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# Predictive Model for TPH Degradation in Soil Amended with Spent Mushroom

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**ABSTRACT:** This study involved the applicability of mathematical model in predicting the amount of residual TPH in contaminated soil. The performances of various concentrations of spent mushroom, mixed with constant weight of TPH contaminated soil were investigated. Although, there was no significant difference in the rate of degradation between 800g to 1000g of spent mushroom, the rate of TPH degradation increased as the amount of spent mushroom was increased. The order of TPH degradation rate in the cells decreased in this order: WF-1>WF-2>WF-3>WF-4>WF-5>WF-0. Thus, the mix with 1000g spent mushroom recorded the highest performance. However, TPH degradation rate in the control soil sample was lowest because no remediating agent was used. There was strong correlation between the experiment and the model, which is an indication that it can be used to predict the concentration of TPH in soil amended by biological agent with time. **KEYWORDS**: bioremediation, degradation, spent mushroom, crude oil, degradation rate

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#### I. INTRODUCTION

Crude oil has both negative and positive effect on the environment and human capital growth. In fact, crude oil is the mainstay of Nigeria's economy since its discovery, relegating other economic sectors to the background. This has also caused a divide in the political and social structure of the nation. However, the region most affected by the negative effects of crude oil is the Niger Delta region of the country. Crude oil damage to the environment has short-term and long-term effects on soil, surface water, groundwater, and air resulting in economic losses<sup>[1].</sup>

Contamination of soil environment by crude oil is perennial challenge across the globe. This is probably due to over dependence on petroleum as major energy source, rapid industrialization and population growth. The release of TPH onto the environment whether by accident or human activities is the main cause of water and soil pollution <sup>[2]</sup>. TPH pollutants disrupt natural equilibrium between the living species and their natural environment. The contamination of the environment either terrestrial or aquatic, by crude oil is estimated at 80% <sup>[3]</sup>.

Lands are polluted by products of petroleum origin used as energy source and chemical in the oil industry <sup>[4] [5]</sup>. The varieties of oil pollutants affecting soil include crude oil and its fractions either as saturated, unsaturated aliphatic, monocyclic or polycyclic hydrocarbons <sup>[5]</sup>. Land pollution by oil can occur naturally, accidentally through pipeline and tanker leakages or intentional destruction of oil facilities.

Pollution of the environment by crude oil has significant effect on humans directly or indirectly. According to Ewetola et al. <sup>[3]</sup>, changes in the environment harmfully affect the quality of human life, animals, microorganism and plants. Crude oil at high concentration inhibited the growth of crops <sup>[4]</sup>. Plant growth in crude oil contaminated soil is adversely affected due to changes in the nutrient status of the soil and disruption of microbial activities. Thus, the effect of the oil spillage on manganese and ferrous elements as soil nutrient was reported by Ezeonu et al. <sup>[6]</sup>. Oyem <sup>[7]</sup> also observed the effect of hydrocarbon contaminated soil on the yield of agricultural produce.

Bioremediation have proven to be an effective technique for decontamination of oil polluted soil. It is the removal of pollutant from soil using biological materials. This method of remediation is cost effective and also lead to complete mineralization of the contaminants in the environment <sup>[8] [9] [10]</sup>.

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Spent mushroom like other amendments for oil decontamination have been reported to be a useful nutrient source for biodegrading organisms for rehabilitation of polluted soil. Mushroom exhibits extra ordinary abilities to transform recalcitrant pollutants and also degrades broad spectrum of structurally diverse toxic environmental pollutants <sup>[11]</sup> <sup>[12]</sup>. Their extra cellular ability made them degrade non-soluble toxic and non-popular compounds <sup>[13]</sup>.

Whilst experimental studies are essential for proper comprehension of bioremediation process of a polluted environment, it is also beneficial to study the degradation of pollutant over time using a mathematical relationship. Thus the degradation rate of TPH in soil amended with spent mushroom substrate was studied using a mathematical model.

Various reported models have been applied for the remedial process of polluted soil under different amendments. Rikea et al. <sup>[14]</sup> developed a model for biodegradation of petroleum hydrocarbons in frozen arctic soils. The rate of hydrocarbon biodegradation and the oxygen diffusion in the soil were investigated through a derived model. Also, Yudono et al. <sup>[15]</sup> showed that the biodegradation process of soil contaminated by crude oil amended by indigenous isolated bacteria followed a first order kinetics. They observed a decrease in TPH concentration. In extension of reported bio-kinetic models <sup>[16] [17] [18]</sup>, Ofoegbu <sup>[19]</sup> developed a predictive model for bioremediation of crude oil contaminated soil amended by organic and inorganic fertilizers, which agreed with experimental data. Other bioremediation models have also been studied in soil environment using different amendments <sup>[20] [21] [22] [23] [24] [25] [26].</sup>

## **II. MATERIALS AND METHODS**

The crude oil for this experiment was obtained from a subsidiary of Nigerian National Petroleum Corporation (NNPC) in Port Harcourt, Rivers State. The spent mushrooms substrate used were collected from Dilomat Farm, Rivers State University, Port Harcourt.

# 2.1 Experimental Procedure

A 5kg each of polluted soil was put into cell (reactors) labeled WF-0 to WF-5. Then, different weights of the spent mushroom: 1000, 950, 900, 850 and 800g was added to the cells WF-1, WF-2, WF-3, WF-4 and WF-5 respectively, after 3 days for baseline analysis of TPH. The spent mushroom supplied nitrogen to the cells for the ten (10) weeks remediation period.

#### 2.2 Analysis of TPH

Three days after pollution, baseline analysis for TPH was conducted before addition of the spent mushroom and water. 10g of each sample was taken and put into sample bottles. 80ml of chloroform was measured and added to each sample, tightly closed and thoroughly shaken for proper mixing. The mixture was left for 4 days to allow extraction of the crude oil by the chloroform. On the 4<sup>th</sup> day, each of the samples was decanted and the clear liquid transferred to fresh sample bottles and then using the UV-VIS spectrophotometer. The UV-VIS spectrophotometer was standardized using chloroform for the blank, with wavelength set at 290nm. The absorbance of sample was measured immediately after completion of the last step and the digital readout of the instrument recorded.

#### 2.3 TPH Degradation Model

The model for prediction of TPH reduction was based on the principle of mass conservation in a batch system. The enzymatic reaction that takes place in the reactor was represented by equation (1).

$$TPH + E + Z \xrightarrow{k_d} X + Z \tag{1}$$

Where: TPH is total petroleum hydrocarbon, E is mushroom substrate concentration, Z is soil, X is the produced biomass and  $k_d$  is the degradation rate constant.

For a batch process, there is no inflow and out flow of mass in/out of reactor. Thus, rate of TPH degradation is given by equation (2).

$$-r_{TPH} = -\frac{dC_{TPH}}{dt} = k_d C_{TPH}$$
(2)

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Where is  $C_o$  initial concentration of TPH (mg/kg),  $C_{(t)}$  instantaneous concentration of TPH (mg/kg),  $r_{TPH}$  is the rate of TPH degradation (mg/kg.day),  $k_d$  is TPH degradation rate constant (day<sup>-1</sup>) and t = time of TPH degradation (day). After integration and simplification, equation (2) yields:

$$\ln C_{(t)} = \ln C_o - k_d t \tag{3}$$

A plot of  $\ln C_{(t)}$  against *t*, gives a linear (straight line) graph with slope equivalent to "k<sub>d</sub>" and intercept equivalent to  $\ln C_a$ .

#### **III. RESULTS AND DISCUSSION**

To predict the degradation of TPH under the influence of spent mushroom amendment in the soil, the degradation rate constant of the model was evaluated. Thus, the plots for determination of  $k_d$  for the control sample and the cells is shown in Fig. 1 to 6. The coefficient of the time variable in the regression equation represents the TPH degradation constant, while the negative sign depicts the loss of TPH with respect to time. The TPH degradation coefficient,  $R^2$  obtained for all the mixes showed that there is strong correlation between the model and experimental results. However, based on the rate of TPH degradation, the mix with 1000g spent mushroom recorded the highest performance. Therefore, it is generally deduced that the developed model predicted the concentration of TPH in all the cells including the control. Hence, the model can be applied in the remediation of TPH contaminated soil under spent mushroom amendment.

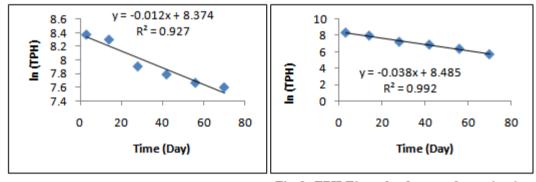
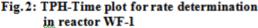
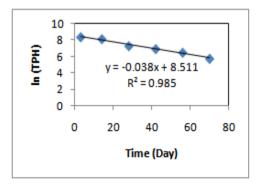
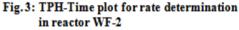


Fig. 1: TPH-Time plot for rate determination in reactor WF-0







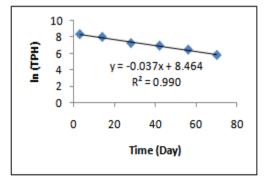
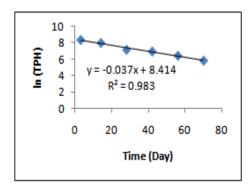


Fig. 4: TPH-Time plot for rate determination in reactor WF-3

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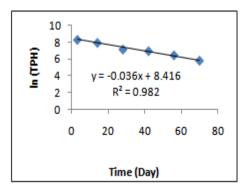


Fig. 1: TPH-Time plot for rate determination in reactor WF-0

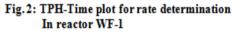


Table 1: Rate constant and correlation coefficient of the reactors		
Sample	Rate constant [k (days <sup>-1</sup> )]	Correlation (R <sup>2</sup> )
WF-0	0.0123	0.9277
WF-1	0.0386	0.9922
WF-2	0.0385	0.9853
WF-3	0.0377	0.9907
WF-4	0.0372	0.9834
WF-5	0.0366	0.9827

Table 1 shows the rate of degradation constant and correlation coefficient of residual TPH concentration for the six cells. The order of the rate constants are as follows: WF-1>WF-2>WF-3>WF-4>WF-5>WF-0. The range of values obtained for TPH degradation rate constant showed no significant difference in the rate of degradation in the cells with mushroom substrate amendment. However, TPH degradation rate constant in the control soil sample was the lowest because no remediating agent was used.

Table 2: Comparison of TPH rate constant	nt (k <sub>d</sub> ) under various amendments
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Type of Amendment	K <sub>d</sub> (day <sup>-1</sup> )	Reference
Poultry Manure	0.058	Fallgren and Jin (2008)
-	0.017	Aghalibe et al. (2017)
Cow Dung	0.0498	Agarry et al. (2013)
-	0.016	Aghalibe et al. (2017)
Pig Dung	0.0266	Agarry et al. (2013)
Groundnut Shell	0.0260	-
Beans Shell	0.0251	-
Cassava Peel	0.0288	-
Melon Shell	0.0257	-
NPK Fertilizer	0.0228	Agarry et al., (2013)
	0.025 0	Aghalibe et al., (2017)
Compost	0.0352	Asgari et al., (2017)
Bacillus megaterium	0.0204	Yudono et al., (2010)
Spent Mushroom	0.0372 - 0.0386	This Study

# **IV. CONCLUSION**

The rates of TPH degradation in soil amended by 800 to1000g spent mushroom showed no significant different, but in comparison to other reported amendments, the degradation rate of TPH was higher than in most amendments. Also, the strong correlation coefficients showed the model fit very well for remediation study. Therefore, it can be used to predict the rate of TPH degradation at any given time under a remediating agent.

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