SJIF Impact Factor (2023): 8.574| ISI I.F. Value: 1.241| Journal DOI: 10.36713/epra2016 ISSN: 2455-7838(Online)
EPRA International Journal of Research and Development (IJRD)
Volume: 8 | Issue: 4 | April 2023 - Peer Reviewed Journal

MODELLING OF THE TOTAL PETROLEUM HYDROCARBON (TPH) DEGRADATION DURING THE BIOREMEDIATION OF CRUDE OIL POLLUTED SOIL USING COW DUNG AND WIRE CROTONS

Ifeanyichukwu Edeh[1*], Milicent Mauren Thomas[2]
[1,2]Department of Chemical Engineering, University of Port Harcourt, Nigeria
* ***Corresponding Author***

Article DOI: https://doi.org/10.36713/epra13084
DOI No: 10.36713/epra13084

ABSTRACT
The contamination of soil due to activities involved in crude oil exploration and production, and oil spillage emanating from pipeline vandalization, sabotage, theft, corrosion of pipeline and the enterprises of artisanal refineries pose health and ecological problems. This is especially as crude oil contains chemical compounds which are grouped into the Total Petroleum Hydrocarbons (TPH), and known to be toxic, mutagenic, and carcinogenic. Bioremediation is currently being explored as a cost effective and environmentally friendly methods of remediating the soil from this contaminant. Thus, the current work is aimed at developing a mathematical model for the bioremediation process. This was carried out while assuming that the process of degradation is a first order reaction, and the principle of the law of conservation of mass was applied. A linear model ($\ln C_{TPH(t)} = \ln C_{TPH(o)} - k_d t$) was developed relating the instantaneous concentration of TPH, initial concentration of TPH and time duration of the bioremediation. The model fitted well to the experimental data as shown by the result of the statistical analysis where the Analysis of Variance (ANOVA) showed a p-value of 0.004 suggesting that the model is statistically significant. The p-values of the model variables such as time duration of the bioremediation was 0.004, this suggested that the variable is significant. The model can be used as a supporting tool in the management of the biodegradation of TPH to predict the degradation concentration of TPH during the bioremediation process at ambient condition of temperature and pressure using cow dung, wire croton and their combination as a carbon source.
KEYWORDS: *Bioremediation; cow dung; wire croton; degradation; Mathematical modelling*

1.0 INTRODUCTION

In Nigeria, the Niger Delta region in the South has been largely affected by oil wastes generated during exploration and production, and spillage since crude oil was discovered in commercial quantity in 1958 at Oloibiri Bayelsa State, Nigeria. Crude oil exploration and production whether onshore or offshore generate high volume if oil wastes, and spillages from pipelines occurring as a result of sabotage, theft, corrosion of pipeline and the activities of artisanal refineries (ISS, 2022). Among other components, crude oil contains chemical compounds which are broadly refereed to as Total Petroleum Hydrocarbon (TPH) (Gustatson, 2007). Such chemicals include hexane, naphthalene, fluorine, other products of petroleum origin, and gasoline constituents (Alinnor and Nwachukwu, 2013). According to ATSDR (1999), due to the complexity in determining the constituent chemicals in crude oil, the total petroleum hydrocarbon is used instead. The impact of the petroleum hydrocarbons in the soil is dependent on its solubility in water, organic carbon affinity in soil, and the properties of the soil including particle size, porosity, organic matter composition, permeability and surface area (Koshlaf and Ball, 2017; Ali et al., 2020). Excess quantity of TPH in the soil reduces the respiration rate of the soil, growth of plants and the activity of the microorganisms. Most petroleum hydrocarbons encountered in the environment are ultimately degraded or metabolized by indigenous bacteria because of their energetic and carbon needs for growth and reproduction, as well as the requirement to relieve physiological stress caused by the presence of petroleum hydrocarbons in the microbial bulk environment (Hazen et al., 2010; Kleindienst et al., 2015). The contamination of soils by petroleum hydrocarbon causes health and ecological problems, especially as these hydrocarbons are toxic, mutagenic, carcinogenic, and have a low flowrate in the soil (Koshlaf and Ball, 2017; Hentati et al., 2013). Crude oil can be harmful to organisms including human and it degradation rate is extremely slow under normal circumstance. The crude oil spill penetrates to a depth of about 10-20 cm which has a major role to play in agricultural activities, resulting in the loss of soil fertility and, initiates environmental degradation (Ofoegbu et al, 2015). This singular process renders the soil impotent, i.e., the soil cannot produce crops as well as it could before the spill. Once the soil has been degraded, it is usually difficult to restore its original state. The majority of the available technologies used for remediating soil are quite expensive and not environmentally friendly compared to bioremediation. Bioremediation is a method that utilizes organisms in the soil such as decayed plants, bacteria and fungi for cleaning up the soil with less environmental impact

(Pilon-Smits, 2005). The method depends on bacteria, plants and fungi to degrade, breakdown, transform or remove contaminants or impairments of quality from the contaminated soil. This organisms require some amounts of nutrients such as nitrogen and phosphorus to carry out their biodegradation function (Margesin and Schinner, 1997; Choi et al., 2002). These nutrients are contained in animal dung and croton leave and the microorganisms utilize them as a carbon source. The microorganisms produced eat up the excess Petroleum Hydrocarbon content present in the soil. Bioremediation is a promising treatment method for crude oil contaminated sites and has a tendency to achieve complete mineralization of organic contaminants into carbon dioxide, water, and inorganic compounds (Ehirim et al 2020).

There is a paucity of knowledge on the hydrocarbon biodegradation in the soil, and prediction of the bioremediation outcome is often complex (Martin et al., 2022). The current work is focused on developing a simple mathematical model to predict the biodegradation of Total Petroleum Hydrocarbon in the crude oil polluted soil using cow dung, wire croton and their combinations as the nutrients for the bioremediation process.

2.0 MATERIALS AND METHODS

2.1 Materials

The soil, cow dung and wire croton were obtained from Obio-Akpor Local Government Area, Rivers State, Nigeria, and the crude oil was collected from Nigeria Agip Oil Company. After washing the wire croton, it was sun dried with the cow dung for one week before grinding into smaller particles, and sieving to obtain homogeneity and remove the unwanted materials.

2.2 Methods

2.2.1 Evaluating the impact of cow dung and wire croton on the bioremediation of crude oil contaminated soil.

This was carried out using the amount of materials shown in Table 1 and 1 kg of soil in each reactor. The experiment was conducted for 42 days (six weeks) and samples taken for analysis every week during this period. The total petroleum hydrocarbon (TPH) was analyzed using gas chromatography equipped with flame ionization detector. Samples were taken from each of the reactor and TPH was extracted using 50 mL of methylene chloride in a 1 L separating funnel. After vortexing for about 20 min and allowing for complete separation, the organic layer was separated from the aqueous layer. Further extractions were carried out from the aqueous layer using 25 mL of methylene chloride. The extract was dried by passing it through a drying column embedded with cotton wool, anhydrous sodium sulphate and silica. The extract was further dried by passing it through streams of nitrogen to a volume of 1.0 mL, and injected into the GC-FID for the TPH analysis.

The TPH at any time was obtained using Equation 1.

$$TPH_R(\%) = \frac{TPH_i - TPH_f}{TPH_i} \times 100\% \quad (1)$$

Table 1. Quantities of materials used for the bioremediation experiments

Batch reactor	Volum of crude Oil (mL)	Cow dung Weight (g)	Croton leaves Weight (g)
Control (1)	-	-	-
Control (2)	200	-	-
3	200	200	-
4	200	30	30
5	200	115	30
6	200	200	30
7	200	30	115
8	200	115	115
9	200	200	115
10	200	30	200
11	200	115	200
12	200	200	200
13	200	-	200

2.2.2Model Development

This was necessary to predict the quantity of TPH at any interval of time during the bioremediation of crude oil polluted soil using cow dung and wire croton. The following assumptions were made:

(i) The process is considered a batch process i.e., there is no flow of materials in and out of the reactor during the process.
(ii) The only components of the reactor are soil sample, crude oil and the nutrients added. Thus, the microorganisms produced from the cow dung and croton consume the crude oil in the contaminated soil.
(iii)The crude oil and soil samples were well mixed to completely simulate homogeneous mixture.
(iv) Cow dung and wire croton are assumed to have the same effect on TPH and are regarded as one nutrient

SJIF Impact Factor (2023): 8.574| ISI I.F. Value: 1.241| Journal DOI: 10.36713/epra2016 ISSN: 2455-7838(Online)
EPRA International Journal of Research and Development (IJRD)
Volume: 8 | Issue: 4 | April 2023 - Peer Reviewed Journal

(v) Temperature is constant throughout the period of the experiment
(vi) The effect of pH was neglected throughout the reaction
(vii) The volume of the reactor was constant throughout the period of the experiment
(viii) The degradation reaction is first order

Materials balance is used to develop the model as shown in Equation 2

$$\begin{Bmatrix}\text{Inflow of}\\ \text{mass into}\\ \text{system}\end{Bmatrix} = \begin{Bmatrix}\text{Outflow of}\\ \text{mass from}\\ \text{system}\end{Bmatrix} + \begin{Bmatrix}\text{Rate of}\\ \text{degradation}\\ \text{due to}\\ \text{reaction}\end{Bmatrix} + \begin{Bmatrix}\text{Rate of}\\ \text{accumulation}\\ \text{of mass}\\ \text{within system}\end{Bmatrix} \quad (2)$$

Where;

Inflow of mass into system $= Q_o C_{TPH(o)}$ (3)

Outflow of mass from system $= QC_{TPH}$ (4)

Rate of TPH degradation $= -r_{TPH}V$ (5)

Rate of accumulation $= \frac{d(C_{TPH}V)}{dt}$ (6)

And;

$Q_o =$ Inlet volumetric flow rate (kg/day); $Q =$ Outlet volumetric flow rate (kg/day); $C_{TPH(o)}$ = Initial concentration of pollutant (TPH) (mg/kg)

$C_{TPH} =$ Instantaneous concentration of pollutant (TPH) (mg/kg); $V =$ Volume of reactor (m^3); $r_{TPH} =$ Rate of TPH degradation (mg/kg. day); $k_d =$ TPH degradation rate constant (day^{-1}); $t =$ Time of TPH degradation (day)

Now, substituting Equations (3) through (6) into Equation (2) gives

$$Q_o C_{TPH(o)} = QC_{TPH} - r_{TPH}V + \frac{d(C_{TPH}V)}{dt} \quad (7)$$

For a batch process; $Q_o C_{TPH(o)} = QC_{TPH} = 0$ (8)

Since, the volume is constant;

Accumulation term becomes

$$\frac{d(C_{TPH}V)}{dt} = V\frac{dC_{TPH}}{dt} \quad (9)$$

Therefore, equation (7) reduces to

$$-r_{TPH}V = -V\frac{dC_{TPH}}{dt}$$

Or $$-r_{TPH} = -\frac{dC_{TPH}}{dt} \quad (10)$$

Assuming first order reaction, the rate of degradation;

$$-r_{TPH} = k_d C_{TPH}$$

And Equation (10) becomes

$$-r_{TPH} = -\frac{dC_{TPH}}{dt} = k_d C_{TPH} \quad (11)$$

By integrating Equation (11) using the separation of variable method, we obtain;

$$\int_{C_{TPH(o)}}^{C_{TPH(t)}} \frac{dC_{TPH}}{C_{TPH}} = -k_d \int_0^t dt \quad (12)$$

$$\ln\left(\frac{C_{TPH(t)}}{C_{TPH(o)}}\right) = -k_d t \quad (13)$$

$$\ln C_{TPH(t)} - \ln C_{TPH(o)} = -k_d t$$

SJIF Impact Factor (2023): 8.574| ISI I.F. Value: 1.241| Journal DOI: 10.36713/epra2016 ISSN: 2455-7838(Online)
EPRA International Journal of Research and Development (IJRD)
Volume: 8 | Issue: 4 | April 2023 - Peer Reviewed Journal

$$\ln C_{TPH(t)} = \ln C_{TPH(o)} - k_d t \quad (14)$$

Equation (14) is likened to the equation of a straight where $-k_d$ is the slope and $\ln C_{TPH(0)}$ is the intercept.

2.2.2 Model validation

The model develop was validated using the result of the TPH degradation obtained during the bioremediation of crude oil polluted soil using cow dung and wire croton. The model was fitted to the data presented in Table 2 to develop models that would be used to determine the concentration of TPH at any given bioremediation duration. Statistical analysis involving the residual plot and ANOVA were carried out to determined the validity of the model developed using the nutrients with 30 g of cow dung and 30 g of wire croton as an example.

3.0 RESULTS AND DISCUSSIONS

3.1 Evaluating the impact of cow dung and wire croton on the bioremediation of crude oil contaminated soil.

This was carried to obtain the required data for the validation of the model developed for the prediction of the quantity of TPH degraded at any point in time during the bioremediation of crude oil polluted soil using cow dung and wire croton. The method used was described in Section 2 and the results obtained are presented in Table 2

Table 2. Effect of nutrients on the degradation of the total petroleum hydrocarbon during a six weeks (42 days) of bioremediation

Sample	Day zero (mg/kg)	Week 1 (mg/kg)	Week 2 (mg/kg)	Week 3 (mg/kg)	Week 4 (mg/kg)	Week 5 (mg/kg)	Week 6 (mg/kg)
30gCD and 30gcroton	55422.3	49026.0	47510.6	46244.0	40941.7	31754.1	29454.4
200g croton	44345.0	33715.8	31568.6	27499.5	24542.7	19127.4	16145.6
30g CD + 115g croton	47560.8	42705.8	38563.5	34276.5	30984.7	27612.3	25370.9
115gCD + 30g croton	45156.6	39028.8	26541.2	21898.1	17297.0	15452.5	10993.8
200g CD	43745.8	35775.9	30871.5	27350.9	23872.1	19486.0	15900.0
30g CD + 200g croton	41372.9	32555.3	29325.6	24552.7	20154.4	17254.5	13076.0
115g CD + 115 croton	39207.3	29959.8	25514.4	21723.2	17868.0	13997.9	13997.9
200g CD + 30g croton	36993.3	27717.4	23413.3	19210.3	14667.9	10093.1	6319.5
115 CD + 200g croton	34730.1	25056.8	20890.2	16781.4	11134.6	8790.9	6319.5
200g CD + 115 croton	30808.6	22778.2	18790.5	14888.3	10878.7	7098.4	7098.4
200g CD + 200 croton	27593.1	20490.2	16105.9	12145.5	8891.0	4900.9	1506.3
Soil + crude oil only	64947.8	64135.6	63834.0	63145.7	62845.9	62054.8	59194.1

Where CD is cow dung

3.2 Model Development

Assuming first order degradation reaction and using material balance, a linear model was developed relating the concentration of TPH at time 0 and time t, and time (t) of TPH degradation as shown in Equation 14. This model is in agreement with that obtained by Ere and Ayodeji (2018) using mushroom as the nutrient in a ten week bioremediation process.

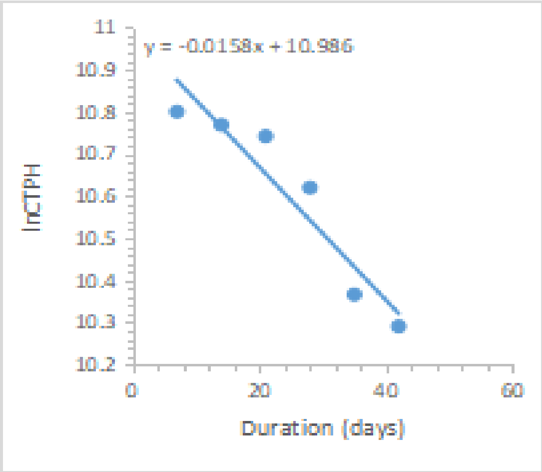
$$\ln C_{TPH(t)} = \ln C_{TPH(o)} - k_d t \quad (14)$$

The experimental data obtained by using cow dung, wire croton and their various combinations are presented in Table 2. The model developed was fitted into the experimental data and the results presented in Figure 1 were obtained. From the figure, y = Ln $C_{TPH\,(t)}$ and x = duration (t). The figure shows that the instantaneous concentration of TPH (concentration at any time during the bioremediation) can be determined if the bioremediation duration (time) is known. For instance, when the model (Equation 14) was fitted to the experimental data obtained from the bioremediation of the crude oil polluted soil using 30 g cow dung plus 30 g wire croton as shown in Figure 1(a), the following model was obtained.

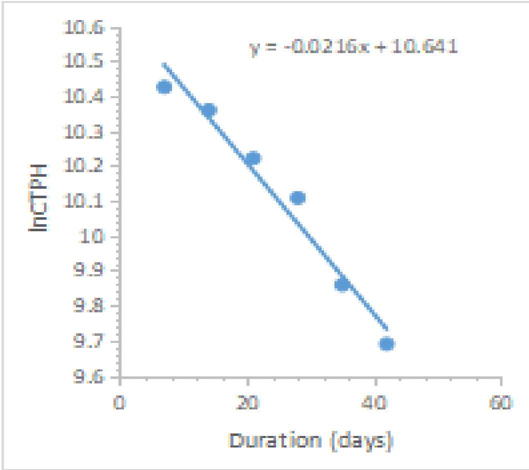
$$\text{Ln}\left(C_{TPH\,(t)}\right) = -0.0158x + 10.986 \quad (15)$$

SJIF Impact Factor (2023): 8.574| ISI I.F. Value: 1.241| Journal DOI: 10.36713/epra2016 ISSN: 2455-7838(Online)
EPRA International Journal of Research and Development (IJRD)
Volume: 8 | Issue: 4 | April 2023 - Peer Reviewed Journal

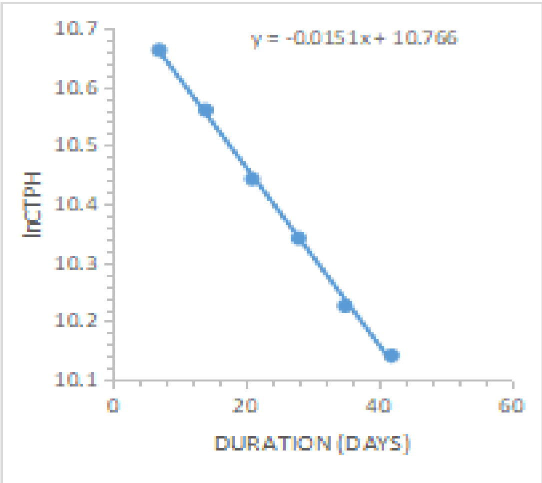
Or $\mathrm{Ln}\left(C_{TPH\,(t)}\right) = -0.0158t + 10.986$



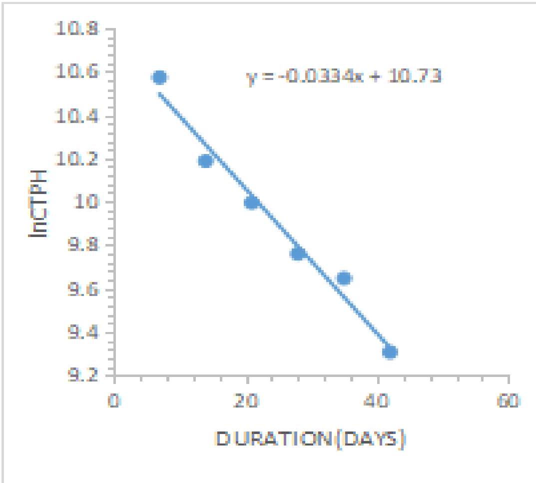
b. 30 g cow dung plus 30 g



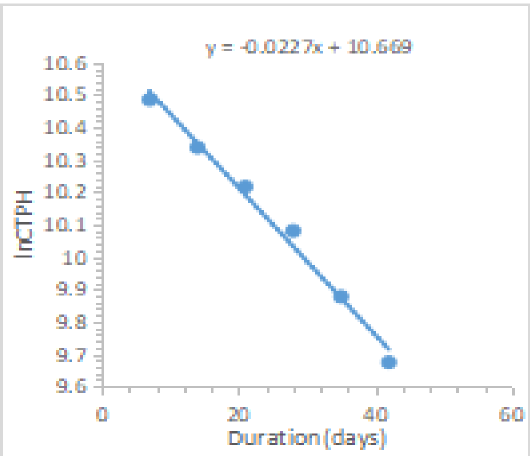
a. 200 g croton only croton



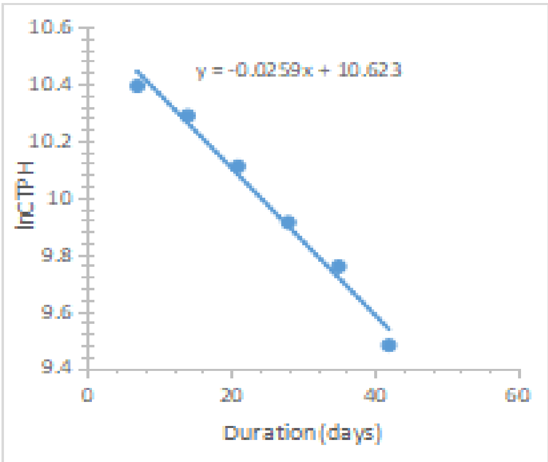
c. 30g cow dung plus 115g croton



d. 115g cow dung plus 30g croton



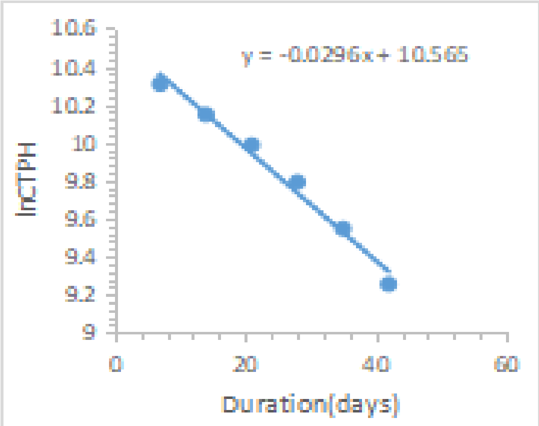
e. 200 g cow dung only



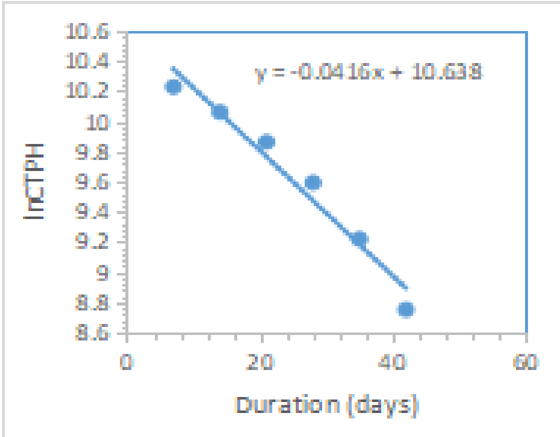
f. 30 g cow dung plus 200 g croton

Figure 1. Determining the initial concentration of TPH and degradation rate constant

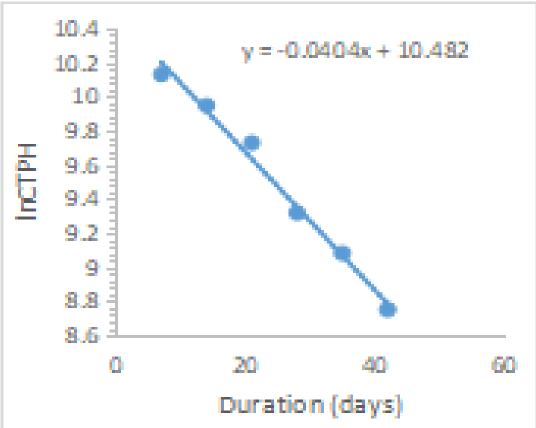
SJIF Impact Factor (2023): 8.574| ISI I.F. Value: 1.241| Journal DOI: 10.36713/epra2016 ISSN: 2455-7838(Online)
EPRA International Journal of Research and Development (IJRD)
Volume: 8 | Issue: 4 | April 2023 - Peer Reviewed Journal



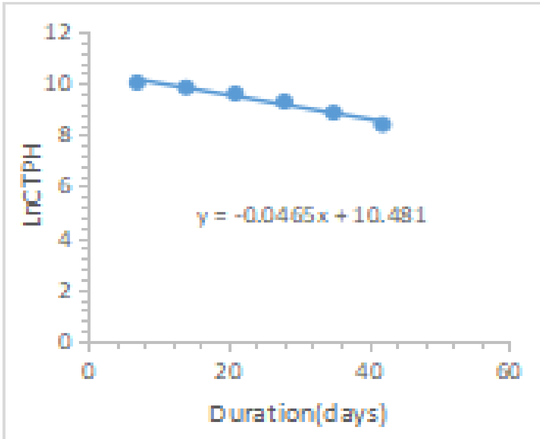
g. 115g cow dung plus 115g croton



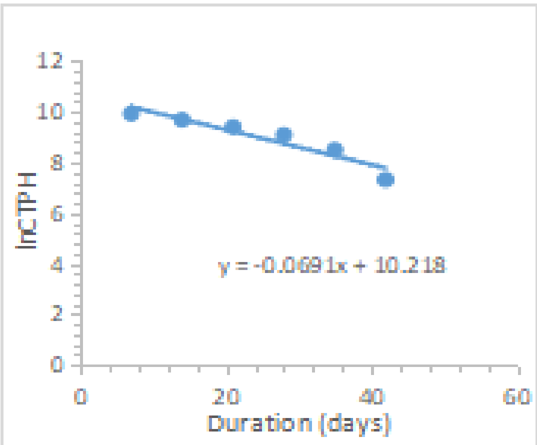
h. 200g cow dung plus 30g croton



i. 115 g cow dung plus 200 g croton



j. 200 g cow dung plus 115 g croton



k. 200 g cow dung plus 200 g croton

Figure 1. Determining the initial concentration of TPH and degradation rate constant (contd).

SJIF Impact Factor (2023): 8.574| ISI I.F. Value: 1.241| Journal DOI: 10.36713/epra2016 ISSN: 2455-7838(Online)
EPRA International Journal of Research and Development (IJRD)
Volume: 8 | Issue: 4 | April 2023 - Peer Reviewed Journal

The model developed for the prediction of the concentration of TPH at any given time during the bioremediation of crude oil polluted soil using 30 g of cow dung plus 30 g of wire croton (Equation 15) was used to predict the $C_{TPH\ (t)}$ at different duration (7, 14, 21, 28, 35 and days, respectively) and the results obtained were compared with the
actual experimental data. This was used to determine the residual of the TPH concentration which was plotted against the TPH concentration at day zero giving rise
to the result presented in Figure 2. The figure shows that the points are scatted fairly randomly around the residual equal zero line indicating that linear model is suitable for describing the experimental data.

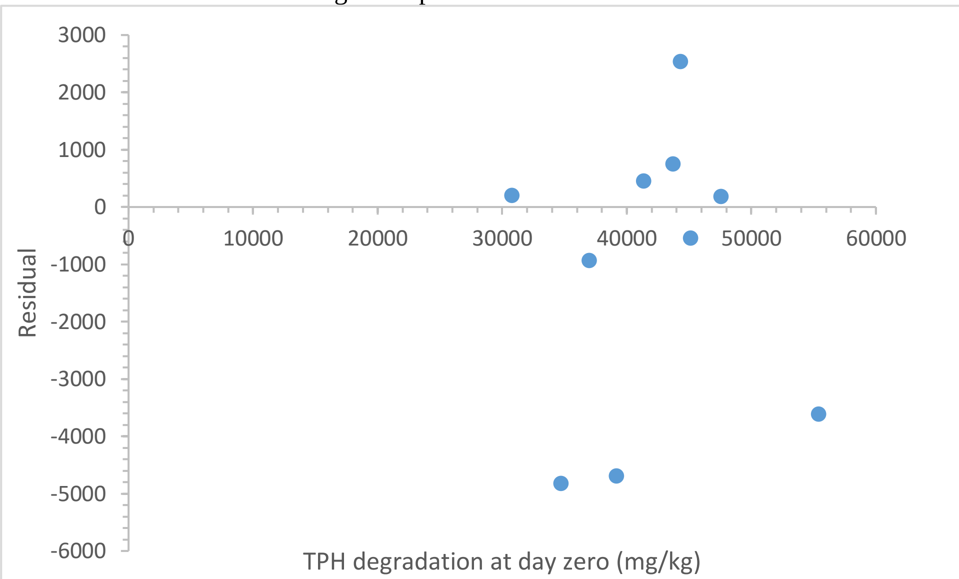


Figure 2. A residual plot

The R square value in Table 3 shows that 89.7 % of the variation in the instantaneous concentration of TPH ($C_{TPH\ (t)}$) can be explained by the initial concentration of TPH and duration of the bioremediation. The standard error value of 0.079 is appreciable (see Table 3). The result of the Analysis of Variance (ANOVA) shows that the significance F or p-value is 0.004 and this means that the model fitted well to the experimental data as this value is less than 0.05 which is within the required range of p-value ($\leq$ 0.05) needed for a model to be statistically significant. The p-values of the intercept ($LnC_{TPH\ (0)}$) and x (duration (t)) are 1.18E-08 and 0.004, respectively are less than a p-value of 0.05 which means that these variables are statistically significant.

Table 3. Linear regression statistics of the model developed using a nutrient with 30 g Cow dung and 30 g Croton composition as an example

	Regression Statistics
Multiple R	0.9470773
R Square	0.8969553
Adjusted R Square	0.8711942
Standard Error	0.0785538
Observations	6

ANOVA

	Df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.214852	0.214852	34.81812	0.004127
Residual	4	0.024683	0.006171		
Total	5	0.239535			

	Coefficient of	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	10.985607	0.07313	150.221	1.18E-08	10.78257	11.18865	10.78257	11.18865
X Variable 1	-0.015829	0.002683	-5.90069	0.004127	-0.02328	-0.00838	-0.02328	-0.00838

SJIF Impact Factor (2023): 8.574| ISI I.F. Value: 1.241| Journal DOI: 10.36713/epra2016 ISSN: 2455-7838(Online)
EPRA International Journal of Research and Development (IJRD)
Volume: 8 | Issue: 4 | April 2023 - Peer Reviewed Journal

4.0 CONCLUSION

It has be demonstrated that Total Petroleum Hydrocarbon in crude oil contaminated soil can be degraded through bioremediation using cow dung, wire croton and their combination as nutrients within a duration of 42 days. The model developed is significant and predicted the bioremediation of TPH appreciably well. Based on this, it can be used as a complementary tool, to support the management of crude oil polluted sites.

REFERENCES

1. *Agency for Toxic Substances and Diseases Registry (ATSDR) (1999). Toxicological profile for total petroleum hydrocarbon Atlanta, G.A: U.S. Department of Health and Human Services, Public Health Service.*
2. *Alinnor, I. J., Nwachukwu, M. A. (2013). Determination of total petroleum hydrocarbon in soil and groundwater samples in some communities in Rivers State, Nigeria. Journal of Environmental Chemistry and Ecotoxicology. 5(11):292-297. DOI: 10.5897/JECE2013.0298*
3. *Ali, N.; Bilal, M.; Khan, A.; Ali, F.; Iqbal, H.M.N. Effective exploitation of anionic, nonionic, and nanoparticle-stabilized surfactant foams for petroleum hydrocarbon contaminated soil remediation. Sci. Total Environ. 2020, 704, 135391.*
4. *Choi, A., Gibson F.N., and Parales, F. (2002). Use of New Kind of Fertilizer of Petroleum Origin Environ. Sci. Technol., 31, 2078 – 2084.*
5. *Ehirim E.O, Walter Cornelius and Ukpaka P. C (2020). Mix Model Formulation for TPH Prediction during Bioremediation of Hydrocarbon Contaminated soils. American Journal Of Engineering Research: Vol 9, pp 01-11.*
6. *Ere, W. and Ayodeji, B. T. (2018). Modeling the Degradation of Total Petroleum Hydrocarbon in Soil using Mushroom. International Journal of Engineering Trends and Technology (IJETT), 66(2):81-91*
7. *Gustafson, J. B. (2007). Using TPH in Risk - Based Corrective action.*
8. *Hazen T. C, Dubinsky E. A., Andersen G.L., (2010). Deep sea oil plume enriches indigenous oil degrading bacteria. National Center for Biotechnology information.*
9. *Hentati, O.; Lachhab, R.; Ayadi, M.; Ksibi, M. Toxicity assessment for petroleum-contaminated soil using terrestrial invertebrates and plant bioassays. Environ. Monit. Assess. 2013, 185, 2989–2998.*
10. *ISS (2022). Endless oil spills blacken Ogoniland's prospect. 24 March 2022, https://issafrica.org/iss-today/endless-oil-spills-blacken-ogonilands-prospects*
11. *Koshlaf, E.; Ball, A.S. Soil bioremediation approaches for petroleum hydrocarbon polluted environments. AIMS Microbiol. 2017, 3, 25–49.*
12. *Kleindienst, S., M. Seidel, K. Ziervogel, S. Grim, K. Loftis, S. Harrison, S.Y. Malkin, M.J. Perkins, J. Field, M.L. Sogin, and others. 2015b. Chemical dispersants can suppress the activity of natural oil-degrading microorganisms.* Proceedings of the National Academy of Sciences of the United States of America *112:14,900–14,905, https://doi.org/10.1073/pnas.1507380112.*
13. *Margesin, F. M. And Schinner, (1997). Biodegredation of Crude Oil in Soil amended with Melon Shell. Auj. T. 13(1): 34-38*
14. *Martins, G.; Campos, S.; Ferreira, A.; Castro, R.; Duarte, M.S.; Cavaleiro, A.J. A Mathematical Model for Bioremediation of Hydrocarbon-Contaminated Soils. Appl. Sci. 2022, 12, 11069. https:// doi.org/10.3390/app122111069*
15. *Ofoegbu, R.U., Momoh, Y.O.L and Nwaogazie, I.L. (2015). Bioremediation of Crude Oil Contaminated Soil Using Organic and Inorganic Fertilizers, Petroleum and Environmental Biotechnology, 6(1): 1-6doi.org/10.4172/2157-7463.1000198*
16. *Pilon-Smits, E., 2005. Phytoremediation. Annu. Rev. Plant Biol. 56, 15–39. doi:10.1146/annurev.arplant.56.032604.144214*