Predictive Model for PAH Degradation in Soil Amended with Mushroom

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Abstract

Experiment investigation was carried out to model the degradation of poly aromatic hydrocarbon (PAH) in crude oil polluted Niger Delta oxisoils as mediated by parasitic, symbiotic and saprophytic mushroom. Predetermined amounts of mushroom were added to fixed amount of the crude oil contaminated soil in six batch reactors and monitored for a period of 90 days. Soil physiochemical properties including PAH, moisture content, organic carbon, Total Hydrocarbon content Total Nitrogen, available phosphorus and pH were determined and used as indices for evaluating the levels of pollution and remediation. Experimental PAH data obtained were then fitted to first – order kinetics. Results showed that the values of the First –order kinetic constant (K_m) across the treatment reactors averaged 0.3623 day^{-1}. Moreover, the predicted PAH data compared well with the experimental results with the coefficient of determination (r^2) averaging 0.9538, suggesting that 98% of the variability in the entire data set was explained by the model.

Keywords - *Poly aromatic Hydrocarbon, Degradation, Soil, Mushroom, Modelling.*

I. INTRODUCTION

Poly-Aromatic Hydrocarbons (PAHs) have been identified as xenobiotic agents toxic, carcinogenic and tetragenic effects on life (Ruma et al, 2007). United States Environmental Protection Agency (USEPA) has designated sixteen poly-Aromatic Hydrocarbons (PAHs) (naphthalene, aceyaphthylene, acenauorine,phenatherene. anthracene, fluoranthene, pyrene, bensz-a-anthracene, chrysene. Benzo-b-fluornethene, benzo-k-fluorenthene, benzo-g-hiperylen and indeno-1,2,3- (d- pyrene), as priority pollutants. They originate from incomplete combustion of fossil fuels, oil spillage, forest fire and pyrolysis of organics (Kanaly et al, 1997). These are liophilic in nature and are relatively insoluble in water, and persist as a potentially hazardous soil contaminants (Johnson et al, 2005, Hafez et al, 2008). Studies in the use of indigenous microflora, microorganisms, priming with bioremediated soil, treatment with nitrogen, phosphorus and potassium have been carried out for the poly aromatic hydrocarbons (PAHs) on polluted soil (Juhasz et al, 2005, Johnson et al, 2005, Hafez et al, 2008) such studies have provided independent variables necessary for the model. The physio-chemical factors control microbial metabolic and nutritional requirements, and the availability of pollutants to the volume of the mushroom (Lion, 1990, Amellal et al, 2001, Johnson et al, 2005).

The contamination of soil environment by poly-Aromatic Hydrocarbons (PAHs) is becoming prevalent across the globe. This is probably due to heavy dependence on petroleum as a major source of energy throughout the world, rapid industrialization population growth and complete disregard for the environmental health.

Poly-Aromatic Hydrocarbons (PAHs) pollutants disrupt natural equilibrium between the living species and their natural environment.

Many techniques of remediation of contaminated soil have been developed, such as physical, chemical degradation, photo gradation. However, most of these methods have some drawbacks in completely remediating poly-aromatic hydrocarbons (PAHs) contaminated soil, because they have behind daughter compounds which are more toxic to the environment than the parent compounds. Biological treatment offers the best environmental friendly method for remediating poly-aromatic hydrocarbons (PAHs) and heavy metal contaminated soil because it utilized the capability of the indigenous microorganisms in the soil environment to break down the poly-aromatic hydrocarbons (PAHs) into innocuous substance.

Bioremediation techniques allow the evaluation of substrate degradation asa well as microbial growth rate. It employs mushroom which is like many bacterial osmotically sensitive growing rapidly to feed on substrate using carbon as energy source (Adams & Stawber, 2004).

Biodegradation as a means of remediation of contaminated site has draw positive attention because of its economic viability and environmental friendliness (Walker and Crawford, 1997; Dinkla et al., 2001). Biostimulation or bioaugmentation technology employs various options as a means of cleaning up of oil polluted sites and one of such options is the use of agro waste which has interestingly proven effective in pollution abatement (Danne et al., 2001).

The availability of nutrients, especially nitrogen and phosphorus significantly control microbial activities (Margesin and Schinner, 1997), and these nutrients are necessary to enhance the biodegradation of oil pollutants (Choi et al., 2002).

Hwang et al., (2001) investigated the bioremediation of diesel contaminated using composting techniques. The results of the applied first order kinetics model agreed to a great extent with the experimental results. They found that the average first order kinetic rate constant of diesel oil was $0.099day^{-1}$.

First –order kinetic is commonly used to describe biodegradation in environmental fate models because mathematically the expression can be incorporated easily into the models (Greene et al, 2000). Many investigators grasp at first –order kinetics because of the ease of presenting and analysing the data, the simplicity of plotting the logarithm of the chemical remaining Versus time as a straight line, and the case of predicting future concentration (Reardon et al, 2002).

The main objective of this work was to develop a model which describes the level of remediation in poly-Aromatic Hydrocarbons polluted soil using mushroom substrates and also to find out the reaction order and reaction rate constant.

II. MATERIALS AND METHODS

A. Sample Collection

Soil Sampling: The soil sample were collected from the Agric farm Niger Delta University, Wilberforce Island, Bayelsa State. The soil samples were collected with hand trowel and transferred into plastic container (sample bottles). The samples were then transported to the department of Soil Science Laboratory in Rivers State University of Science and Technology, Nkpolu, Port Harcourt, for further analysis to be conducted on the soil characteristics.

Crude oil Collection: The crude oil for this experiment was obtained from Nigeria National Petroleum Company (NNPC) in Port Harcourt, Rivers State.

B. Experimental Design

The soil was divided into six treatment sample cells in six different container (bucket). The different samples were coded as AS-1 to AS-6. Cell AS-1 was the control volume, i.e. did not receive any treatment, whereas cells AS-2, AS-3, AS-4, AS-5, AS-6, were marked to receive 1000g and 800g of mushroom respectively during the remediation period.

C. Microbial Sampling

The soil were later transported in the department of microbiology in Rivers State University of Science and Technology, Nkpolu, Port Harcourt for the purpose of isolation, identification and characterization of possible microorganism present in the soil.

D. Tilling

All the cells were tilled twice in one month to provide necessary aeration and adequate mixing of nutrients and microbes with contaminated soil. The tilling was done in line with the work of Christofi et al., (1998) which reviewed that agro-technical method such as tilling and loosening provides proper aeration that could decrease the contamination level due to the oxidation of easily degradable petroleum components.

E. Laboratory Analysis

Soil physiochemical parameters such as; moisture content, Poly Aromatic Hydrocarbon (PAH), Total Hydrocarbon Content (THC), Total Organic Content (TOC), Soil PH were determined using standard methods. The parameters obtained were used as indices for evaluating the levels of pollution and remediation. The soils were stirred properly and transferred into well labelled polyethylene bags, using a sterile knife. Care was taken to clean up the sampling knife with mentholated spirit before introducing into each soil. Each sample was collected in the triplicate and sent to laboratories. After sampling, the soil samples were air dried and crushed. The crushed soil samples were then passed through a 2mm sieve and collected into clean well-labelled polyethylene bags, for further analysis.

F. Moisture Content (M.C)

This was determined using the oven drying method . 20g of wet soil (W_1) was put into an aluminium foil and place in an oven to dry at 105^oC. After 24hours the soil sample in the oven were removed and reweighed. The dry weight therefore becomes an index for determining the moisture content of the soil sample. The final weight (W_2) of each sample is recorded using an electronic weighing balance (Sansui and Japan, 2001), and the moisture content ($W_1 – W_2$) is determined

Water Content (W %) = $\frac{Mass\ of\ water}{Mass\ of\ dry\ soil}.\times\ 100$

Where mass of water = mass of wet soil – mass of dry soil.

The moisture content in soil samples is measured in percentages (Smith 1998).

G. Poly Aromatic Hydrocarbons (PAH)

100ml solvent (n- hexane & dichloromethane, V: V = 1:1 was added to 5g of soil sample in a soxhlet. After 14h, contents of the flask were evaporated and concentrated exactly to 3ml. the poly Aromatic Hydrocarbon (PAH) content in each soil sample was measured by observing absorbance at 220nm (Tsai et al., 2002).

H. Total Hydrocarbon Content (THC)

In determining the total hydrocarbon content of the soil, 5g of contaminated soil was weighed in a tripe beam balance and put in a conical flask and 10ml of tolune (Hydrocarbon Solvent) was added to the 5g contaminated soil and then stirred vigorously. The solution was then filtered using a filter paper via funnel into test tube and the residue was thrown away. The filter was then tested for using a spectonic ZID spectrophotometer at 420nm wavelength. This wavelength guaranteed the maximum absorption of hydrocarbons. These filtrates were then transferred in different test tube one after the other and absorbent readings was taken in the process. A blank sample (toluene alone) was first tested for its absorbent, and then the machine was adjusted to the zero mark before other readings were taken. A chart of absorbent again St THC (Mg/Kg) was then used to read the total. The total hydrocarbon content was calculated with reference to Odu et al, (1985) using the standard curve, and multiplication by the appropriate dilution factor.

I. Model Development

The degradation of non-conservative substance is usually modelled as a first order reaction. It is assumed that the rate of loss of substance is proportional to the amount of substance that is present (Gilbert and Masters, 2006).

Considering a steady state system with non-conservative pollutant, many contaminants undergo biochemical reaction at a rate sufficient to treat them as a non-conservative substance.

From Michaels Menten's equation

$X + Y + Z \xrightarrow{k_m} P + Q + S$

Where

X = Soil under consideration

Y = Poly aromatic hydrocarbons

Z = Mushroom Substrate

K_m = Rate Constant

P = Gases

Q = Heat and

S = New biomass

J. Applying the Mass Balance Principle

Input of poly aromatic hydrocarbon to the soil = Output rate + Disappearance due to biochemical reaction + Accumulation.

Let PC_o = Input of poly aromatic hydrocarbons to the soil

Input = PC_o

Let PC = Output of poly aromatic hydrocarbon from the soil

Output = PC

Let $\propto$ = Rate of disappearance due to biochemical reaction

μ = Accumulation rate

From mass balance

$PC_o = PC + \propto + \mu$ (1)

Let $\propto = M_S V$

Where

M_S= Mushroom substrate

V = Volume of the soil

$\mu = \frac{Vdc}{dt}$ (2)

$\propto = M_S V$ (3)

Substituting eq 2, 3 into eq1

$PC_o = PC + M_S V + V\frac{dc}{dt}$ (4)

Dividing all through eq 4 by V

$\frac{PCo}{V} = \frac{PC}{V} - M_S + \frac{dc}{dt}$ (5)

$$\frac{P}{V}\ C_o = \frac{PC}{V} - M_S + \frac{dc}{dt} \quad (6)$$

The –ve sign implies loss of substance with time (i.e rate of disappearance of PAHs from the soil).

$$\frac{dc}{dt} = \frac{P}{V}\ (C_o - C) - MS \quad (7)$$

Making C = O for complete removal of contaminant from the soil

Where C = Final concentration

Since C = O

As C_o tends to C, we have:

$$\frac{dc}{dt} = M_S \quad (8)$$

$$MS = K_mC \quad (9)$$

Where K_m = rate of degradation

C = concentration

$$\frac{dc}{dt} = -K_mC \quad (10)$$

Separation of Variables

$$\frac{dc}{C} K_m dt \quad (11)$$

Integrating both sides

$$\int_{Co}^{C} \frac{dc}{C} = -K_m \int_o^t dt \quad (12)$$

$$\text{In } C / C_o = -K_m \int_o^t t \quad (13)$$

$$\text{In } C - \text{In } C_o = -K_m \int_o^t (t - o) \quad (14)$$

$$\text{In } C - \text{In } C_o = -K_m \quad (15)$$

Taking exponential

$$e^{In \frac{C}{Co}} = e^{-kmt} \quad (16)$$

$$\frac{C}{Co} = e^{-kmt} \quad (17)$$

Determining the rate of biodegradation of poly aromatic hydrocarbon (PAHs) therefore, model equation can be written as:

$$C = C_o e^{-kmt} \quad (18)$$

Where

C_o = Initial concentration of PAHs (Mg/L)

C = Final concentration of PAHs (Mg/L)

K_m = Reaction coefficient ($time^{-1}$)

t = Time in weeks

III. RESULTS

To predict the degradation of PAHs under the influence of saprophytic, parasitic and symbiotic mushroom amendment in the soil, the degradation rate constant of the model was evaluated. Thus the plots for determination of rate constant K_m for the parasitic, symiotic and saprophytic mushroom is shown in fig 1 to 3. The coefficient of the time variable in the regression variable represent the PAHs degradation constant, while the negative sign depict the loss of PAHs with respect to time. The correlation coefficient in the three reactors (cells) is presented in table3.4. The high correlation coefficient R2 obtained for all the mixes showed that there is strong correlation between the model and experimental results. However based on the rate of PAHs degradation, the mix with 1000g parasitic mushroom recorded the highest performance.

Therefore, it is generally deduced that the developed model predicted the concentration of PAHs in all the cells. Hence, the model can be applied in the remediation of PAHs contaminated soil under mushroom amendment.

DETERMINATION OF RATE CONSTANT K_m

The rate constants were calculated by linearizing the model equation and ploting ln [PAH] against time for parasitic, symbiotic and saprophytic mushroom respectively.

linearizing eq 18 gives

$$\text{In } C = -K_m t + \text{In } C_o \quad (19)$$

From general linear equation

$$Y = Mx + C$$

Where

Y = InC

M = Gradient of the graph =K_m

X = t (time)

C = Intercept of the graph = InC_o

Therefore, plotting a graph of final concentration of PAHs against time using 1000g of mushroom substrate for parasitic, symbiotic and saprophytic rate constant (km).

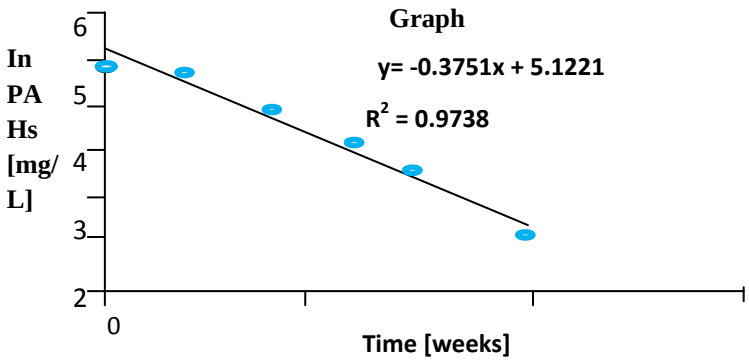

Figure 3.1 Graph of In [PAHs] vs Time for Parasitic Mushroom.

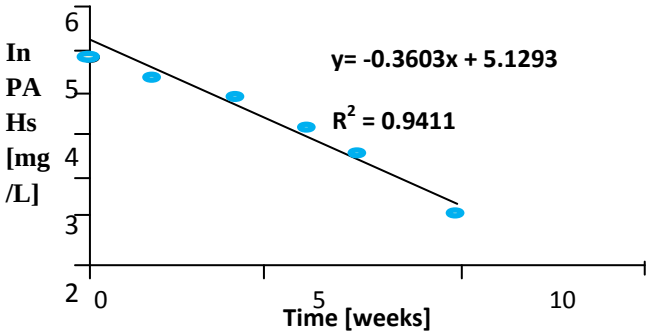

Figure 3.2 Graph of In [PAHs] vs Time for Symbiotic Mushroom.

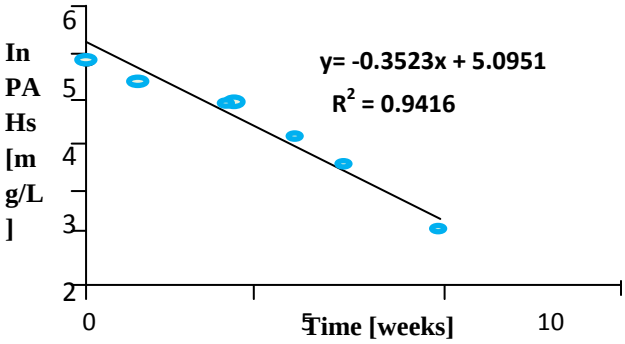

Figure 3.3 Graph of In [PAHs] vs Time for Saprophytic Mushroom.

Table 3.1 1000g of Parasitic Mushroom.

Time (Weeks)	In [PAHs] in mg/l
0	4.88
2	4.36
4	3.75
6	3.31
8	2.63
10	1.07

Table 3.2 1000g of Symbiotic Mushroom.

Time (Weeks)	In [PAHs] in mg/l
0	4.88
2	4.35
4	3.84
6	3.35
8	2.53
10	1.02

Table 3.3 1000g of Saprophytic Mushroom.

Time (Weeks)	In [PAHs] in mg/l
0	4.88
2	4.49
4	3.71
6	2.98
8	2.37
10	1.04

Table 3.4. Rate constant and correlation coefficient of the reactors

Mushroom	Rate Constant [K (day^{-1})]	Correlation (R^2)
Parasitic	0.3751	0.9738
Symbiotic	0.3603	0.9411
Saprophytic	0.3523	0.9416

Table 3.4 showns the rate of degradation constant and correlation of residual PAHs concentration for the three cells. The range of values obtained for PAHs degradation rate constant showed no significance difference in the rate of degradation in the cells with mushroom amendment.

IV. CONCLUSION

The rate of PAHs degradation in soil amendment by 1000g to 800g of mushroom showed no significant difference. The strong correlation coefficient showed that, the model is fit very well for remediation study. Therefore, it can be used to predict the rate of PAHs degradation at any given time under a remediating agent.

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