Determining The Degradation Rate Constant for Model Prediction of TPH in Soil

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Abstract- This study explores the degradation of Total Petroleum Hydrocarbons (TPH) in soil through various kinetic models, focusing on the first-order, second-order, and Michaelis-Menten models. Extensive research has highlighted the first-order degradation rate as the predominant model for predicting TPH decay over time. To enhance the predictive accuracy of TPH degradation, this study compares the effectiveness of these models by applying them to soils amended with moringa and elephant grass. Key to this process is the accurate determination of kinetic parameters. The first-order degradation rate constant was calculated using experimental data and evaluated through graphical plots. These plots illustrate the relationship between TPH concentration and time, allowing for the extraction of degradation rate constants (k) for different soil treatments. For instance, the data indicated that the degradation rate constant (k) increased with the weight of moringa applied, suggesting a higher degradation efficiency with greater amounts of the treatment. The study also contrasts the obtained constants with previous literature values, showing that the constants fall within established ranges for various treatments, including beans shell and compost. Tables 1 and 2 summarize the degradation rate constants for different treatment scenarios and compare them with values reported in prior studies. This comparison underscores the validity of the obtained results and provides a framework for predicting TPH degradation based on the applied soil amendments. Ultimately, this study contributes to a deeper understanding of TPH bioremediation in soil environments by evaluating and comparing kinetic models for practical application.

I. INTRODUCTION

There is growing alarm over the escalating environmental degradation driven by the increased production and use of fossil fuels. Oil exploration and utilization pose significant threats to ecosystems and human health across all continents. Oil spills, defined as the release of petroleum hydrocarbons into the environment, can occur from various sources, including tankers, offshore platforms, drilling rigs, and wells. These spills can involve crude oil, refined products like gasoline and diesel, or heavier fuels such as bunker fuel used by large ships, as well as oily refuse or waste oil [1-2]

Historical spills, such as those in Alaska, the Gulf of Mexico, the Galapagos Islands, France, and the Niger Delta in Nigeria, illustrate the extensive damage caused by such events. The volume of spilled oil varies greatly, from a few hundred tons to several hundred thousand tons, as seen in incidents like the Deepwater Horizon Oil Spill, the Atlantic Empress, and the Amoco Cadiz. Even smaller spills can have severe impacts on ecosystems, particularly in remote areas or regions with limited emergency response capabilities, such as the Niger Delta [3-5].

The consequences of oil contamination are profound. Oil disrupts the insulating properties of birds' plumage and mammals' fur, making them more susceptible to temperature changes and reducing their buoyancy in water. Additionally, the strong odor of oil can interfere with animals’ ability to locate their young or mates, leading to abandonment, starvation, and death [5-7].
The degradation of Total Petroleum Hydrocarbons (TPH) in soil environments is a critical area of study for advancing bioremediation technologies aimed at mitigating crude oil contamination. Various kinetic models have been employed to understand and predict the dynamics of TPH degradation, with the first-order model being the most frequently utilized due to its simplicity and effectiveness in many scenarios [8-10]. This model assumes that the degradation rate of TPH is proportional to its concentration, making it a

straightforward tool for predicting the rate of degradation over time.

However, the effectiveness of the first-order model can be influenced by various factors, including soil type and the nature of the amendments applied. To enhance the predictive accuracy and better understand the degradation process, it is valuable to explore alternative kinetic models. This study compares the first-order model with the second-order and Michaelis-Menten models to evaluate their effectiveness in predicting TPH degradation in soils amended with moringa and elephant grass. The second-order model accounts for scenarios where the rate of degradation depends on the concentrations of both TPH and the degrading agents, while the Michaelis-Menten model provides insights into enzyme kinetics, which may be relevant in bioremediation contexts involving biological amendments [11-15].

II. METHODOLOGY

Experimental Procedure

The swampy and clay soils were each divided into eleven 1 kg portions, resulting in a total of 22 samples. Each soil sample was placed into one of 22 reactors, to which 100 ml of crude oil was added. The mixture was then thoroughly stirred and allowed to settle undisturbed for three days to ensure proper stabilization before treatment began. After the stabilization period, 20g, 40g, 60g, 80g, and 100g of moringa leaf and elephant grass particles were introduced into the reactors containing the swampy and clay soils. Additionally, one reactor of each soil type was left untreated to serve as control samples. This setup aimed to evaluate the efficacy of the different treatment options [16].

Reactors with swampy and clay soil treated with moringa were labeled MST, while those treated with elephant grass were labeled EAST. Every two days, the reactors were stirred to ensure even distribution of the treatments. Soil samples, approximately 10g each, were collected from three separate sample bottles every two weeks (14 days) for laboratory analysis. This analysis, which continued for 84 days, included measurements of pH, moisture content, total organic content (TOC), total nitrogen, phosphorus content, and electrical conductivity. Additionally, Total Petroleum Hydrocarbon (TPH) and Total Hydrocarbon Degrading Bacteria (THDB) were analyzed every 14 days. A detailed description of the process and analyses is illustrated in Figure 1.

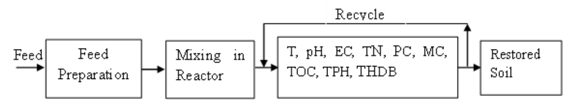

Figure 1: Process Description of the Bioremediation

The First Order Biodegradation Rate Kinetic Model

The first order biodegradation rate kinetic model for prediction of TPH reduction was developed using the principle of mass conservation in a batch reactor. A typical batch reactor is represented in Figure 1.

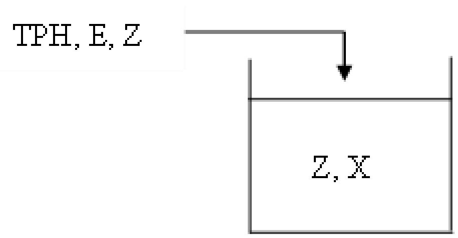

Figure 2: Batch Reactor

The principle of mass conservation is stated as

$$\begin{Bmatrix}\text{Inflow of} \\ \text{mass into} \\ \text{system}\end{Bmatrix} = \begin{Bmatrix}\text{Outflow of} \\ \text{mass from} \\ \text{system}\end{Bmatrix} + \begin{Bmatrix}\text{Rate of} \\ \text{degradation} \\ \text{due to} \\ \text{reaction}\end{Bmatrix} + \begin{Bmatrix}\text{Rate of} \\ \text{accumulation} \\ \text{of mass} \\ \text{within system}\end{Bmatrix} \quad (1)$$

The degradation reaction that takes place in the reactor can be represented by equation (2).

$$TPH + E + Z \xrightarrow{k_d} X + Z \quad (2)$$

Where:

TPH = Total hydrocarbon (pollutant) (g)

E = Bacteria

Z = Soil (kg)

X = Biomass (g)

k_d = Degradation rate constant (unit according to model used)

From equation (1) we have

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 $= -\dfrac{d(C_{TPH}V)}{dt}$ (6)

Thus,

$$Q_oC_{TPH(o)} = QC_{TPH} = 0 \quad (7)$$

Also, for a batch process, volume of reactor (vessel) is constant hence, the accumulation term is

$$\frac{d(C_{TPH}V)}{dt} = V\frac{dC_{TPH}}{dt} \quad (8)$$

Therefore, equation (3.11) reduces to

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

Or $$-r_{TPH} = -\frac{dC_{TPH}}{dt} \quad (9)$$

Assuming that the degradation of TPH is described by first order kinetics, then, we have

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

Where:

$Q_o =$ 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)

Integration of equation (10) by the separation of variable method yields the following

$$\int_{C_{TPH(o)}}^{C_{TPH(t)}} \frac{dC_{TPH}}{C_{TPH}} = -k_d\int_0^t dt \quad (11)$$

$$\ln\left(\frac{C_{TPH(t)}}{C_{TPH(o)}}\right) = -k_dt \quad (12)$$

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

$$\ln C_{TPH(t)} = \ln C_{TPH(o)} - k_dt \quad (13)$$

Equation (13) can be simply written as

$$\ln C_{(t)} = \ln C_o - k_dt \quad (14)$$

Equation (15) can be compared with the general linear equation of the form

$$y = mx + C \quad (15)$$

Where:

$y = \ln C_{(t)}$

$x = t$

$m = k_d$

$C = \ln C_o$

A plot of $\ln C_{(t)}$ against t, gives a linear (straight line) graph with slope equivalent to "k_d" and intercept equivalent to $\ln C_o$.

However, to obtain the instantaneous TPH concentration, exponential of both sides of equation (15) is taken to give

$$C_{TPH(t)} = C_{TPH(o)}\exp(-k_1t) \quad (16)$$

Equation (17) is the predictive first order kinetic model for TPH reduction during the treatment process.

III. RESULTS AND DISCUSSION

The degradation of TPH in soil environment has been extensively studied via kinetic models, which has been a useful tool for understanding of the reaction dynamics of crude oil during bioremediation. In literature, the first order degradation rate kinetics has been the most applied model for prediction of TPH with time. However, in addition to the first order rate model, the second order rate and the Micaelis-Menten models were used in this study. This is to compare the predictability of the models, and suggest which model best suited the study of TPH degradation in soil amended with moringa and elephant grass.

First Order Degradation Rate

The degradation rate constant in the first order rate kinetic model was determined by using equation.

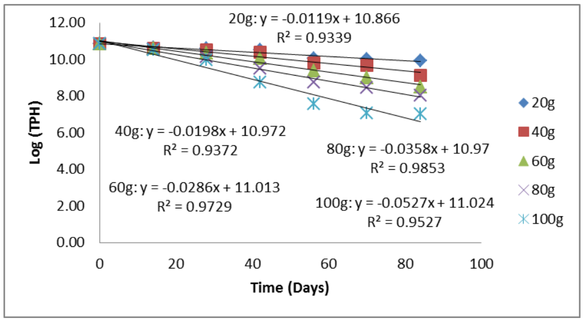

Figure 3: First Order Rate Data Evaluation Plot for Swampy Soil Treated with Moringa

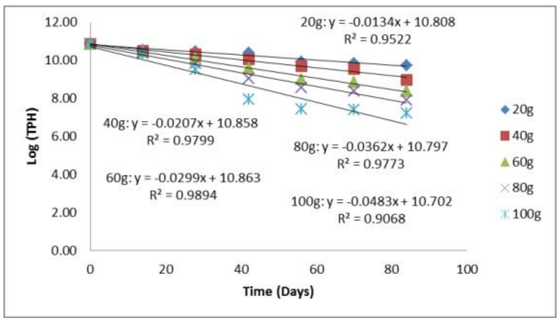

Figure 4: First Order Rate Data Evaluation Plot for Clay Soil Treated with Moringa

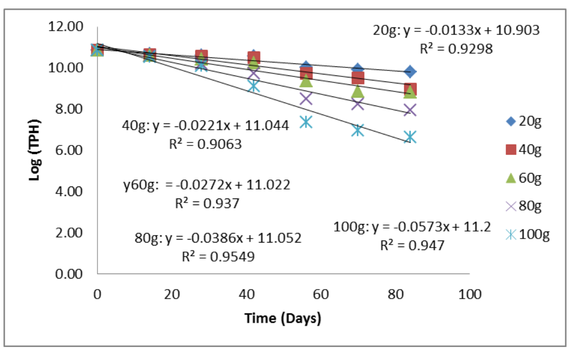

Figure 5: First Order Rate Data Evaluation Plot for Swampy Soil Treated with Elephant Grass

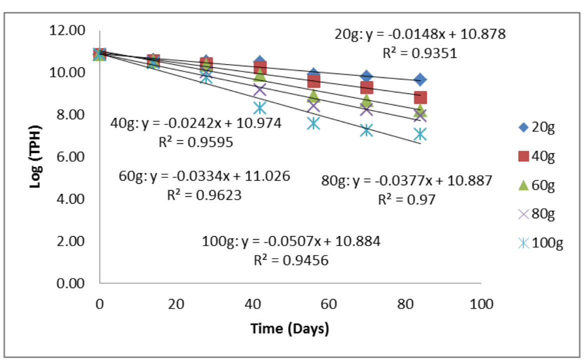

Figure 6: First Order Rate Data Evaluation Plot for Clay Soil Treated Elephant Grass

Figures 3 to 6 were used to calculate the degradation rate constant, *k* for the first order rate kinetic model. Thus, from the given equations on the plots, the respective predictive model can be obtained for each of treatment in the soils. For instance, the respective predictive model determined from the first order rate model for swampy soil treated with moringa is summarized in Table 1. Also, the TPH degradation rate constants obtained through the plots for the treatments have been evaluated.

Table 1: Degradation Constant and First Order Rate Model

Weight (g)	Regression Equation	*k* (day^{-1})	Predictive Model
20	$\ln C_{TPH} = -0.0119t + 10.866$	0.0119	$C_{TPH} = 51067.73e^{-0.00119t}$
40	$\ln C_{TPH} = -0.0198t + 10.972$	0.0198	$C_{TPH} = 51067.73e^{-0.00198t}$
60	$\ln C_{TPH} = -0.0286t + 11.013$	0.0286	$C_{TPH} = 51067.73e^{-0.00286t}$
80	$\ln C_{TPH} = -0.0358t + 10.970$	0.0358	$C_{TPH} = 51067.73e^{-0.00358t}$
100	$\ln C_{TPH} = -0.0527t + 11.024$	0.0527	$C_{TPH} = 51067.73e^{-0.00527t}$

From Table 1, it was observed that the degradation rate constant, *k* increased with increase in the weight of moringa treatment. The variable *x* in the regression equation stands for time, while the coefficient of *x* is the TPH degradation constant *k*. The negative sign in the equation indicates that TPH is reduced with time, and R^2 is the correlation coefficient, which shows the degree of agreement between the experimental value and the predicted counterpart. Also, the degradation rate constant, *k* reported in previous works for first order rate model are summarized in Table 2. Hence, the TPH degradation constant *k* obtained in this study are within the reported values in previous works.

Table 2: Reported TPH Degradation Rate Constant (k_d) for different Treatments

Treatment	k_d (day^{-1})	Reference
Beans Shell	0.0251	[1]
Cassava Peel	0.0288	-
Cow Dung	0.0498	-
Groundnut Shell	0.0260	-
Melon Shell	0.0257	-
NPK Fertilizer	0.0228	-
Pig Dung	0.0266	-
Cow Dung	0.016	[2]
NPK Fertilizer	0.025	-
Poultry Manure	0.017	-
Compost	0.0352	[4]
Spent Mushroom	0.0366 - 0.0386	[3]
20g treatment	0.0119-0.0148	This Work
40g treatment	0.0198-0.0242	This Work
60g treatment	0.0272-0.0334	This Work
80g treatment	0.0358-0.0386	This Work
100g treatment	0.0483-0.0573	This Work

CONCLUSION

The results from the predictive models indicate that the Michaelis-Menten rate model and the first-order degradation rate model both performed similarly in predicting TPH degradation, showing superior results compared to the other models that has been previously used by other authors in similar researches.

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