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Kinetic Approach to Biodegradation of Poly Aromatic Hydrocarbon Polluted Soil using Mushroom Substrate

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ABSTRACT

Bioremediation of poly aromatic hydrocarbon (PAHs) contaminated soil was investigated using micro scale land farming. The mushroom species: namely saprophytic, symbiotic and parasitic were applied by broadcasting them to the relevant cell at 10 cm depth. 100 g of mushroom substrate was applied once in 6 weeks to the cells. These quantities of mushroom supplied enough nitrogen to the cells for the 10 weeks of remediation period. The biodegradation rates of PAHs contaminated soil in the presence of the mushroom were studied using chemical kinetics approach. The reaction orders were studied using the differential method but the reaction rate constants were computed using the integral method. -1Results show that reaction rate constants were 0.0503, 0.0536 and 0.0515 day^{-1}, for saprophytic, parasitic and symbiotic mushrooms respectively. The reaction orders and rate constants show no significant difference. However, parasitic mushroom degrade the PAHs faster than the other species.

Introduction

Polycyclic aromatic hydrocarbon (PAH) is a class of organic compound that consists of two or more fused benzene rings and/or pent acyclic molecules that are arranged in various structural configurations (Harvey, 1998). They are highly recalcitrant molecules that can persist in the environment due to their hydrophobicity and low water solubility. PAHs are ubiquitous in the natural environment, and originate from two main sources: these are natural (biogenic and geochemical) and anthropogenic sources (Harvey 1997).

The latter source of PAHs is the major cause of environmental pollution and hence the focus of many bioremediation activities.

Biological remediation is the use of microorganisms or plants to detoxify or remove organic and inorganic xenobiotic compounds from the environment. The remediation option offer green technology solution to the problem of environmental degradation. The process relies on microbial enzymatic activities to transform or degrade the contaminants in the environment (Philip, 2005). It is a cost effective remediation technique when compared with other methods as it is natural and does not usually produce toxic by-products. It also provides a permanent solution as a result of complete mineralization of the contaminants in the environment (Perelo, 2010).

Poly aromatic Hydrocarbon (PAH) contamination is caused by leakage of crude oil and their refined products and the spills of coal tar and creosote from coal gasification and wood treatment sites (Mueller et al., 1998). Contaminated soil has elevated concentrations of PAH's or other substances deriving from man's use of the soil.

This soil contamination negatively influence human health, surface and groundwater quality, nature and viability of ecosystems, condition of buildings, other materials and archaeological artifacts within the ground area (Vegher, 2002).

Thus, regulatory agencies have set acceptable limits of concentrations of many soil contaminants depending on the intended use of the soil.

Mushroom serves as an important source of food for a variety of animals ranging from insect to large mammalian herbivore such as Deer (Alexopolus et al, 1996). It is often used in thickening popular agusi – melon soup and serves as a substitute for egusi – melon (*cigrullus vulgaris*) in south eastern Nigeria (Nwokolo, 1987; Okhuoya and Isikhwemhen, 1999). It is a good source of vitamins, minerals low in sugar, lowers blood cholesterol (Kenada and Tokuda, 1996), and a selective medicinal for diabetes (Bano, 1976; change and miles, 1982; Gupta, 1989) as well as contributes to longevity in human being (Flynn, 1991).

Mushroom contains good quality protein, low fat content and vitamins B1, B2 and C. It also has effects on tumours, blood pressure and viruses. It has ability to degrade lignin and cellulose. Emuh (2009) reported that mushroom inoculated in locally sourced substrates showed promise in bioremediation of hydrocarbon polluted soil.

This paper seeks to examine the efficiency of different species of mushroom applied on the surface of a soil for bioremediation of Poly Aromatic Hydrocarbons.

Materials and Methods

Description of Study

The Poly Aromatic Hydrocarbon (PAHs) used for this experiment was obtained from Nigeria National Petroleum Company (NNPC) in Port Harcourt, Rivers State.

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The Mushrooms used were bought from Santana Market in Benin, Nigeria. The experimental cells were located at the University Research Green House in Niger Delta University, Wilberforce Island, Bayelsa State. Electrical weighing and electronic balance was used to determine the density of the PAHs and also the volume of mushroom used. A mathematical model was developed to describe the remediation process.

Design of Experiment

The soil was divided into 6 treatment cells that were made into 6 different containers, each with dimension 0.2m x 0.2m and tilled to a depth of 0.1m. The different beakers of samples were coded as AS-1 to AS-6. The beakers were use in order to control the temperature, concentration and moisture content simultaneously (Emuh, 2009).

Soil Treatment

Poly aromatic hydrocarbon obtained from Department of Petroleum Resources (DPR) in NNPC was added to each treatment cell. The cells were left undisturbed for three days, at the end of which the treatment options were then applied. The three day period allowed degradation to commence and following the work of Odokuwa & Dickson (2003).

Soil Sampling

Different random spot were augured using a 9 – inch hand due soil anger capable of obtaining uniform cores of equal volume at the desired depths (Smith & Atkinson 1975), bulked together (composite soil samples) and put in well labeled polyethylene bags. The samples for total Hydrocarbon Content (THC) measurement were placed in 1L glass bottles and sealed with aluminum foil to ensure accurate results. This procedure was done three times to form replicates. The bags and glass bottles were immediately transferred to the laboratory for analysis. The procedure was similar to that reported by Odokuwa & Dickson (2003).

Mushroom Application

Different types of mushroom were applied, broadcast to the relevant cell and worked into 10cm depth in each cell. Various quantities of mushroom applied to the different cells were noted earlier in this work. About 100g of the mushroom substrate was applied once in 6 weeks to cells. These quantities of mushroom supplied nitrogen to the cells for the 10 weeks remediation period. In a related study, Odokuma & Dickson (2003) applied a total of 400kg/ha of mushroom substrate to the relevant cells for a 9 week remediation period.

Tilling

The entire cells were tilled twice in a month to provide necessary aeration and adequate mixing of nutrients and microbes with contaminated soil. The tilling was tone in line with 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.

Laboratory Methods

Soil physiochemical parameters which include Moisture content, PAHs, Total Hydrocarbon content (THC), Total Organic Content (TOC), and soil pH, were determined using standard methods. The parameters obtained were used as indices for evaluating the levels of pollution and remediation. Soil samples collected from the remediation cells were air-dried, homogenized and made to pass through a 2mm mesh sieve (Johnsen, et. al., 2005).

Model Derivation

The degradation of non-conservative substance is usually modeled 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, 2006).

Considering a steady state system with non-conservative pollutant, many contaminants undergo biochemical reactions at a rate sufficient to treat them as a non-conservative substance. Using the mass balance principle,

[Soil + PAHs] + Mushroom Substrate $\xrightarrow{k}$ Gases + Heat + New biomass (1a)

k = Rate of reaction, PAHs is the Pollutant

Applying the principle of mass balance;

Input of Poly aromatic hydrocarbon to soil = output rate + Disappearance due to biochemical reaction + Accumulation (1b)

Let PC_0 = Input of PAH to the soil

Input = PC_0 (2)

Let PC= Output of Poly aromatic hydrocarbon from the soil

Output = PC (3)

Let α = Rate of disappearance due to biochemical reaction $\alpha = M_S V$ (4)

Where, M_S = Mushroom Substrate, V = Volume

Let γ = Rate of accumulation

$$\gamma = \mathbf{V}\frac{\mathbf{dc}}{\mathbf{dt}} \quad (5)$$

Where, $\mathbf{V}$ = Volume of soil

Substituting Eq. 2 to 5 into Eq. 1 we have

$$\mathbf{PC_0 = PC + RM_S V + V\frac{dc}{dt}} \quad (6)$$

Dividing all through Eq. 6 by V

$$\mathbf{\frac{PC_0}{V} = \frac{PC}{V} + M_S + \frac{dc}{dt}} \quad (7)$$

$$\mathbf{\frac{P}{V}C_0 = \frac{PC}{V} - M_S + \frac{dc}{dt}} \quad (8)$$

$$\mathbf{\frac{dc}{dt} = \frac{P}{V}(C_0 - C) - M_S} \quad (9)$$

If C = 0 for complete removal of contaminant from the soil.

As C_0 tends to C, we have:

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

$$\mathbf{M_S = K_m C} \quad (11)$$

Where, K_m = rate of degradation

$$\mathbf{\frac{dc}{dt} = -K_m C} \quad (12)$$

The above equation can be solved using separation of variable method.

$$\mathbf{\frac{dc}{dt} = -K_m C}$$

$$\mathbf{\frac{dc}{C} = -K_m dt} \quad (13)$$

Integrating both sides of Eq.13

$$\mathbf{\int_{C_0}^{C} \frac{dC}{C} = -K_m \int_0^l dt}$$

In

$$\mathbf{C|_{C_o}^{C} = -K_m \int_0^t t} \quad (14)$$

In

$$C - \ln C_0 = -K_m(t - 0) \quad (15)$$

In $C - \ln C_0 = -K_m$ (16)

$$\ln \frac{C}{C_0} = -K_m t \quad (17)$$

Taking exponential on both sides of equation

$$\frac{C}{C_0} = e^{-K_m t} \quad (18)$$

Therefore, the Model Equation can be written as:

$$C = C_0 e^{-K_m t} \quad (19)$$

Where,

C_0 = Initial concentration of PAH (mg/L)
C = Final concentration of PAH (mg/L)
k_m = Reaction coefficient ($time^{-1}$)
t = Time in weeks

Linearizing Eq. 19 we have

ln PAH = -kt + ln $PAH_{(0)}$ (20)

Comparing Eq. 20 with the general linear equation y = mx + c

Where,

y = ln PAH
m = gradient = k
x = Time
c = Intercept = ln $PAH_{(0}$

Results and Discussion

Experimental Data

Table 1 and 2 shows the experimental results obtained from the initial assessment of the soil and the soil characteristic after contamination. From Table 1 it could be observed that the soil pH level is 4.65 which indicate that the soil is acidic and it does not favor the condition for bioremediation.

Table 3 shows the effect of mushroom on bioremediation, this indicates that mushroom substrate is time dependent in bioremediation. This is in agreement with the findings of Olatunji & Horsfall (2014).

Table 3. The PAHs concentration in treated soil.

Time (weeks)	PAHs Concentration (mg/L) in soil treated by Mushroom		
	Parasitic	Saprophytic	Symbiotic
0	131.42	131.42	131.42
2	89.21	78.26	77.48
4	40.94	42.52	46.53
6	19.71	27.37	28.50
8	10.74	13.92	12.55
10	2.84	2.92	2.77

Rate of Reaction (k_m)

The rates of reaction constants were obtained from the graph of ln PAHs against time, where K_m is the slope of the graph from Figure 1, plotted from the linearized equation of the mathematical model (Eq. 19). The k_m values show that Parasitic mushroom will degrade PAHs faster than Saprophytic and Symbiotic mushrooms of 100g. The kinetic parameters are shown on Table 4.

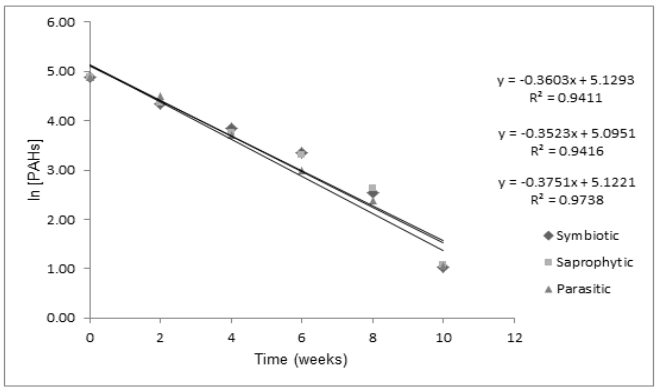

Figure 1. Graph of ln [PAHs] vs. Time.

Table 4.Kinetic Parameters.

Mushroom Substrate	k_m (day^{-1})
Saprophytic	0.0503
Parasitic	0.0536
Symbiotic	0.0515

Moisture Content

Table 5 and Figure 2 shows the effect of mushroom on moisture content of the soil in bioremediation of PAHs. Effect of moisture content in bioremediation using mushroom substrate; symbiotic mushroom reduced the moisture content faster than the other two species

Table 5. Moisture content in treated soil.

Time (weeks)	Moisture content (mg/g) in soil treated by Mushroom		
	Parasitic	Saprophytic	Symbiotic
0	20.48	20.48	20.48
2	22.38	23.32	20.38
4	20.33	19.31	18.35
6	14.35	14.48	14.42
8	14.27	14.27	14.14
10	14.27	14.17	14.12

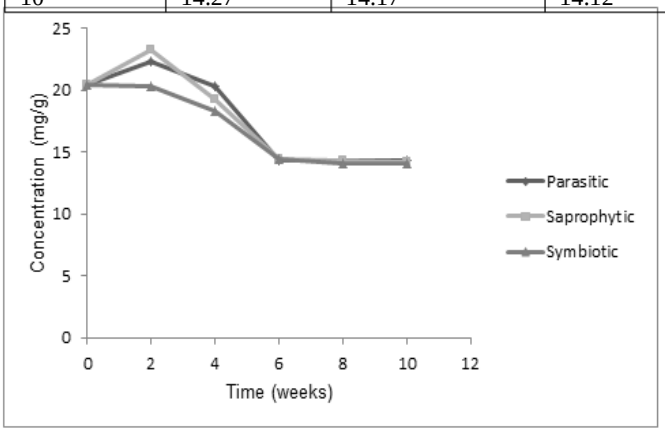

Figure 2. Moisture content in soil treated by Mushroom substrate.

Table 1. Initial Assessment of Soil.

Percentage (%)				pH 1 : 2.5	EC (µ/cm)	Percentage (%)		C/N Ratio
Sand	Silt	Clay	Moisture content			Organic C	Total N	
13.7±0.5	41±0.2	45±0.5	14±1	4.65±0.1	29±2	0.18±0.02	0.62±0.3	0.4±0.01

Results represent the means ± standard deviation of three replicates

Table 2. Physiochemical Characteristics of soil after contamination, prior to remediation.

Percentage (%)				pH 1 : 2.5	EC (µ/cm)	Percentage (%)		C/N Ratio	Potassium (cµ/kg)	PAHs (ppm)
Sand	Silt	Clay	Moisture content			Organic C	Total N			
79.0	10.0	11.0	20.48	5.8	4.71	0.49	0.13	4	1.29	120.23 ±0.007

Results represent the means ± standard deviation of three replicates

pH Effect

As the pH of contaminated sites can often be linked to the pollutant, the result shows that there is no significant change in pH as time increases, in a duration of three months, the pH value increased from 5.8 – 7.2 which indicates a favorable condition for bioremediation (Table 6).

Table 6. pH (1 : 2.5) in treated soil.

Time (weeks)	pH (1: 2.5) in soil treated by Mushroom		
	Parasitic	Saprophytic	Symbiotic
0	5.80	5.80	5.80
2	6.42	6.58	6.41
4	6.40	6.51	6.40
6	6.39	6.52	6.40
8	7.03	6.91	7.15
10	7.07	7.06	7.19

Conclusion

From the results obtained it could be deduced that from the numerical computation and model validation, there is a strong correlation between the experiment and the mathematical model for the bioremediation of Poly Aromatic Hydrocarbons polluted soil with mushroom substrate. The mathematical model developed can be used to predict the rate of remediation of PAHs polluted soil using mushroom as a remediating agent.

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