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Comparative Analysis of TPH Degradation Rate Kinetics in Amended Polluted Soil

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ABSTRACT

The rate of Total Petroleum Hydrocarbon (TPH) degradation in soil amended with mash food wastes (MFW) and fish wastes (FW) was investigated in this study. Experimental analysis was performed for a period of 56 days, while samples were collected weekly for analysis. The first and second order kinetic models were applied to study the TPH degradation rate. The result revealed that the rate of TPH removed from the control sample was low compared to samples amended by MFW and FW. Over 90% of TPH was removed from the amended samples, while only about 48% was removed from sample under natural attenuation. Analysis of the 1st and 2nd order kinetic models showed high correlation coefficient, but the rate of TPH degradation was better interpreted by the second order kinetics. The 1st order degradation rate constant were recorded as 0.0422day^{-1} and 0.0430day^{-1} for soil amended by MFW and FW respectively, while in the 2nd order, the degradation rate constant were as 1.0 x 10^{-5} kg.mg^{-1}.day^{-1}. The rate of TPH degradation increased rapidly within the first 14 days to 237.961mg.kg^{-1}.day^{-1} and 292.486mg.kg^{-1}.day^{-1} in soil amended by MFW, while in soil amended by FW, it increased to 225.386mg.kg^{-1}.day^{-1} and 262.390mg.kg^{-1}.day^{-1} for the 1st and 2nd order models respectively. However, the rate of TPH also decreased sharply after attaining maximum rate. Conclusively, food and fish wastes are recommended for treatment of hydrocarbon polluted soil as they increase TPH degradation rate. Also, the models could be useful, especially during the design stage of a bioremediation process to predict the rate of TPH degradation and time to achieve the bioremediation.

Key words: Crude Oil, Food and Fish wastes, Bio-kinetics, TPH Degradation Rate

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1. INTRODUCTION

The protection of the environment against all form of pollution should be the primary concern of every stakeholder, especially as human activities are on the rise daily. Globally, there are agencies charged with the responsibility to regulate and monitor the activities of all potential sources environmental pollution such Environmental Protection Agency (EPA) in the United State, National Environmental Standards and Regulations Enforcement Agency (NESREA) and National Oil Spill Detection & Response Agency (NOSDRA) in Nigeria. In spite of these agencies, the environment still suffers great impact of industrial activities.

Most notable environmental pollution is through petroleum, which often contaminates the soil, water and the air. It was on this premise that agencies are established to legislate on environmental pollution [1], though much is still expected in the case of Nigeria as report of oil pollution and other environmental degradations are still high [2]. As previously noted, crude oil has both negative and positive effect on the environment and economic growth [3]. Therefore, it is imperative that individuals and organizations assist in reducing environmental disasters.

Although soil has the ability to purify itself, but while some of its pollutants may be removed naturally, others such as hydrocarbons may not be easily removed [4]. Hydrocarbon polluted soil has serious negative effect on agriculture and aquifer, and this could impair on the overall yield of crops as well as contamination of groundwater [5, 6]. Thus, at elevated concentration of crude oil in soil, the growth of crops may be inhibited due to changes in the nutrient availability and interference on microbial activities [7].

Different techniques have been applied for the removal of petroleum contaminants from soil, such as the use of adsorbents [8, 9, 10], but application of bioremediation either via direct application of microorganism or the use of stimulants like fertilizer, plants and animal wastes have proved effective [11]. Bioremediation technology is cost effective [12]. Investigations show biodegradation can be influenced by several factors like temperature, pH nutrient and oxygen availability, but proper understanding the pollutant will enhance an effective bioremediation process [11, 13].
Mathematical relationship has been used for the study and prediction of bioremediation process. Though, this has been studied with specific objectives, such as crude oil penetration rate in soil [14]. Abdulkadir and Yahaya [15] developed a polynomial regression model to describe the dispersion of crude oil in soil as a function of remediation time and depth. Also, the interaction of microorganism and hydrocarbon substrate was studied via mathematical model [16]. Akpoveta *et al*. [17] described the degradation of TPH in kerosene polluted soil amended by microorganism with linear regression model, while the michealis-Menten model was used by Ukpaka [18]. While in other studies, the bulk flow and molecular diffusion of crude oil in soil was studied through mathematical model, which showed that the rate of diffusion of contaminant in soil depended on dispersion coefficient and seepage velocity [19, 20]. Second order quadratic regression model has equally been used by some researchers [21, 22].
Similarly, the mathematical models for prediction of biodegradation rate of petroleum hydrocarbon content in soil amended by agricultural and biological materials or microorganism have been largely studied via the first order kinetics [3, 23, 24, 25, 26, 27]. Also, second order degradation rate kinetics has been applied for the study of TPH degradation in soil [28]. However, this study investigated the effectiveness of the first and second order degradation kinetics in describing the TPH degradation rate in soil amended by fish waste (FW) and mashed food wastes (MFW).

2. MATERIALS AND METHODS

Collection of samples

The soil sample was collected from Enito II Village in Ahoada West Local Government Area of Rivers State, Nigeria. Enito II village play host to an oil and gas facilities owned by Nigerian Agip Oil Company (NAOC), one of the major multinational companies in Nigeria, and this made the Community vulnerable to crude oil pollution caused by leakage of the oil facilities. However, the soil sample was collected within 10cm and 30cm depth. Food and fish wastes were gathered from various kitchens in same Community. The food wastes are combination of yam, cassava, plantain and banana peels, while the fish wastes include intestine, gills, fins and scales. Crude oil sample was collected from a licensed Oil and Gas Company in Rivers State, Nigeria.

Experimental procedure

The yam, cassava, plantain and banana wastes were mashed together (mash food wastes). Similarly, the fish wastes were crushed together. 600g of soil samples were weighed into three different containers, and then, contaminated with 100ml of crude oil. The mixture was stirred vigorously for homogeneity, and left undisturbed for three days to stabilize. Thereafter, 100g of the mashed food wastes was added to one of the samples and labelled MFW. Also, 100g of the mashed fish wastes was added to another of the remaining two samples and labelled FW, while the third sample was left without the addition of MFW or FW (only soil and crude oil) and labelled control. Every two days, the content of the containers was stirred to ensure the content of the container is homogeneous. 10g from each of the representative samples were collected at the first day immediately after the samples were prepared, and at every fourteen (14) day for laboratory analysis to determine the total petroleum hydrocarbon content (TPH).
The TPH analysis was carried in line with American Society for Testing Materials method D3921 [29]. The TPH in the representative soil samples was extracted with dichloromethane and treated with 2ml of activated silica gel, and thereafter analysed with the aid of Gas Chromatography-Flame Ionization Detector (GCFID), Model HP 5890 Series II, manufactured in the USA. The percentage of TPH removed from the soil was calculated using the expression:

$$TPH_t(\%) = \frac{TPH_i - TPH_t}{TPH_i} \times 100\% \qquad (1)$$

Where TPH_i and TPH_t are the initial and instantaneous concentrations of TPH (mg/kg)

Biodegradation kinetics

Previous studies have studied the degradation rate of TPH in various soil types, and most notably applied in these studies was the first order degradation rate model [3, 26]. This is expressed according to equation (1).

$$-r_{TPH} = -\frac{dC_{TPH}}{dt} = k_d C_{TPH} \qquad (1)$$

Where:

$-r_{TPH}$ = Rate of TPH degradation (mg.kg^{-1}.day^{-1})

TPH = Total petroleum hydrocarbon (kg)

C_{TPH} = Instantaneous TPH concentration (mg.kg^{-1})

k_d = TPH degradation rate constant in first order (day^{-1})

t = Time of TPH degradation (day)

Equation (1) was finally expressed as follows (Amagbo and Ere, 2019)

$$\ln C_{TPH(t)} = \ln C_{TPH(o)} - k_d t \quad (2)$$

where $C_{TPH(o)}$ = Initial TPH concentration in the soil (mg.kg^{-1})

A plot of $\ln C_{TPH(t)}$ against t gives a slope equivalent to k_d and $\ln C_{TPH(o)}$ as intercept.

Another biodegradation rate kinetic model that has been applied to the study of TPH degradation in polluted soil is the second order rate kinetics [27, 30]. This is expressed according to equation (3).

$$-r_{TPH} = -\frac{dC_{TPH}}{dt} = k_d C_{TPH}^2 \quad (3)$$

To obtain the second order degradation rate constant, equation (3) was further solved via integration, which after simplification, resulted to equation (4).

$$\frac{1}{C_{TPH(t)}} = \frac{1}{C_{TPH(o)}} + k_2 t \quad (4)$$

A plot of $\frac{1}{C_{TPH(t)}}$ against t gives k_2 as slope and $\frac{1}{C_{TPH(o)}}$ as intercept

where: $C_{TPH(o)}$ and $C_{TPH(t)}$ are the initial and instantaneous TPH concentration

t = Time (day)

k_2 = TPH degradation rate constant in second order (kg.mg^{-1}.day^{-1})

3. RESULTS AND DISCUSSION

Table -1 Physicochemical characteristics of soil before contamination

Parameters	Value
Temperature (ºC)	27
pH	6.46
Moisture content (%)	33.37
TOC (%)	1.14
Nitrogen content (%)	2.12
Phosphorus content (mg/kg)	2.23
TPH(mg/kg)	7.73
Porosity	0.673
Bulk Density (g/cm^3)	1.22
Sand (%)	21.54
Silt (%)	63.08
Clay (%)	15.38

The temperature, pH, moisture content, total organic carbon (TOC), nitrogen content, phosphorus content, the porosity and bulk density of the soil shown in Table 1 were analysed before being polluted by crude oil. The total petroleum hydrocarbon (TPH) content in the soil was lower than the 50mg/kg maximum permissible limit set by Department of Petreleum Resources [31]. In addition, the particle size distribution (PSD) analysis revealed that the soil can be classified as silt loam soil.

TPH degradation in soil

The residual TPH in soil recorded with time for control sample as well as the samples amended by mash food wastes (MFW) and fish wastes (FW) are presented in Table 2, while the extent of degradation is shown in terms of percentage in Table 3.

Table -2 Residual TPH in soil

Time (Days)	Control (mg/kg)	MFW (mg/kg)	FW (mg/kg)
0	13786.7	13786.7	13786.7
14	14456.8	5408.2	5122.4
28	13071.4	2597.4	2341.6
42	10468.4	1713.2	1648.4
56	8159.7	1278.7	1194.8

Table -3 Percentage TPH degradation in soil

Time (Days)	Control (%)	MFW (%)	FW (%)
0	0	0	0
14	16.90	60.77	62.85
28	26.95	81.16	83.02
42	31.32	87.57	88.04
56	48.07	90.73	91.33

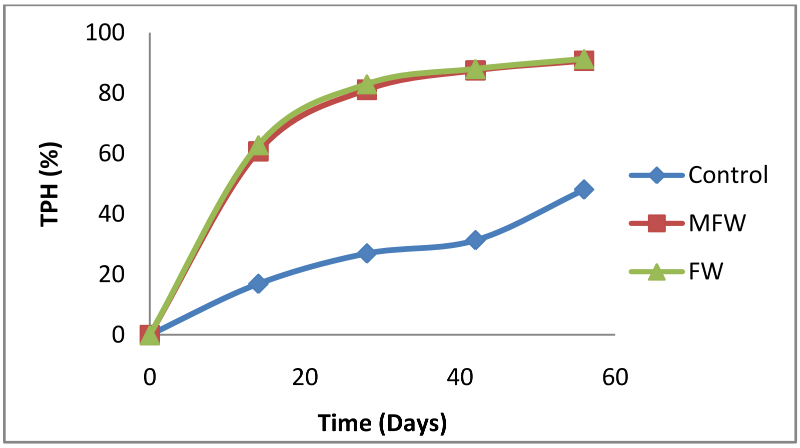

Fig. 1 Extent of TPH removal polluted silt loam soil

Figure 1 shows the percentage degradation of TPH in the soil as time increases. As shown in the figure, the percentage of TPH removed from the soil increases with increase in time for both the control and amended samples. However, the rate of TPH removed from the control sample was low compared to samples amended by MFW and FW. This is because the wastes supplied nutrients to the soil that was subsequently utilized by microorganisms for metabolism, therefore, enabling the microorganisms to attack the hydrocarbon substrate in the soil. As shown in Table 1, the content of TPH at the end of the analysis (56th day) reduced from an initial concentration of 13786.7mg/kg to 8159.7mg/kg, 1278.7mg/kg and 1194.8mg/kg, representing 48.07%, 90.73% and 91.33% of TPH removed from the soil for control, MFW and FW samples respectively.

On comparison, both MFW and FW showed high efficiency in TPH reduction from the polluted soil, but FW slightly edged MFW. Although, different conditions and proportions were adopted by authors in the experimental design, the performance of MFW and FW can be comparable to amendments previously studied for TPH removal from soil. Thus, 89.82% TPH was removed from soil amended by cassava peels [30], about 70 to 85% with cow dung, poultry manure and NPK fertilizer [26], 71.56% with immature compost [27] and about 92% with spent mushroom [32].

Biodegradation rate evaluation

The kinetic evaluation of TPH degradation in soil is useful for understanding of the reaction dynamics of crude oil during bioremediation. To use the biodegradation models, the TPH biodegradation constant must first be evaluated. Thus, Figures 1 to 3 were used to estimate the degradation rate constants in the first and second order rate models.

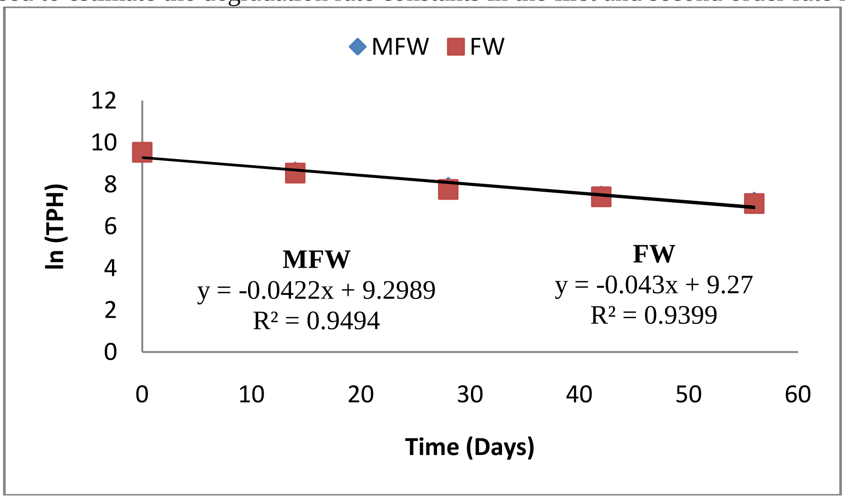

Fig. 2 First order degradation rate

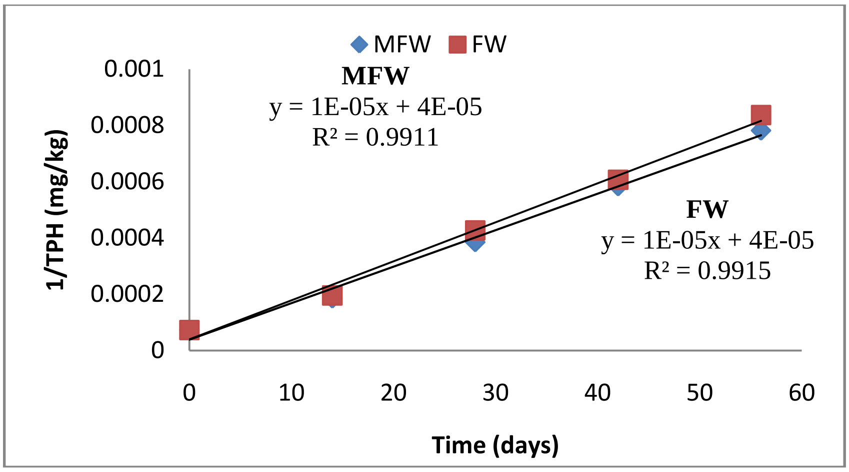

Fig. 3 Second order degradation rate

Figure 2 shows the first order degradation rate model, while Figure 3 is for the second order. In the first order, the regression line for both MFW and FW cannot be easily distinguished as they overlapped, which is an indication that both amendments performed very closely with R^2 values obtained as 0.9494 and 0.9399 respectively, while the TPH degradation rate constant, k_1 are obtained as 0.0422day^{-1} and 0.0430day^{-1} for soil amended by MFW and FW respectively. On the other hand, the second order rate model regression line for MFW and FW can be distinguished, though, close to each other. Again, the R^2 values were obtained as 0.9911 and 0.9915 for soil amended by MFW and FW respectively, while the TPH second order degradation rate constants k_2 were both obtained as 1.0 x 10^{-5} kg.mg^{-1}.day^{-1}. The R^2 values obtained for the second order are higher those the first order. However, very high R^2 values between 0.9732 and 0.9932 was reported by Aghalibe *et al*. [26], while between 0.982 and 0.992 was obtained by Amagbo and Ere [3] for first order rate constant.

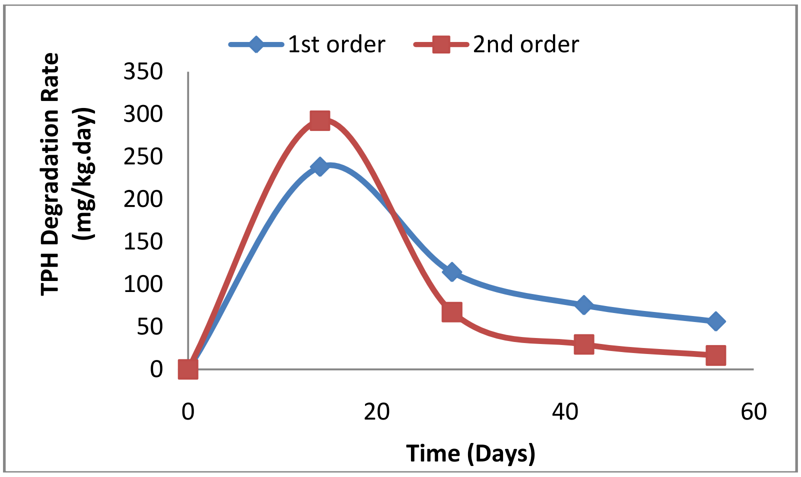

Fig. 4 TPH degradation rate with time under MFW amendment

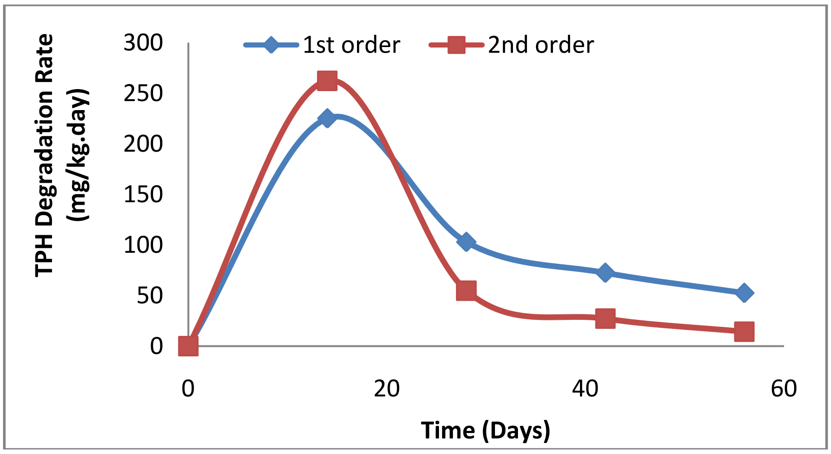

Fig. 5 TPH degradation rate with time under FW amendment

Figures 4 and 5 compare the progression of TPH degradation rate at the instant of time during the amendment period for first and second order rate kinetics. Initially, the TPH degradation rate for soil amended by MFW, increased tremendously within the first 14 days to 237.961mg.kg^{-1}.day^{-1} and 292.486mg.kg^{-1}.day^{-1} for the 1st and 2nd order models respectively, while for soil amended by FW, it increased to 225.386mg.kg^{-1}.day^{-1} and 262.390mg.kg^{-1}.day^{-1} for 1st and 2nd order models. The rapid rate of degradation depicts the active metabolic process of microbial attack on the substrate hydrocarbon, which was influence by the increase population of the hydrocarbon degrading bacteria in the media. However, it was noticed that the degradation rate profile sharply decreased almost at same rate of initial increase before maintaining a relative steady decrease. This was observed across the treatment options and also, the rate orders (Table 4). This stage of sharp decreases indicates the depletion of nutrients necessary to metabolise the cell energy, and also due to reduced concentration of the hydrocarbon, while the phase of insignificant decrease implied low relative activities of degrading bacteria in the media. It was also noticed that the 2nd order degradation rate was higher than the 1st order within the first 14 days, but from about 22 to 23 days of remediation, the 1st order degradation rate increased more than the 2nd order. Generally, from the value of R^2, the rate of TPH degradation would be more predicted by the 2nd order degradation rate kinetics. This result also agrees with earlier studies on comparison of the 1st and 2nd order kinetics for amendment of crude oil polluted soil [27, 28].

Table -4 TPH degradation rate

Time (Days)	$-r_{TPH}$ (mg/kg/day): MFW		$-r_{TPH}$ (mg/kg/day): FW	
	1st order	2nd order	1st order	2nd order
0	0	0	0	0
14	237.961	292.486	225.386	262.39
28	114.286	67.4649	103.03	54.8309
42	75.3808	29.3505	72.5296	27.1722
56	56.2628	16.3507	52.5712	14.2755

CONCLUSION

This study revealed that food and fish wastes can be useful for treatment of hydrocarbon polluted soil, rather than being discarded as waste; which could constitute environmental hazard if not properly disposed of. Thus, MFW and FW were able to remove above 90% of TPH from the soil as compared to just about 48% with natural attenuation. This indicates that the kitchen wastes are good amendments for crude oil polluted soil. However, the investigation on the degradation rate of TPH in soil proved effective as both the first and second order kinetic models showed high correlation coefficient with the measured laboratory data. Though, the rate of TPH degradation was better interpreted by the second order kinetics in both treatment options. Finally, application of mathematical model for bioremediation studies will help to reduce cost and time especially in large scale remediation process.

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