ABUAD Journal of Engineering Research and Development (AJERD)
ISSN: 2645-2685

Volume 3, Issue 2, 1-11

Investigating the Rate of Uptake of TPH, TOC, Organic Matter and Some Heavy Metals by Melon Grass in a Crude Oil Polluted Soil in the Tropical Region

Modestus Chidera UWAZIE[1], Okechukwu Dominic ONUKWULI[2], Akinpelu Kamoru BABAYEMI[3], Jonah Chukwudi UMEUZUEGBU[3]

[1]*Department of Chemical Engineering, Imo State Polytechnic Umuagwo, Imo State, Nigeria*
uwaziemodestus@gmail.com

[2]*Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria*
onukwuliod@yahoo.com

[3]*Department of Chemical Engineering, Chukwuemeka Odumegwu Ojukwu University, Anambra State, Nigeria*
akinbabs40@yahoo.com/umejonah@gmail.com

Corresponding Author: akinbabs40@yahoo.com

Date Submitted: 26/01/2020
Date Accepted: 16/03/2020
Date Published: 31/12/2020

Abstract: This research was aimed at finding the rate at which melon grass take up TPH (total petroleum hydrocarbons), TOC (total organic carbon) and heavy metals like lead, zinc, nickel, potassium, calcium, from a petroleum contaminated soil. Four wooden boxes were made and 7.5 kg of soil was added in each of the boxes. These two boxes were also polluted with 150 g of crude oil, one out of these two boxes were amended with 150g of cow dung. The other two boxes were also polluted with 75 g of crude oil, also one box out of these two was amended with 150g of cow dung. A control box which has no crude oil contamination was also grown to aid comparisons. At the end of the three months growth period, melon grass was able to remediate TPH from an initial 6.784 µg/g (for 75 g pollution) to 6.356 µg/g, and from an initial 9.109 µg/g (for 150 g pollution) to 7.713 µg/g. Lead was reduced from 0.699 mg/kg to 0.002 mg/kg, zinc was reduced from 0.851 mg/kg to 0.506 mg/kg. It was discovered that a close corresponding value of what was remediated from the soil was found in plant. Nickel, however, did not show any significant change in value. A predictive mathematical model was developed to predict how long it will take to remediate TPH and the heavy metals and bring the soil back to its original state.

Keywords: Phytoremediation, melon grass, total petroleum hydrocarbon, heavy metals, moving boundary models.

1.INTRODUCTION

Prior to the period of oil boom, the Niger Deltans were predominantly farmers. They provided the nation with most of the agricultural produce like fish, palm oil, etc, but now most of these farm produces are being imported [1].

It is also an obvious fact that even in the case of oil spillages, the communities that were affected are after compensation by the oil company concerned rather than the clean-up of the affected area. Consequently, a lot of spilled sites are left unattended to, thus reducing the available fishing, farming and even building spaces. Again, there are cases of remediation attempts by the oil companies but most of them were inconclusive and abandoned. Based on the above issues, it is imperative to find a remediation method that will be affordable, and at the same time available to the rural dwellers before oil spillage will turn to a norm in the Niger Delta region.

Quantification of risks and impacts associated with environmental management options, and design of remediation systems are also needed [2]. To achieve this, a reliable predictive tool (usually in the form of numerical simulation models) is required. However, this work tries to assert the application of predictive models to achieve an efficient phytoremediation of petroleum contaminated soil.

Achieving remedy to oil polluted sites (soil) has always been the concern of several studies [3]. A wide range of remediation measures have been preferred with the aim of offering solution to the damages caused by crude oil on nature of the soil and its physiochemical characteristics. Over the years, the biological methods of remediating the environment have received much interest. This is due to its ability to reduce, detoxify and mineralize chemical contamination, bringing chemical balance at low cost. Phytoremediation is associated by numerous advantages such as its cost friendliness, environmental friendliness, non-complexity in technology, preservation of soil texture and properties and its ability to produce non-toxic end products. This is opposing other physiochemical treatment methods whose demerits include; movement of pollutants from one place/phase to another, being a rigorous technology and capital intensive to implement at commercial scale [4]. Due to the limitations of the physiochemical technologies stated above, great deal of literature has reported that phytoremediation methods are the best option and/or supplements to these methods.

Phytoremediation is a non-destructive, cost-friendliness, on site technology that helps in a large extent to remediate polluted soils. If pollution is caused by petroleum hydrocarbons, plants can stimulate microbes to break down the contaminant in the rhizosphere. The potential for success of this technology for the tropics is high due to the prevailing climatic conditions enhancing plant growth and stimulating microbial activity [5].

Plants can bring to harmless state, extract or stabilize a contaminant in soil, thereby making the contaminant(s) unreachable for other organisms and reducing environmental hazards. Mechanism of this technology called phytoremediation depends on the type of contaminant, bioavailability and soil properties [6].

Besides the varying rates of biodegradation, researchers have consistently documented a lag time after oil is spilled before indigenous microbes begin to break down the oil molecules [7]. This lag time is related to the initial toxicity of the volatile fractions of the oil, which evaporate in the first few days of a spill. Microbial populations must begin to use oil and expand their population before measurable degradation takes place, a period usually lasting several days. This fact becomes very important when considering the appropriateness of phytoremediation as a quick or first response technique. Soil pollution is widespread in Nigeria leading to varying forms of degradation and is associated with loss of bioresources especially plant materials [8]. In reaction to this, it becomes imperative to use biological techniques in restoring and resisting further degradation.

This research pays attention to the investigation of the phytoremediation potential of a selected legume plant on a petroleum contaminated soil using the plant as remediation agent. This was ascertained following two main stages of work; establishing relevant characterization parameters before and after polluting the collected soil sample and then analyzing the grown plant (at the end of the phytoremediation period) to compare its characterizing properties relative to that grown on the control soil.

2.1 Materials

2.1.1 Sample/Material collection

The soil sample used for the experiments was collected within Umuanunu Community in Obinze Town located in Owerri-West L.G.A of Imo State, Nigeria, tropical rain forest. The melon seeds used for the work was also purchased from same locality. The crude oil used was collected from the Shell Petroleum development company (SPDC), Etelebou flow station, Bayelsa state. The soil sample was collected from a fertile farmland location of the village communal farm area, with a large nylon bag and well labelled before being delivered to the laboratory for the laboratory tests.

2.1.2 Soil sample/Material preparation

The soil sample was superficially dried for two days after which it was further meshed and then sieved through 2mm mesh size. The sieved soil samples were then used for the laboratory analysis.

Four soil sample groups, each weighing 7.5kg were measured out and separated for the experimental purpose. One more sample weighing the same (7.5kg) was reserved as the control sample. Two out of these four groups were contaminated with petroleum to the concentrations of 1w/w%. The other two groups were also contaminated with petroleum to concentrations of 2w/w%. Again, to the pair of the polluted samples, one of each group were further enriched with organic manure (cow dung), while the others were not. This was basically to check the effect of enrichment on the polluted soil, in the phytoremediation of the soil.

2.2 Methods

2.2.1 Experimental procedure

The phytoremediation study took place from the month of August to October 2017. The treatment was subdivided into four groups. Each of the treatment groups 1-4 constitutes three (3) replicate treatments. The only common proportion of all was the petroleum contaminated soil of 7.5kg. The target was to find out how different levels of contamination and enrichment would affect the degradation of a petroleum contaminated soil. The objective of the variation in the treatment levels was to investigate the most appropriate quantity of each treatment option that will give the best remediating result.

The soil set-up/grouping for the remediation study is as follows:

Group B: The constituent replicates in this group were made up of 7.5kg of soil + 75g of crude oil + 150g cow dung, each of which were analyzed at intervals of approximately six weeks during the twelve-week study period.

Group C: The constituent replicates in this group were made up of 7.5kg of soil + 150g of crude oil + 150g cow dung, each of which were analyzed at intervals of approximately six weeks during the twelve-week remediation study.

Group D: The constituent replicates in this group were made up of 7.5kg of soil + 75g of crude oil, each of which were analyzed at approximately six-week intervals for the period of twelve weeks.

Group E: The constituent replicates in this group were made up of 7.5kg of soil + 150g of crude oil, each of which were analyzed at intervals of approximately six weeks for the period of twelve weeks.

It is worthy of mention the necessity of oxygen in phytoremediation of oil-contaminated soil, hence all the replicates were supplied with little watering and exposed to oxygen by milled tilling in order to facilitate degradation.

Table1 shows how the experiment was divided into four treatment groups; each treatment had 7.5kg of soil plus different proportions (75g or 150g) of crude oil and then either with or without organic manure.

Table1: Experimental design for the phytoremediation study

Options	Treatment/enrichment
Group B	7.5kg soil + 75g crude oil + 150g cow dung
Group C	7.5kg soil + 150g crude oil + 150g cow dung
Group D	7.5kg soil + 75g crude oil
Group E	7.5kg soil + 150g crude oil

The experimental layout is shown in Table 2 below;

Table 2: Experimental Layout

	Treatment Groups			
Treatment number	B	C	D	E
1 (Before planting)	S_{B1}	S_{C1}	S_{D1}	S_{E1}
2 (Within planting period)	S_{B2}	S_{C2}	S_{D2}	S_{E2}
3 (After planting)	S_{B3}	S_{C3}	S_{D3}	S_{E3}

where:

S_{B1} - 7.5kg soil + 75g crude oil + 150g cow dung (Before planting)
S_{B2} - 7.5kg soil + 75g crude oil + 150g cow dung (Within planting period)
S_{B3} - 7.5kg soil + 75g crude oil + 150g cow dung (After planting)
S_{C1} - 7.5kg soil + 150g crude oil + 150g cow dung (Before planting)
S_{C2} - 7.5kg soil + 150g crude oil + 150g cow dung (Within planting period)
S_{C3} - 7.5kg soil + 150g crude oil + 150g cow dung (After planting)
S_{D1} - 7.5kg soil + 75g crude oil (Before planting)
S_{D2} - 7.5kg soil + 75g crude oil (Within planting period)
S_{D3} - 7.5kg soil + 75g crude oil (After planting)
S_{E1} - 7.5kg soil + 150g crude oil (Before planting)
S_{E2} - 7.5kg soil + 150g crude oil (Within planting period)
S_{E3} - 7.5kg soil + 150g crude oil (After planting)

This research work was conducted for approximately twelve weeks, during which soil and plant samples were taken to the laboratory for analysis at six weeks interval.

2.2.2 Model formulation

Continuity Equation was used to derive from different mass balance the general absorption equation for nutrient as;

$$\frac{\partial c}{\partial t} = \frac{1}{x^*}\frac{\partial}{\partial t}\left(x^* D\frac{\partial c}{\partial x}\right) - f(c) \quad (1)$$

C(x,t) in Equation (1) above denotes the concentration of the nutrient diffused at a distance x from the outer surface of the absorbing medium at time t, D is the diffusion coefficient, and f(c) represent the rate of consumption of the nutrient by the plant.

For this work, D is assumed to be constant for different nutrients, and the rate of nutrient consumption is constant for nutrients that are been consumed by the plant. For nutrients that are been absorbed but not consumed by the plant, the equation reduces to:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \quad (2)$$

and for nutrient consumed, we have

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - f(c) \quad (3)$$

At the initial phase of nutrient entering the surface of the plant, the boundary condition is

$$C = C_O \text{ at } x = 0, t \geq 0 \quad (4)$$

Where the surface concentration Co is a constant

At point x, when the gradient of the concentration becomes zero, then a steady state is obtained in which the concentration at the upward part of the tree becomes constant. The nutrient cannot diffuse beyond the point x unless a new boundary condition is obtained. The following conditions exist at this point;

$$C = 0 \text{ at } x \geq X, t \geq 0 \quad (5)$$

$$\frac{\partial c}{\partial x} = 0 \text{ at } x \geq X, t \geq 0 \quad (6)$$

For f(c) = β, for steady state condition for nutrient consumption, the equation solution is gotten as;

$$C = \frac{\beta}{2D}(x - X)^2 \quad (7)$$

$$X = \sqrt{(\frac{2DCo}{\beta})} \quad (8)$$

And for non-consuming nutrients which satisfy the condition in (2) and (3), we have

$$C = \frac{(x-X)^2}{2D} \quad (9)$$

$$X = \sqrt{(2DCo)} \quad (10)$$

At the point below x, where the nutrient exist at every point in its varying amount, and unsteady state is experienced. For the consuming nutrient, at these points, the nutrients are been consumed which makes their absorption more rapid, while for the non-consumed nutrients store up at the pores of the plant. The part of the diffusion and absorption can be represented by the following equations;

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - \beta \text{ at } 0 \leq x \leq X \text{ for consuming} \quad (11)$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \text{ at } 0 \leq x \leq X \text{ for non-consuming} \quad (12)$$

$$\frac{\partial c}{\partial x} = 0 \text{ at } x = 0, t \geq 0 \quad (13)$$

$$C = 0 \text{ at } x = X(t), t \geq 0 \quad (14)$$

$$\frac{\partial c}{\partial x} = 0 \text{ at } x = X(t), t \geq 0 \quad (15)$$

$$C = \frac{\beta}{2D}(x - X)^2 \text{at } 0 \leq x \leq X, t = 0 \text{ for consuming} \quad (16)$$

$$C = \frac{1}{2D}(x - X)^2 \text{at } 0 \leq x \leq X, t = 0 \text{ for non-consuming} \quad (17)$$

Using finite difference numerical solutions to solve Equations (11) and (12), we have for consuming nutrients

$$C_{i,j+1} = (\frac{D\Delta t}{\Delta x^2})C_{i+1,j} + (1 - \frac{2D\Delta t}{\Delta x^2})C_{i,j} + (\frac{2D\Delta t}{\Delta x^2})C_{i-1,j} - \beta \quad (18)$$

For non-consuming nutrients, we have

$$C_{i,j+1} = \left(\frac{D\Delta t}{\Delta x^2}\right)C_{i+1,j} + \left(1 - \frac{2D\Delta t}{\Delta x^2}\right)C_{i,j} + \left(\frac{2D\Delta t}{\Delta x^2}\right)C_{i-1,j} \qquad (19)$$

By defining new sets of variables,

$$y = \frac{x}{X}, \quad \tau = \frac{D}{x^2 t}, \quad \Theta = \frac{C}{2Co} = \frac{D}{\beta x^2}$$

and denoting $y_o(\tau)$as the value of y corresponding to x(t), Equations (11) to (17) reduces to:

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial Y^2} - 1 \qquad 0 \le y \le y_o(\tau) \qquad (20)$$

$$\frac{\partial \theta}{\partial y} = 0 \quad \text{at } y = 0,\ \tau \ge 0 \qquad (21)$$

$$\Theta = 0 \quad \text{at } y = y_o(\tau),\ \tau \ge 0 \qquad (22)$$

$$\frac{\partial \theta}{\partial y} = 0 \quad \text{at } y = y_o(\tau),\ \tau \ge 0 \qquad (23)$$

$$\Theta = 0.5(1-y)^2,\ 0 \le y \le 1,\ \tau = 0 \qquad (24)$$

For non-consuming nutrients,

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial Y^2} \qquad (25)$$

The above equations represent a moving boundary problem, and since not only the concentration of the nutrient is always zero at the boundary, but also, no nutrient diffuses across the boundary at any time, there is no relationship which contains the velocity of the moving boundary explicitly.

3.0 RESULTS AND DISCUSSION

3.1 Results presentation

Results of the laboratory tests conducted on the soil and plant samples obtained are presented below:

Table 3: Result for unpolluted soil sample

S/N	PARAMETER	RUN 1	RUN 2	RUN 3	AVERAGE
1	TPH, µg/g	0.014	0.010	0.016	0.013
2	TOC, %	1.60	1.70	1.60	1.63
3	Organic matter, %	5.98	5.47	5.88	5.78
4	Potassium, mg/kg K	40.00	45.00	50.00	45.00
5	Calcium, mg/kg Ca	12.62	12.66	11.30	12.19
6	Nickel, mg/kg Ni	0.15	0.13	0.14	0.14
7	Zinc, mg/kg Zn	1.57	1.58	1.62	1.60
8	Lead, mg/kg Pb	2.06	2.04	1.83	1.98

Table 4: Textural class of unpolluted soil sample

S/N	TEXTURAL CLASS	MESH SIZE (mm)	SOIL SIZE (%)
1	Pebble Stone	4.750	-
		3.350	-
2	Very Coarse Sand	1.180	0.61
3	Coarse Sand	1.000	0.87
4	Medium Coarse Sand	0.425	31.44
		0.300	18.86
5	Fine Sand	0.212	30.90
		0.125	8.96
		0.106	2.98
6	Very Fine Sand	0.075	2.13
		0.053	0.05
7	Silt	< 0.053	3.20

3.1.1 Soil analysis before planting, 18th August 2017

Table 5: Result for polluted soil sample (amended)

S/N	PARAMETER	B (7.5 kg Soil polluted with 75 g crude oil + 150 g Cow dung)				C (7.5 kg Soil polluted with 150 g crude oil + 150 g Cow dung)			
		B_1	B_2	B_3	Average	C_1	C_2	C_3	Average
1	TPH,µg/g	6.783	6.785	6.785	6.784	9.394	9.175	8.757	9.109
2	TOC, %	5.40	5.70	5.60	5.57	5.84	5.93	5.79	5.85
3	Organic matter, %	20.98	20.76	19.56	20.43	22.73	24.47	23.75	23.65
4	Potassium, mg/kg K	46.00	47.00	47.00	46.67	44.58	43.74	44.57	44.30
5	Calcium, mg/kg Ca	11.56	11.34	11.48	11.46	10.74	11.05	11.17	10.99
6	Nickel, mg/kg Ni	0.029	0.029	0.031	0.030	0.032	0.030	0.034	0.032
7	Zinc, mg/kg Zn	0.984	0.823	0.793	0.867	0.904	0.804	0.846	0.851
8	Lead, mg/kg Pb	0.456	0.472	0.512	0.48S	0.674	0.695	0.729	0.699

Table 6: Result for polluted soil sample (unamended)

S/N	PARAMETER	D (7.5kg Soil polluted with 75g crude oil)				E (7.5kg Soil polluted with 150g crude oil)			
		D_1	D_2	D_3	Average	E_1	E_2	E_3	Average
1	TPH,µg/g	7.247	7.937	7.573	7.59	9.95	10.05	10.12	10.04
2	TOC, %	6.46	7.17	7.04	6.89	8.03	8.15	9.02	8.40
3	Organic matter, %	14.48	13.96	14.26	14.23	15.15	15.10	15.07	15.11
4	Potassium, mg/kg K	45.17	44.63	45.73	45.18	44.26	42.74	43.16	43.39
5	Calcium, mg/kg Ca	11.36	11.28	11.25	11.30	11.27	11.28	11.15	11.23
6	Nickel, mg/kg Ni	0.005	0.003	0.002	0.003	0.000	0.000	0.000	0.000
7	Zinc, mg/kg Zn	0.843	0.853	0.786	0.827	0.850	0.854	0.852	0.852
8	Lead, mg/kg Pb	0.346	0.329	0.362	0.436	0.404	0.402	0.398	0.401

3.1.2 Soil analysis within planting period, 26th September 2017

Table 7: Result for polluted soil sample (amended)

S/N	PARAMETER	B (7.5kg Soil polluted with 75g crude oil + 150g Cow dung)				C (7.5kg Soil polluted with 150g crude oil + 150g Cow dung)			
		B_1	B_2	B_3	Average	C_1	C_2	C_3	Average
1	TPH, µg/g	6.493	6.515	6.481	6.500	8.419	8.673	8.236	8.443
2	TOC, %	5.21	5.27	5.18	5.22	5.42	5.38	5.29	5.36
3	Organic matter, %	16.46	15.43	15.38	15.76	20.04	21.46	20.92	20.81
4	Potassium, mg/kg K	23.84	25.29	22.22	23.78	18.94	20.17	19.73	19.61
5	Calcium, mg/kg Ca	11.13	10.84	10.88	10.95	10.67	11.80	11.72	11.40
6	Nickel, mg/kg Ni	0.025	0.035	0.033	0.031	0.053	0.061	0.057	0.057
7	Zinc, mg/kg Zn	0.784	0.693	0.663	0.713	0.746	0.772	0.809	0.776
8	Lead, mg/kg Pb	0.127	0.174	0.211	0.171	0.244	0.219	0.259	0.241

Table 8: Result for polluted soil sample (unamended)

S/N	PARAMETER	D (7.5kg Soil polluted with 75g crude oil)				E (7.5kg Soil polluted with 150g crude oil)			
		D_1	D_2	D_3	Average	E_1	E_2	E_3	Average
1	TPH, µg/g	6.37	7.47	6.99	6.94	7.89	7.92	8.11	7.97
2	TOC, %	6.09	5.67	5.95	5.90	7.58	7.30	8.06	7.65
3	Organic matter, %	13.83	13.73	12.96	13.51	15.78	15.64	15.47	15.72
4	Potassium, mg/kg K	18.754	16.947	21.196	18.966	24.67	22.76	19.85	22.43
5	Calcium, mg/kg Ca	10.63	10.46	11.04	10.71	11.02	11.17	11.21	11.13
6	Nickel, mg/kg Ni	0.043	0.051	0.049	0.0477	0.018	0.030	0.026	0.025
7	Zinc, mg/kg Zn	0.653	0.715	0.863	0.744	0.780	0.556	0.704	0.680
8	Lead, mg/kg Pb	0.164	0.229	0.172	0.188	0.207	0.184	0.191	0.194

3.1.3 Soil analysis after planting, 24th October 2017

Table 9: Physico-chemical parameters for polluted soil sample (amended)

S/N	PARAMETER	B (7.5kg Soil polluted with 75g crude oil + 150g Cow dung)				C (7.5kg Soil polluted with 150g crude oil + 150g Cow dung)			
		B_1	B_2	B_3	Average	C_1	C_2	C_3	Average
1	TPH,µg/g	6.236	6.485	6.356	6.359	7.473	7.483	8.183	7.713
2	TOC, %	5.18	5.04	4.75	4.99	5.36	5.37	3.49	14.22
3	Organic matter, %	16.84	15.74	14.95	15.84	17.37	16.38	15.59	16.45
4	Potassium, mg/kg K	3.379	3.337	3.603	3.440	3.205	3.301	3.395	3.300
5	Calcium, mg/kg Ca	10.26	10.73	10.29	10.43	10.00	10.05	10.02	10.02
6	Nickel, mg/kg Ni	0.043	0.042	0.044	0.043	0.052	0.061	0.058	0.057
7	Zinc, mg/kg Zn	0.565	0.568	0.546	0.560	0.502	0.497	0.518	0.506
8	Lead, mg/kg Pb	0.0580	0.058	0.058	0.058	0.0572	0.059	0.062	0.059

Table 10: Physico-chemical parameters for polluted soil sample (unamended)

S/N	PARAMETER	D (7.5kg Soil polluted with 75g crude oil)				E (7.5kg Soil polluted with 150g crude oil)			
		D_1	D_2	D_3	Average	E_1	E_2	E_3	Average
1	TPH,µg/g	6.537	6.836	6.756	6.710	6.936	6.904	7.059	6.966
2	TOC, %	4.72	4.63	4.44	4.60	5.12	5.03	4.95	5.03
3	Organic matter, %	14.72	13.82	12.38	13.64	16.94	15.37	15.98	16.10
4	Potassium, mg/kg K	8.103	7.937	8.073	8.038	12.783	12.750	12.762	12.765
5	Calcium, mg/kg Ca	8.26	9.49	9.92	9.22	9.82	9.38	9.86	9.69
6	Nickel, mg/kg Ni	0.033	0.038	0.037	0.036	0.021	0.021	0.026	0.023
7	Zinc, mg/kg Zn	0.483	0.485	0.492	0.487	0.404	0.412	0.382	0.399
8	Lead, mg/kg Pb	0.020	0.027	0.021	0.023	0.000	0.000	0.006	0.002

3.1.4 Analysis on plant

Table 11: Physico-chemical parameters for control plant

S/N	PARAMETER	RUN 1	RUN 2	RUN 3	AVERAGE
1	Moisture content, %	18.44	19.03	18.37	16.61
2	Ash content, %	12.87	11.97	12.06	12.30
3	Organic matter, %	87.68	88.73	87.28	87.91
4	Nitrate-Nitrogen, mg/kg NO_3-N	9.47	10.06	10.18	9.90
5	Potassium, mg/kg K	28.46	31.17	29.03	29.55
6	Calcium, mg/kg Ca	16.83	17.08	16.56	16.82
7	Nickel, mg/kg Ni	1.652	1.652	1.652	1.652
8	Mercury, mg/kg Hg	0.988	0.988	0.974	0.983
9	Cadmium, mg/kg Cd	0.072	0.075	0.072	0.073
10	Lead, mg/kg Pb	0.430	0.432	0.430	0.431

Table 12: Physico-chemical parameters for plant from polluted soil sample (amended)

S/N	PARAMETER	Plant from Pot B (7.5 kgSoil polluted with 75 g crude oil +150 g Cow dung)				Plant from Pot C (7.5 kg Soil polluted with 150 g crude oil + 150 g Cow dung)			
		B_1	B_2	B_3	Average	C_1	C_2	C_3	Average
1	Moisture content, %	14.28	14.37	14.73	14.46	13.83	14.13	13.92	13.96
2	Ash content, %	15.48	15.37	15.87	15.57	15.89	15.76	15.66	15.77
3	Organic matter, %	78.28	76.38	79.47	78.04	76.93	77.04	77.33	77.10
4	Nitrate-Nitrogen, mg/kg NO_3-N	8.94	9.02	8.94	8.97	8.76	9.94	8.34	9.01
5	Potassium, mg/kg K	15.72	14.93	14.78	15.14	13.93	14.07	13.77	13.92
6	Calcium, mg/kg Ca	11.10	10.92	10.98	11.00	11.07	10.70	10.38	10.72
7	Nickel, mg/kg Ni	1.646	1.603	1.588	1.612	2.188	1.908	1.986	2.027
8	Mercury, mg/kg Hg	1.908	2.007	2.111	2.009	2.807	3.104	3.012	2.974
9	Cadmium, mg/kg Cd	0.016	0.029	0.012	0.019	0.027	0.034	0.022	0.028
10	Lead, mg/kg Pb	3.750	3.738	3.750	3.746	4.081	3.828	3.857	3.922

Table 13: Physico-chemical parameters for plant from polluted soil sample (unamended)

S/N	PARAMETER	Plant from Pot D (7.5kg Soil polluted with 75g crude oil)				Plant from Pot E (7.5kg Soil polluted with 150g crude oil)			
		D_1	D_2	D_3	Average	E_1	E_2	E_3	Average
1	Moisture content, %	13.36	14.08	13.82	13.75	11.16	11.44	10.94	11.18
2	Ash content, %	15.88	15.29	14.85	15.34	15.64	15.37	15.38	15.46
3	Organic matter, %	75.12	76.64	76.11	75.96	73.84	75.02	74.93	74.60
4	Nitrate-Nitrogen, mg/kg NO_3-N	7.97	7.58	7.86	7.80	7.86	7.83	7.94	7.88
5	Potassium, mg/kg K	13.63	13.85	14.03	13.84	13.22	13.70	13.28	13.40
6	Calcium, mg/kg Ca	12.73	11.70	11.85	12.09	11.07	10.70	10.38	10.72
7	Nickel, mg/kg Ni	1.583	1.701	1.685	1.656	2.328	2.448	2.392	2.389
8	Mercury, mg/kg Hg	2.204	2.187	2.417	2.269	2.811	2.920	3.144	2.958
9	Cadmium, mg/kg Cd	0.022	0.026	0.023	0.024	0.027	0.034	0.022	0.028
10	Lead, mg/kg Pb	3.864	3.868	3.899	3.877	3.998	3.897	4.126	4.007

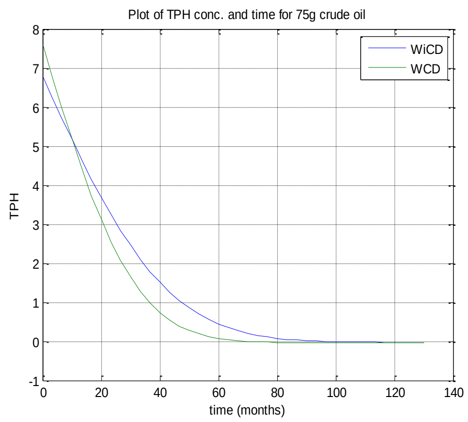

Fig. 1: Comparison of TPH values for 7.5kg polluted soil with 75g crude oil with and without cow dung

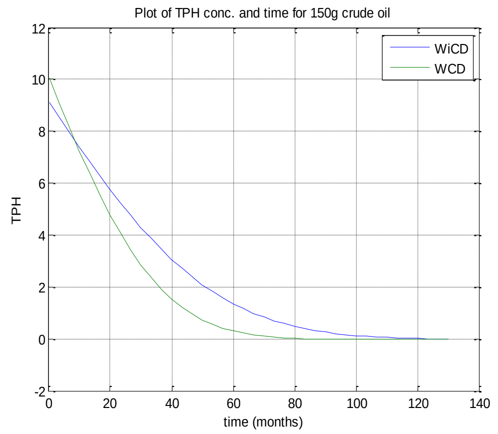

Fig. 2: Comparison of TPH values for 7.5kg polluted soil with 150g crude oil with and without cow dung

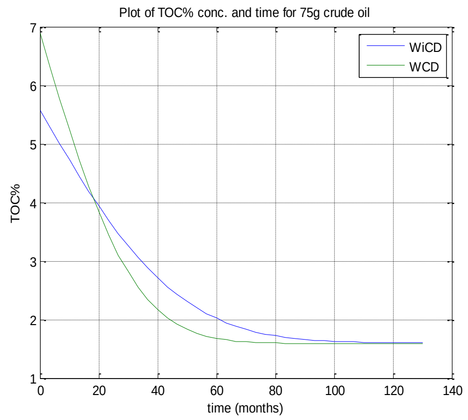

Fig. 3: Comparison of TOC values for 7.5kg polluted soil with 75g crude oil with and without cow dung

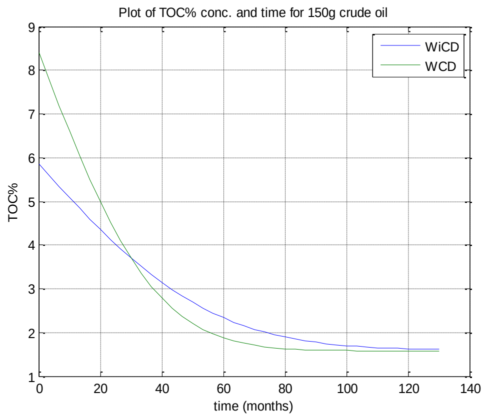

Fig. 4: Comparison of TOC values for 7.5kg polluted soil with 150g crude oil with and without cow dung

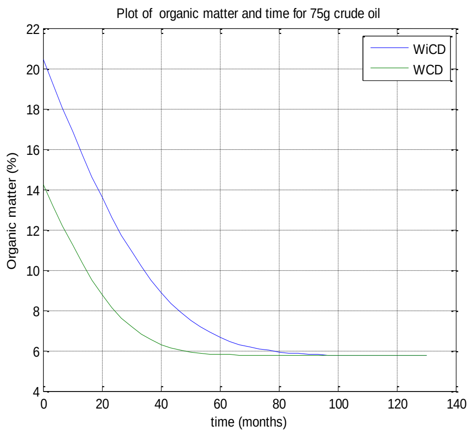

Fig. 5: Comparison of organic matter for 7.5kg polluted soil with 75g crude oil with and without cow dung

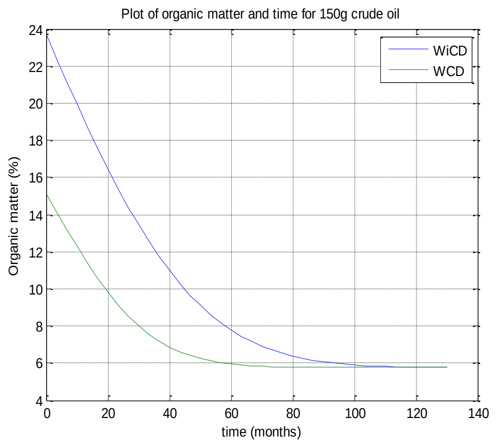

Fig.6: Comparison of organic matter for 7.5kg polluted soil with 150g crude oil with and without cow dung

KEY

WCD	Without cow dung
WiCD	With cow dung

3.2 Discussion of Results

The modelled results show comparison of every sample for without cow dung (un-amended) and when cow dung was introduced (amended). The model shows at what time the nutrient is likely to normalize at the original state of the soil as in Table 1 for all parameter considered. The model only considers for time period when TPH, TOC and organic matter will normalize to soil value.

Continuity equation was used to derive from different mass balance the general absorption equation for nutrients (1) and was used as starting point for the various models developed for nutrients absorbed but not consumed, and nutrients absorbed and consumed, where Equation (1) was reduced to Equations (2) and (3) respectively. Moving boundary conditions were then applied on the equations to develop models which were solved numerically with the aid of the computer software (MATLAB 7.9) using the finite difference technique, and the generated solutions made as comparative plots for the nutrient absorption by the plants in the different soil samples (i.e with and without amendment). The results are as shown in Figures 1 – 6, for three key phytoremediation parameters: total petroleum hydrocarbon (TPH), total organic carbon (TOC) and organic matter.

The result in Figure.1 shows the value of TPH concentration with and without cow dung for 75g crude oil contaminated soil. Though at initial values, TPH with cow dung was higher than without cow dung, the cow dung was absorbed faster than without cow dung. This shows higher rates of absorption for the introduction of cow dung in the mixture as it will take about 63months for the soil to come to initial state as compared to without cow dung which will take about 96 months for complete absorption. For 150g contaminated crude oil as shown in Figure.2 for with and without cow dung, more time will be required to normalize the soil to its initial condition. Addition of cow dung influenced the absorption rate which reduced the needed time from approximately 112 months to 78 months.

For the percentage TOC value, despite the high value as at when cow dung was not added, the rate of absorption of the nutrient was faster and normalized at 65 months with cow dung for 75g crude oil contaminated soil from about 104 months (Figure 3), while for 150g crude oil contaminated soil, despite the large difference when cow dung was added, the absorption was far much faster and normalized at about 80 months as against 120 months when cow dung was not added as shown in Figure .4.

The organic matters initially reduced drastically with the addition of cow dung and could normalize at 60 months with addition of cow dung for 75 g crude oil contaminated soil as shown in Figure 5 as against the 88 months when cow dung was not added. For 150g contaminated crude oil as shown in Figure 6, the introduction of cow dung reduced the percentage organic matter normalization time from 100 months to about 60 months.

From the results discussed above, it is clear that cow dung had a great impact on the absorption of contaminant from soil to bring the soil back to its original state. Apart from some metals like potassium, calcium and zinc which had no significant change in its initial state, others were greatly affected by the addition of cow dung. The TPH value which is the main focus, gave an improved rate of absorption with the addition of cow dung.

The model developed with a moving boundary condition was used to describe the movement or absorption of the materials by the plant. The model showed that the cow dung will effect a better rate of absorption of the materials and bring the soil back to its original state, and at a reduced time as at when cow dung was not added.

4.0 CONCLUSION

Based on the results obtained from these experiments, the following conclusions can be drawn; Remediation of the oil contaminated soil at the end of twelve weeks revealed a positive impact of the contaminated soil enrichment with cow dung. Petroleum removal efficiency in terms of TPH can be minimized by 34.4% for (cow dung+ contaminated soil) over a period of 10 weeks within the range of experimental conditions investigated in this study. The above result indicates that the bio-stimulant employed in this study offer significant reduction in the hydrocarbon content.

This study demonstrates that at optimum load of bio-stimulant, the rate of nutrient absorption increases, and this corroborates the result obtained when cow dung was added to the contaminated soils before the legume planting. It was observed that the treatment measures employed in this work followed a moving boundary model with the ultimate contaminant concentration not being zero when the bio-stimulant was applied. Therefore, the moving boundary model approach employed in this work provided a good description of an effective phytoremediation process.

This study demonstrates that at optimum load of bio-stimulant, the rate of nutrient absorption increases, and this corroborates the result obtained when cow dung was added to the contaminated soils before the legume planting. It was observed that the treatment measures employed in this work followed a moving boundary model with the ultimate contaminant concentration not being zero when the bio-stimulant was applied. Therefore, the moving boundary model approach employed in this work provided a good description of an effective phytoremediation process.

REFERENCES

[1] Osoka, E.C.&Onyelucheya,O.E. (2011). Data-Driven Model for Palm Bunch Ash-Enhanced Bioremediation of a crude oil contaminated soil, 362-363.

[2] Oyoh, K.B & Osoka, E.C. (2002). Rate Model for Bioremediation Based on Total Petroleum Hydrocarbon Content, *Journal of Nigerian Society of Chemical Engineers*, 22 (2007),50-56.

[3] Leahy, J.G. & Crowell, R. R. (1990). Microbial Degradation of Hydrocarbons in theEnvironment. Microbio. Rev. 3, 305.

[4] Vidali, M. (2001). Bioremediation*:* An overview. *J. Appl. Chemistry*, 73(7), 1163–1172.

[5] Ikhajiagbe, B. & Anoliefo, G.O. (2011). Natural attenuation of a 14-month-old waste engine oil polluted soil. *J Soil Sci Environ Manage* 2: 184-192.

[6] Ebere, J.U., Wokoma, E.C.& Wokocha, C.C. (2011). Enhanced remediation of a hydrocarbon polluted soil, Research journal of environment and earth science.

[7] Thies, J.E. &Rillig, M.C. (2009). Characteristics of biochar: Biological properties. Ind. Microbial. Biotechnology, 30,260.

[8] Agarry, S.E., Aremu, M.O. & Aworanti O.A. (2013). Kinetic modelling and half- life study on enhanced soil bioremediation of bonny light crude oil amended with crop andanimal-derived organic waste. *J Pet Environ Biotechnol* 4: 137.