.316	91.579	128.947	117.368	130.526	138.947	152.632
12	34.211	25.789	35.789	89.474	42.632	80.000	98.421	104.737
16	17.368	23.158	32.105	85.263	40.000	73.684	95.263	102.105
20	12.632	21.579	28.421	74.737	34.737	69.474	91.053	95.263
24	11.053	20.526	26.316	72.105	28.947	66.842	83.684	86.316
28	6.316	17.368	21.053	26.842	27.895	46.842	71.579	81.579
32	5.263	16.842	21.579	24.737	32.105	47.368	70.000	80.526

Note: Where $B_1=50$ ml, $B_2=70$ ml, $B_3=90$ ml, $B_4=110$ ml, $B_5=130$ ml, $B_6=150$ ml, $B_7=170$ ml and $B_8=190$ ml

- Total petroleum hydrocarbon concentration (C_{TPH}) effect as a function of petroleum quantity discharged and exposure time with cow dung nutrient (WN).
- Modelling total petroleum hydrocarbon concentration (C_{TPH}) as a function of variable dimensions of petroleum polluted loamy soil with no cow dung nutrient (NN).
- Modelling total petroleum hydrocarbon concentration (C_{TPH}) as a function of variable dimensions of petroleum polluted loamy soil with cow dung nutrient (WN).
- Comparison analysis of total Petroleum Hydrocarbon concentration (C_{TPH}) at NN and WN.

Physicochemical properties at CTR, NN: Results of physicochemical properties of loamy soil for CTR are compared with those 50 ml petroleum polluted loamy soil for the study period of 0-32 days exposure time. The results were observed to show higher deviational values of NN than those of CTR for pH, electrical conductivity (EC), Total organic carbon. While the values of physicochemical properties for total nitrogen, total organic matter and total phosphorus for NN were less than those of CTR. Interestingly, it is observed that the total potassium value for CTR and NN are the same. These observations are well presented in Tables 4 and 5. In other words, the effect of oil pollution in loamy soil environment does not alter the total potassium values. Also in Tables 4 and 5, a remarkable observation deduced from the results

demonstrated great deal of effect as the exposure time increases. The physicochemical properties of the NN at longer exposure time of 32 days normalizes the physicochemical properties to the same level of those in the CTR. This might be due to the natural attenuation (RENA) of the bio degradability of the hydrocarbon by the atmospheric micro-organisms. This observation is in conformity with the works of Ofoegbu et al. [10]. Hence, in the earlier periods of oil pollution, the methods adopted were RENA which actually enhances soil amendments through vertical and horizontal windowing. This process used to be accomplished via tilling and breaking of the impacted soil.

Physicochemical properties at CTR, WN: Similarly, results of physicochemical properties of loamy soil for CTR were compared with those 50 ml petroleum polluted loamy soil with cow dung nutrient for the study period of 0-32 days exposure time. The results were observed to show mild upper deviational values of WN than those of CTR for pH, total organic carbon, total organic matter, total nitrogen, total phosphorus and total potassium. These observations are well presented in Tables 4 and 5. Also in Tables 4 and 5, a remarkable observation deduced from the results with the addition of the cow dung nutrient demonstrated great deal of effect as the exposure time increases. The physicochemical properties of the WN at longer exposure time of 32 day components like total organic matter (TOM), total organic carbon (TOC), total phosphorus and total potassium. This observation seems to be real because the chemistry of the cow dung contains

the above mentioned elements as depicted in the literature review. Interestingly, the soil facility depends on these physiochemical properties. Hence the addition of the cow dung to the petroleum polluted site enhances rapid bioremediation process.

Similarly, critical comparison analysis of the physiochemical properties of NN and WN were very interesting in that the physiochemical properties of the polluted soil normalizes faster with the addition of the cow dung nutrient as evident in Tables 6 and 7. This may also be due to the coupled atmospheric micro-organism and the augmented cow dung nutrients in enhancing the bio degradability of the hydrocarbon. This observation is again, in conformity with the works of Ofoegbu [10]. As reflected in the literature, it is recommended clearly that the soil augmentation through organic nutrients such as cow dung coupled with the natural attenuation process enhances faster remediation of petroleum impacted sites.

Petroleum quantity effect on TPH concentration (C_{TPH}) for NN: Based on the experiment conducted, the results obtained shows non linearity behaviour with respect to TPH concentration as a function of volume of crude oil for varying exposure time (t). The TPH concentration increases with increase in the volume of petroleum discharged for various time of the investigation. This observation is well presented in Figure 8.

Petroleum quantity effect on TPH concentration (C_{TPH}) for WN: Conversely TPH Concentration (C_{TPH}) vs petroleum quantity spilled with cow dung nutrient (WN) for varying exposure time plotted and the results shows that the TPH concentration (C_{TPH}) increases with increase in the quantity of petroleum spilled at various exposure time (t) this observation is well depicted and presented in Figure 9.

A critical observation was deduced from the results in Figures 8 and 9 on the TPH concentration (C_{TPH}) vs petroleum volume for both NN and WN both graphs demonstrated non linearity behavior. The TPH concentration (C_{TPH}) values of WN seems to be higher than those of NN at various exposure time (t). This critical observation showed that the cow dung nutrient entails higher hydrocarbon contents that boosted the TPH concentration (C_{TPH}) values.

A plot of TPH concentration vs petroleum quantity discharged at exposure time of 32 days as presented in Figure 10 demonstrated this deviation. The Biodegradable rate of polluted site for a longer exposure time is faster with cow dung nutrient and also acted better than those without nutrients N). Although at the initial time of 4 days, the reverse is the case as in Figure 11. This may be due to the fact that, the cow dung is composed of hydrocarbon elements, so this seems to shoot up the TPH concentration (C_{TPH}) and eventually reduced at loner exposure time (t).

Exposure time effect on TPH concentration (C_{TPH}) for NN: The results as presented in Table 6 were carefully examined to ascertain the TPH concentration behaviour as a function of exposure time for a polluted site with no cow dung nutrient (NN). The results showed that TPH concentration decreased with increase in time for various quantity of petroleum spills discharged into the environment. The graphs also demonstrated non linearity with rather parabolic or quadratic behaviour. This characteristic behaviour of TPH concentration (C_{TPH}) decrease with increase in exposure time (t) might be motivated due to natural attenuation

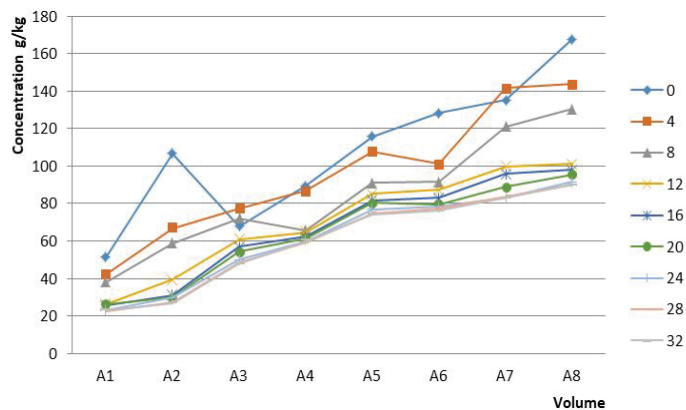


Figure 8: TPH concentration (C_{TPH}) vs volume for contaminated soil without nutrient NN.

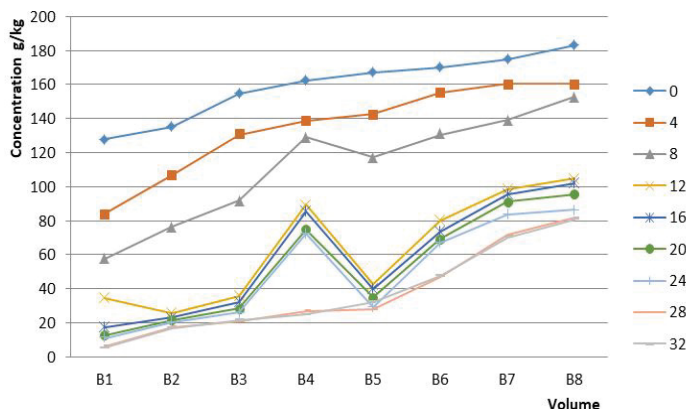


Figure 9: TPH concentration vs volume for polluted soil with nutrient (cow dung) WN.

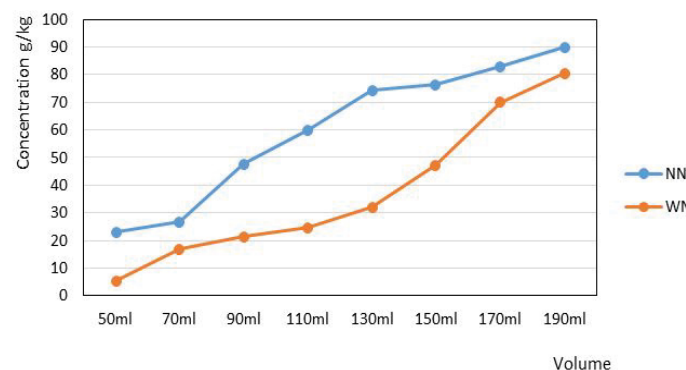


Figure 10: TPH concentration vs petroleum quantity discharged at 32 days.

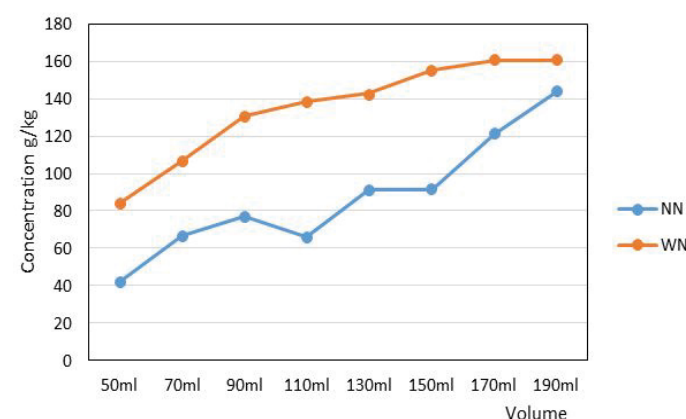


Figure 11: TPH concentration vs petroleum quantity discharged at 4 days.

process (RENA) taking place. Figure 12 shows this characteristic behaviour as discussed above. The outcome of this result is also compatible with previous works of Omogoye and Ayotamuna et al. [14,15].

Exposure time effect on TPH concentration (C_{TPH}) for WN: Similarly, the results obtained in Table 7 were plotted for TPH concentration (C_{TPH}) vs time for various quantities of petroleum considered in this study for a polluted site with cow dung nutrient (WN). The results observed were quite interesting in the sense that the TPH concentration (C_{TPH}) decreases with increase in exposure time for all the petroleum quantities spilled into the loamy soil environment. Figure 13 showed the plot of TPH concentration vs time and the characteristic behaviour is confirmed as claimed in this text above. The results of TPH concentration (C_{TPH}) vs time for various volumes of petroleum quantities for polluted loamy soil environment for without nutrient (NN) and with cow dung nutrient (WN) were compared [16-18]. The results demonstrated that the TPH concentration (C_{TPH}) at the earlier exposure time of 4-8 days interval at various volumes of petroleum for polluted site with no nutrient (NN) are less than those with nutrient (WN) [18-22]. The plot of TPH concentration (C_{TPH}) vs exposure time for constant 50 ml quantity of petroleum discharged for NN and WN is presented in Figure 14. The profile as in Figure 14 confirms as claimed above. As the volume of petroleum quantity discharge increases, the TPH Concentration level for both NN and WN increases simultaneously [23,24]. This observation is obvious that the degree of impactation of a polluted site increases with increase in the quantity of oil spilled, this is well observed in Tables 6 and 7.

Modelling TPH concentration (C_{TPH}) variable dimensions for polluted site with no nutrient (NN): In order to establish the dimensionless constant, (ϕ_{MNN}) as in equation (14), and recalling accordingly and putting ϕ_{MNN} gives that:

$$C_{TPH} = \phi_{MNN} \left[(tK_L \mu_p \sigma_p) / V^{2/3} \right] \quad (27)$$

From the plot, in Figure 14, extrapolation is made of TPH concentration (C_{TPH}) was made for constant petroleum quantity and found out that C_{TPH} is correlated to exposure time (t) and is given by

$$C_{TPH} = 2.08t^{0.4} \quad (28)$$

In order to evaluate ϕ_{MNN} , equation (28) is compare with equation resulting to;

$$\phi_{MNN} = \left(2.08V^{2/3}t^{0.4} \right) / (tK_L \mu_p \sigma_p) \quad (29)$$

Equation (29) can further be simplified as;

$$\phi_{MNN} = \left(2.08V^{2/3}t^{-0.6} \right) / (K_L \mu_p \sigma_p) \quad (30)$$

The dimensionless constant ϕ_{MNN} signifies the predictive factor that can be used to confirm the effect of TPH concentration of petroleum polluted site as a function of petroleum physical properties, soil conductivity but is independent of petroleum density with no nutrient (NN) [25-28].

Modelling TPH concentration (C_{TPH}) variable dimensions for polluted site with nutrient (WN): In the same vein, in order

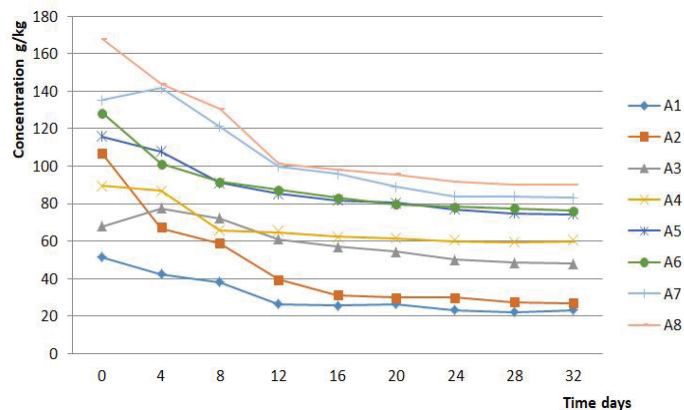


Figure 12: TPH concentration vs exposure time (t) for various petroleum quantities NN.

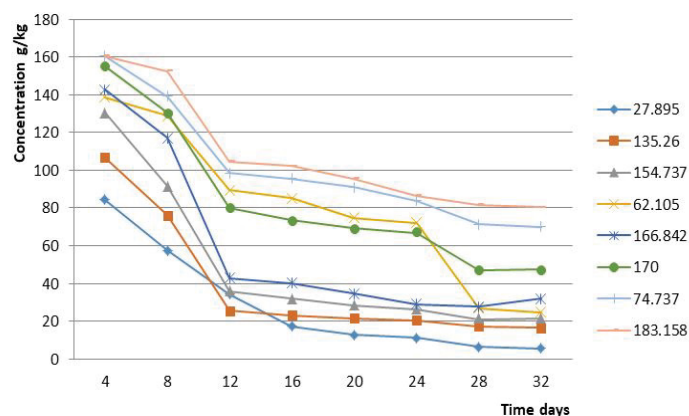


Figure 13: TPH concentration vs exposure time (t) for various petroleum quantities WN.

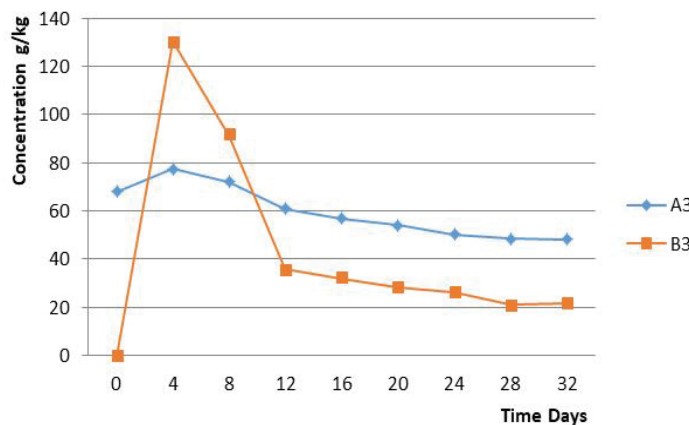


Figure 14: TPH concentration vs exposure time (t) for NN and WN at 50 ml.

to correlate TPH concentration (C_{TPH}) variable dimensions for polluted sites with nutrients, we recall equation (26) and putting $C_{TPH} =$, then equation 26 is given as;

$$C_{TPHWN} = \phi_{MWN} \left[\frac{(tM_{cd}K_L \mu_p \sigma_p)}{\left(\rho_p^2 V_p^{7/3} \right)} \right] \quad (31)$$

Similarly, from the plot as in Figure 14, extrapolation is made using graphical method and C_{TPH} is established to be:

$$C_{TPH} = 2.08t^{0.5} \quad (32)$$

In order to evaluate the dimensionless constant as a function of crude oil physical properties, quantity spilled, mass of cow dung and loamy soil conductivity, equation 31 and 32 are compared:

$$.08t^{0.5} = \phi_{MWN} \left[\left(tM_{cd}K_L\mu_p\sigma_p \right) / \left(\rho_p^2 V_p^{7/3} \right) \right] \quad (33)$$

Therefore, equation 33 upon further simplification gives:

$$\phi_{MWN} = \frac{2.08t^{-0.5} \rho_p^2 V_p^{7/3}}{M_{cd}K_L\mu_p\sigma_p} \quad (34)$$

Equations 30 and 32 can be called Omoruwou, Abowei, Tumininu dimensionless constant for the evaluation of the effect of the TPH concentration for polluted sites for no nutrient and with nutrient respectively [29].

CONCLUSION AND RECOMMENDATIONS

Evaluation of cow dung effectiveness for bioremediation in petroleum polluted loamy soil site is studied. The results obtained showed that cow dung nutrient is ideally effective for bioremediation of petroleum polluted site. In addition predictive models for the simulation of Total petroleum Hydrocarbon concentration is developed. The developed equation was expressed for C_{TPH} as a function of petroleum physical properties, soil conductivity, and quantity of cow dung. The predictive models show that C_{TPH} is independent of petroleum density for polluted site with no nutrient but density dependency with polluted site with nutrient. The developed models are generalized and can be applied in any polluted site.

From the outcome of the studies, cow dung should be used as a nutrient for the remediation of oil spill polluted sites. Secondly, it is my obvious recommendations that further work should be done in the following areas:

1. The effectiveness of cow dung on other soil properties for petroleum polluted sites as this work was limited to the investigation of C_{TPH} .
2. The diffusion rate as a function of C_{TPH} for oil spill polluted environment with and without cow dung nutrients.

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