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Crude Oil Degradation on the Influence of Palm Oil-Fermented Wastewater Used as Biostimulant

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Abstract

The total petroleum hydrocarbon (TPH) degradation was monitored in a batch reactor with the addition of biostimulants like palm oil processed wastewater (POPWW) acting as nutrients, to effectively enhance high efficiency in contaminants remediation in clay soil. The kinetic components were evaluated in terms of specific rates of petroleum hydrocarbon degradation, maximum specific rate of total petroleum hydrocarbon degradation as well as the equilibrium constant of total petroleum hydrocarbon degradation. The effect on the variations on the concentration of the dosages 30 g, 60 g, 90 g, 120 g, 150 g, and the control samples were evaluated as presented in this research in relationship of reciprocal of specific rate of TPH against Reciprocal of TPH Degradation for nutrient sample application of POPWW. The obtained data for the maximum specific rate of total petroleum hydrocarbon degradation and the equilibrium constant of total petroleum hydrocarbon degradation demonstrates values of Vmax and Ks for 30 g dosage as 16666.67 $(ppm/day)^{-1}$ and 14488.33 $(ppm)^{-1}$ as well as the regression value of the best fit (R^2 = 99.51%). In the case of 60 g dosage the values are Vmax = 2000 $(ppm/day)^{-1}$, Ks = 21768 $(ppm)^{-1}$ and R^2 = 96.11% as well as for 90 g dosage we have Vmax = 1250 $(ppm/day)^{-1}$, Ks = 5563.5 $(ppm)^{-1}$ and R^2 = 92.5%. Also, in the case of 120 g, 150 g, and the control sample of the functional parameters and coefficients are obtained as Vmax = 476.19 $(ppm/day)^{-1}$, 909.09 $(ppm/day)^{-1}$, Vmax = 25.71 $(ppm/day)^{-1}$, respectively. The Ks values are 5483.89 $(ppm)^{-1}$, 44626.36 $(ppm)^{-1}$, 33601.54 $(ppm)^{-1}$, respectively, as well as the R^2 values of 99.31%, 99,76%, 99.75%, respectively. This investigation has revealed that kinetic parameters and coefficients are dependent on the rate of total petroleum degradation at interval of sampling.

Keywords: Biostimulant, degradation, fermented, fertilizer, modeling, oil

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INTRODUCTION

Anaerobic digestion modeling allows one to track the changes in the composition of the biogas generated over time as organic matter breaks down [1]. The hydrolysis step is to solubilize the substrate; it is performed by extracellular enzymes excreted by specific bacteria. There is no metabolism; therefore, this is not a biological process. The metabolic steps are acidogenic, acetogenesis, and methanogenesis where the organic substrate is consumed and effectively converted by bacteria. The biokinetics of the reaction processes are described by three phenomena: growth and bacterial decay, substrate consumption, methane generation, and inhibition of bacterial activity [2].

One of the main areas of attention for biochemical reactions and correctional control efforts related to corrosion of industrially based equipment and

facilities is inhibition. These days, a variety of biological research make extensive use of computer modeling and mathematics to forecast or evaluate the behavior of such complex systems as biological systems. But the study also looks at mathematical modeling to forecast the uncompetitive suppression of the decomposition of petroleum hydrocarbons [3].

This study's primary goal is to provide the findings from the breakdown of crude oil in a loamy soil environment, analyze bio-substrate enzymatic processes in the presence of uncompetitive inhibitors, and provide a detailed description of the inhibitory effects. Using various software programs, four uncompetitive inhibition models were created [4]. Studies have focused on uncompetitive inhibitors of the first and second enzyme-substrate complexes. By employing identical kinetic parameters across all models, the simulation enabled the examination of response behavior and revealed some intriguing details regarding the impact of various instances of uncompetitive inhibition [5, 6].

Ever since it was discovered, petroleum has become a useful source of energy to the world. As an oil-rich country, Nigeria is globally known as a hub of oil and gas activities. However, these activities, such as exploitation, refining, transportation, and storage, cause environmental pollution – the unintended discharge of petroleum hydrocarbon into the environment. Measures are taken to arrest the situation and they include: Chemical injection, bioremediation, and so on. Some of these methods are good but not so cost-effective like bioremediation [7, 8].

Bioremediation is the deployment of microorganisms in degrading petroleum hydrocarbon. The microbes are sometimes indigenous species in the affected area, and they require the hydrocarbon contaminant for energy and carbon. According to field and lab studies, dissolved oxygen, temperature, pH, biological, and chemical oxygen demands, moisture content, and the solubility of the pollutants can all affect the treatment method [9, 10]. The important requirement is the presence of microorganisms with the appropriate metabolic capabilities [11]. Meaning, it is necessary to deploy microbes that can mineralize hydrocarbon contaminant effectively. This very important requirement has caused many scientists to develop methods in tackling hydrocarbon contaminants. Some of these methods include [12–15]:

- Phytoremediation (use of plants to manage hydrocarbon degradation).
- Genetically Engineered Microorganisms, GEMs (this employs the use of genetically encoded microorganisms to tackle hydrocarbon degradation. This means is yet to be adopted in fieldwork).
- Use of Enzymes.

MATERIALS AND METHODS

Modeling and Kinetics

Mathematical Model

Model for competitive inhibition relationship of crude oil degradation and the inhibiting parameters were developed. The non-growth Monod Equation describing the biodegradation of petroleum hydrocarbon when present as the sole substrate is:

- $E + S \rightarrow E.S$ ……. Step 1.
- $E + I \leftrightarrows E.I$ ……. Step 2.
- $E.S \rightarrow E + P$ …… Step 3.

Assume, we have low concentration of P. Now, the rate of degradation of petroleum products is given below:

$$RHC_e = K\,[E.S]. \quad (1)$$

Note that steps 1 and 2 above have constants, Km, and Ki, respectively. From the principle of rate determining step, Km, and Ki are derived below:

$$K_m = \frac{[E][S]}{[E.S]} \quad (2)$$

From mathematical manipulation, Equation (2) becomes:

$$[E.S] = \frac{[E][S]}{K_m} \quad (3)$$

$$K_i = \frac{[E][I]}{[E.I]} \quad (4)$$

Also, from change of subject formula, Equation (4) becomes:

$$[E.I] = \frac{[E][I]}{K_i} \quad (5)$$

Mass balance of enzyme is constant, i.e., ET = 0 and it is given as:

$$E_T = [E] + [E.S] + [E.I] \quad (6)$$

Substituting Equations (3) and (5) into Equation (6), we have:

$$E_T = [E] + \frac{[E][S]}{K_m} + \frac{[E][I]}{K_i} \quad (7)$$

Factorizing [E], we have:

$$E_T = [E]\left(1 + \frac{[S]}{K_m} + \frac{[I]}{K_i}\right) \quad (8)$$

From Equation (8) above, we make [E] subject of formula:

$$[E] = \frac{[E_T]}{\left(1 + \frac{[S]}{K_m} + \frac{[I]}{K_i}\right)} \quad (9)$$

Substitute the value of from Equation (9) into Equation (3), we have:

$$[E.S] = \frac{[E][S]}{K_m}$$

$$[E.S] = \frac{[E][S]}{K_m} = \frac{[E_T][S]}{K_m\left(1 + \frac{[S]}{K_m} + \frac{[I]}{K_i}\right)} \quad (10)$$

Now that an expression for [E.S] is known, it will be substituted into Equation (1) above to derive the rate of degradation of the crude oil:

$$RHC_e = \frac{K[E_T][S]}{K_m\left(1 + \frac{[S]}{K_m} + \frac{[I]}{K_i}\right)} \quad (11)$$

Equation (11) can be written to resemble Michaelis–Menten (M–M) Equation:

$$V = \frac{V_{max}[s]}{K_{m\,+\,[S]}} \text{ (M–M Equation)}$$

$$RHC_e = \frac{V_{max}[S]}{K_m\left(1 + \frac{[I]}{K_i}\right) + [S]} \quad (12)$$

$$RHC_e = \frac{K_{HCe\ S\ X}}{S + K_{SHC}} \quad (13)$$

where $V_{max} = K[E_T]$.

Rewriting Equation (12) using the two-compound competitive inhibition equation and in terms of petroleum hydrocarbon effluent and influent yields Equation (14):

$$RHC_e = \frac{K_{HCe}\, S\, X}{S + K_{SHC}\left(1 + \frac{I}{K_I}\right)} \tag{14}$$

where

- RHC_e = degradation rate of petroleum hydrocarbon (effluent when present alone (mgHc/l–d).
- KHC_e = maximum specific degradation rate of hydrocarbon (Hc) (g/g vss-d).
- S = Liquid concentration of hydrocarbon (mg Hc/l).
- X = biomass concentration (mg Vss/l).
- K_{SHC} = half saturation concentration of hydrocarbon (mgHc/l).
- I = liquid concentration of a competing compound (mg/l) and,
- K_i = inhibition constant (mg/l).

Equation (14) is a representation of competitive inhibition. However, many studies have shown that the inhibition effect of a compound can be described by the Ks of the compound since the Ks represents the relative enzyme affinity. An extension from two-compound competitive inhibition to four compounds for the interactive effect of influent hydrocarbon, HC on the effluent degradation is:

$$RHC_{em} = \frac{K_{HCe}\, S_e\, X}{S_e + K_{SHCe}\left(1 + \frac{S_{in}}{K_{SHCin}}\right)} \tag{15}$$

Before we proceed to derive equations for every individual, note that the subscripts, “in” and “e” stands for influent and effluent, respectively:

$$R_{cnem} = \frac{K_{cne}\, S_{cne}\, X}{S_{cne}\, K_{scne}\left(1 + \frac{S_{cnin}}{K_{scnin}}\right)} \tag{16}$$

where

n = 5, 6, 7, 8, 9, 10, 11, etc.

R_{CHem} = Degradation rate individual hydrocarbon in the mixture with other component of petroleum milligrams per liter per day.

S_{cnin} = Liquid concentration of another individual hydrocarbon present in the influent (mg/l).

K_{SCnin} = Half – saturation concentration (mg/l).

Similarly, an extension from two-compound competitive inhibition to eleven compounds for the interaction effect of C6 to C11 on C5 degradation is:

$$R_{C5em} = \frac{K_{C5}\, S_{C5}\, X}{S_{C5e} + K_{SC5e}\left(1 + \frac{S_{C6in}}{K_{SC6in}} + \frac{S_{C7in}}{K_{SC7in}} + \frac{S_{C8in}}{K_{SC8in}} + \frac{S_{C9in}}{K_{SC9in}} + \frac{S_{C10in}}{K_{SC10in}} + \frac{S_{C11in}}{K_{SC11in}}\right)} \tag{17}$$

where K_{SC6in}, K_{SC7in}, K_{SC8in}, K_{SC9in}, K_{SC10in}, and K_{SC11in} = half-saturation concentration of C_6, C_7, C_8, C_9, C_{10}, and C_{11}, respectively (mg/l). Then, combining Equations (13) and (17) yields:

$$\frac{R_{C5em}}{R_{HCe}} = \frac{S_{C5} + K_{SC5}}{S_{C5e} + K_{SC5e}\left(1 + \frac{S_{C6in}}{K_{SC6in}} + \frac{S_{C7in}}{K_{SC7in}} + \frac{S_{C8in}}{K_{SC8in}} + \frac{S_{C9in}}{K_{SC9in}} + \frac{S_{C10in}}{K_{SC10in}} + \frac{S_{C11in}}{K_{SC11in}}\right)} \tag{17a}$$

where K_{SC6in}, K_{SC7in}, K_{SC8in}, K_{SC9in}, K_{SC10in}, and K_{SC11in}, Equation (17a) can be reduced to Equation (18) below:

$$\frac{R_{C5em}}{R_{HCe}} = \frac{S_{C5} + K_{SC5}}{S_{C5e} + K_{SC5e} + S_{C6e} + S_{C7e} + S_{C8e} + S_{C9e} + S_{C10e} + S_{C11e}} \quad (18)$$

Assume, RHCe = RCne Equation (18) becomes:

$$\frac{R_{C5em}}{R_{Cne}} = \frac{S_{C5} + K_{SC5}}{K_{SC5} + \sum S_{C6in}\, S_{C7in}\, S_{C8in}\, S_{C9in}\, S_{C10in}\, S_{C11in}} \quad (19)$$

where $\sum S_{C6in}\, S_{C7in}\, S_{C8in}\, S_{C9in}\, S_{C10in}\, S_{C11in} = S_{C6in} + S_{C7in} + S_{C8in} + S_{C9in} + S_{C10in} + S_{C11in}$= Total liquid concentration of hydrocarbon (mg Hc/l). If SC5 >> KSC5, Equation (19) reduces to:

$$\frac{R_{C5em}}{R_{Cne}} \approx \frac{S_{C5}}{\sum S_{C6in}\, S_{C7in}\, S_{C8in}\, S_{C9in}\, S_{C10in}\, S_{C11in}} \quad (20)$$

Kinetic Model

In this research the substrate kinetic model, microbial kinetic model, first order kinetic model and second order kinetic model were considered for the determination of the functional parameters and coefficient of the crude oil degradation upon the action of the remediant and microbial activities in each bioreactor set-up.

Kinetics of First Order Reaction

The kinetics of the first order reaction in this case were established by considering the mixtures of the reactant as demonstrated in the equation of reaction as well as the experimental set-up as shown in Figure 1 for the equation of reaction, we have:

$$[Cs] + [M] + [Co] \; K_1 \; [P] + [M] + [Cs]$$

where:

- [Cs] is denoted as clay soil.
- [M] is denoted as microorganisms.
- [Co] is denoted as crude oil.

Considering the experimental set-up, the flow diagram is demonstrated in Figure 1, as:

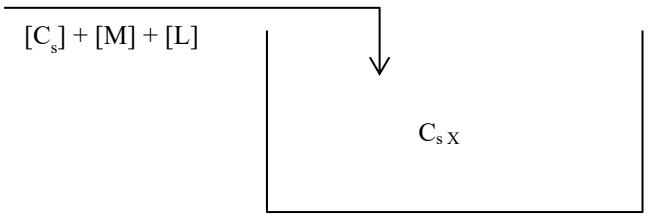

Figure 1. Demonstration of a batch bioreactor set-up for the research.

Considering the mass balance of reaction process as illustrated in Figure 1 reveals that:

$$\begin{pmatrix} Therateof \\ massinputof \\ thesubstrate \\ int\ o\ thesystem \end{pmatrix} = \begin{pmatrix} Therateof \\ massoutput \\ ofthesubstrate \\ fromthesystem \end{pmatrix} + \begin{pmatrix} Therateofmassof \\ substratedisapprance \\ duetobiochemical \\ reactionfrom \rightleftarrows the \\ system \end{pmatrix} + \begin{pmatrix} Therateofmass \\ ofsubstrate \\ accumulation \\ withinthesystem \end{pmatrix} \quad (21)$$

The reactor type is grouped as batch process thus the rate or mass input of the substrate into the system is equal to the rate of mass output of the substrate from the system, that is:

$$\begin{pmatrix} The\,rate\,of\,mass\,input\,of\,the \\ substrate\,int\,o\,the\,system \end{pmatrix} = \begin{pmatrix} The\,rate\,of\,mass\,output \\ of\,the\,substrate\,from \\ the\,system \end{pmatrix} = O \tag{22}$$

Applying condition of Equation (22) into Equation (21), therefore, Equation (21) can be written

$$\begin{pmatrix} The\,rate\,of\,mass\,substrate \\ accumulation\,within\,the\,system \end{pmatrix} = \begin{pmatrix} The\,rate\,of\,mass\,of\,substrate \\ disapprance\,due\,to\,biochemical \\ reaction\,from\,the\,system \end{pmatrix} = \tag{23}$$

From Equation (20) defining each of the rate expressions, we have:

- The rate of mass input of the substrate into the system = λ GPHco (24)
- The rate of mass output of the substrate from the system = λ GTP (25)
- The rate of mass of substrate disappearance due to biochemical reaction from the system = – α TPH^V (26)
- The rate of mass of substrate accumulation within the system = $\frac{d\left(C_{TPH}{}^{V}\right)}{dt}$ (27)

However, considering Equations (24) to (27) and then substituting it into Equation (21), we have:

$$\lambda_o\, C_{TPH} = \lambda C_{TPH} + \left(-^{\alpha}\, TPH^{V}\right) + \frac{d\left(C_{TPH}{}^{V}\right)}{dt} \tag{28}$$

Indeed, it is revealed that change in crude oil degradation is a function of time, provided that the organisms are feeling in the substrate. Therefore, the rate of accumulation of the substrate within the system can be written as:

$$\frac{d\left(C_{TPH}{}^{V}\right)}{dt} = {}^{\alpha}TPH^{V} \tag{29}$$

According to Equation (29), the rate at which substrate mass enters the system is equal to the rate at which substrate mass exits the system, and both are equal to zero. Also, Equation (29) can be achieved by substituting Equations (26) and (27) into Equation (23).

The volume of a batch reactor is considered to be equal; therefore, Equation (30) can be written as:

$$-^{\alpha}TPH^{V} = -\frac{vd^{C}TPH}{dt} \tag{30}$$

In Equation (30), V is constant, therefore, diving through the expression with V, we have:

$$-^{\alpha}TPH = -\frac{d^{C}TPH}{dt} \tag{31}$$

The change of substrate concentration as a function of time can be in terms of equation of the kinetic as:

$$-\frac{dC_{TPH}}{dt} = -K_1 C_{TPH} \tag{32}$$

However, Equation (31) can further be written as:

$$-^{\alpha}TPH = -\frac{dC_{TPH}}{dt} = K_1 C_{TPH} \quad (33)$$

where:

- K_1 denotes the TPH degradation in system.
- λo denotes the final concentration of TPH output volumetric rate of flow (kg/day).
- λ denotes the final concentration of TPH output volumetric rate of flow (kg/day) $C_{TPF(o)}$ denotes the initial concentration of TPH (mg/kg).
- V denotes reactor volume (m^3).
- *t* denotes degradation time (day).
- ^{C}TPH denotes the final concentration of TPH (mg/kg).

Equation (32) can be written and simplified as:

$$\int_{^{C}TPH(O)}^{^{C}TPH} \frac{d^{C}TPH}{dt} = -K_1 \int_{o}^{t} dt \quad (34)$$

$$\left[InC_{TPH}\right]_{^{C}TPH(O)}^{^{C}TPH} = -K_1 [t]_{o}^{t} \quad (35)$$

$$\text{In } C_{TPH} - \text{In } C_{TPH(o)} = -K_1 (t - o) \quad (36)$$

$$In \frac{C_{TPH}}{C_{TPH_{(o)}}} = -K_1 t \quad (37)$$

Considering the experimental of Equation (37), we have:

$$C_{TPH(t)} = C_{TPH(o)} e^{-k1t} \quad (38)$$

Or

$$C_{TPH(t)} = C_{TPH(o)} \exp^{k1t} \quad (39)$$

Equation (39) can be expressed in terms of equation of the line, thus:

$$Y = Mx + C \quad (40)$$

In relationship between Equations (40) and (39) can be written as:

- $Y = C_{TPH(t)}$ this denotes the output.
- $M = K_1$ this denotes the slope.
- $C = C_{TPH(o)}$ this denotes the constant.
- T = x this denotes the coordinate or coefficient.

Plot of In CTPH(*t*) versus *t* and establishment of the linear equation for the determination of the slope and intercept. In this case slope of K1 = m as well as intercept of C = In $C_{TPH(o)}$.

Kinetics of Second Order Reaction

The kinetics of the second order reaction for substrate (crude oil) degradation was established as:

$$-^{\alpha} TPH = \frac{dC_w}{dt} = K_1 C_w^2 \tag{41}$$

From Equation (41), we have:

$$\frac{dC_w}{dt} = K_1 C_w^2 \tag{42}$$

By integrating Equation (42) we have:

$$\int_{Cw(o)}^{Cw(t)} C_w^{-2} dC_w = \int_o^t K_1 dt \tag{43}$$

From Equation (43), we have:

$$\frac{1}{C_{w(t)}} = \frac{1}{C_{w(o)}} = K_1 t \tag{44}$$

Equation (44) can be written as:

$$\frac{1}{C_{w(t)}} = \frac{1}{C_{w(o)}} + K_1 t \tag{45}$$

However, Equation (45) can be written as:

$$C_{w(t)} = \frac{C_{w(o)}}{1 + C_{w(o)} K_d t} \tag{46}$$

Equation (46) can be expressed in terms of crude oil (TPH) degradation:

$$C_{TPH(t)} = \frac{C_{TPH(o)}}{1 + C_{TPH(o)} K_d t} \tag{47}$$

where:

- $C_{w(o)}$ and $C_{w(t)}$ represent the initial and final crude oil (TPH) concentration.
- K_1 represents the rate constant of crude oil (TPH) degradation of the second order *t* represents the time.
- Plot of $1/C_{w(t)}$ against + and K1 representing the slope and $1/C_{w(o)}$ representing the intercept.

Michaelis–Menten Model

The Michaelis–Menten Model deals with the rate of substrate degradation (TPH or crude oil degradation) upon the action of microbes. The equation expressing the action of microbes in substrate degradation is demonstrated in Equation (3.68) below:

$$[C_0] + [M] \underset{K_2}{\overset{K_1}{\rightleftharpoons}} [M][C_0] \xrightarrow{K3} [P] + [M_1] \tag{48}$$

where:

- [Co] denotes the substrate or crude oil (TPH).

- [M] denotes the enzyme.
- [M] [Co] denotes enzyme – substrate complex.
- [P] denotes the product.
- [M_1] denotes the free enzyme.

The general rate Equation of Michaelis–Menten Kinetic is expressed as:

$$R = \frac{R_{\max}[C_o]}{R_{co}+[C_o]} = \frac{R_{\max}[S]}{R_s+[S]} \tag{49}$$

where:

- R denotes the specific rate of substrate degradation.
- R_{max} denotes the maximum specific rate of substrate degradation.
- $[C_o]$ = [S] denotes the substrate concentration or TPH or crude oil.
- K_{co} = Ks denotes dissociation constant of substrate degradation.

For the determination of the functional parameters and coefficient Equation (49) was expressed in terms of Lineweaver–Burk plot and the general solution of equation is presented in Equation (50) and (51) as:

$$1/R = \frac{K_s}{R_{\max}(S)} + \frac{1}{R_{\max}} \tag{50}$$

or

$$1/R = \frac{K_{co}}{R_{\max}(C_o)} + \frac{1}{R_{\max}} \tag{51}$$

Relating Equations (50) and (51) into equation of line graph 1 of Y = Mx + C.

Therefore:

$$Y = \frac{1}{R_{TPH}}$$

$$M = \frac{K_s}{(R_{TPH})_{\max}} = \frac{K_{co}}{(R_{TPH})_{\max}}$$

$$X = [S] = [C_o]$$

$$C = \frac{1}{(R_{TPH})_{\max}} = \text{int } ercept.$$

$$Slope = \frac{K_s}{(R_{TPH})_{\max}} = \frac{K_{co}}{(R_{TPH})_{\max}}$$

Plot of $1/R_{TPH}$ versus $1/[s]$ or $1/[C_O]$ and then the established equation of the linear graph result in the evaluation of the intercept value and the slope as intercept = $1/(R_{TPH})_{\max}$ and

$$\text{slope} = \frac{K_s}{(R_{TPH})_{\max}} \text{ or } \frac{K_{co}}{(R_{TPH})_{\max}}$$

Monod's Model

The activity of microbes was evaluated using the kinetic of Monod's in terms of substrate degradation and microbial activities. The Monod's model evaluated the functional parameters of the microbial kinetics:

$$\mu = \frac{\mu_{\max}[S]}{K_m + [S]} = \frac{\mu_{\max}[C_o]}{K_m + [C_o]} \tag{52}$$

where:

- μ denotes the specific rate of biomass concentration.
- $\mu_{\max}$ denotes the maximum specific rate of biomass concentration.
- K_m denotes the dissociation constant of microbes or biomass.

The Equation (51) can be related to the Lineweaver Burk plot for the determination of the functional parameters and coefficient of, and Km. Therefore, the general solution to Equation (3.31) can be expressed as:

$$\frac{1}{\mu} = \frac{K_m}{\mu_{\max}[S]} + \frac{1}{\mu_{\max}} \tag{53}$$

$$\frac{1}{\mu} = \frac{K_m}{\mu_{\max}[C_o]} + \frac{1}{\mu_{\max}} \tag{54}$$

RESULTS AND DISCUSSION

Results of Biokinetics

The biokinetics parameters were determined by plotting the reciprocal of specific rate against reciprocal of TPH and the results obtained are presented from (Figures 2 to 7).

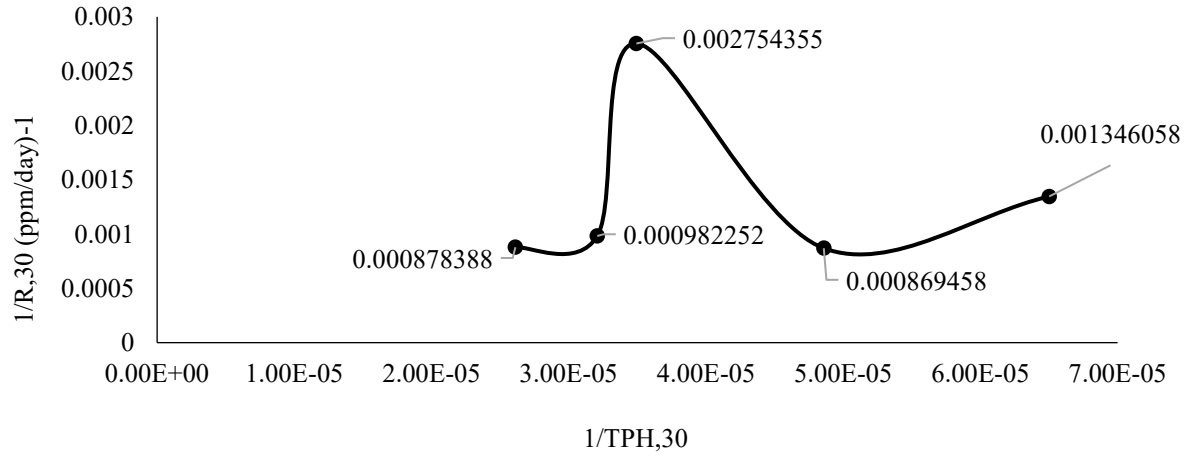

Figure 2. Dosage 30 g of reciprocal of specific rate of TPH against reciprocal of TPH degradation for nutrient sample application of POPWW.

Figure 2 shows the relationship between the $^1/_R$ and $(^1/_{TPH})_{30g}$ (which is referred as the reciprocal of R and the reciprocal of TPH. The regression equation of Y_{30} = 11.693x + 0.0006 and best fit value

of $R_{30}^2 = 0.9951$ was obtained. The reliability of acceptability of the research revealed 99.51% showed the effectiveness of the process to enhance TPH degradation by the action of the THB and THF inoculated in the bioreactor with biostimulant of 30 g dosage. The rate of TPH degradation can be obtained through the application of Michaelis–Menten Model. Therefore, $V_{max} = \frac{1}{\text{intercept}}$ and $K_{TPH} = V_{max}$ (slope) which $V_{max} = \frac{1}{0.0006}$ reveals = 1666.67 day/ppm and K_{TPH} = 1666.67 (11.693) = 19488.33 (ppm^{-1}); Hence, $V_{30} = \frac{1666.67\,[TPH]}{19488.33 + [TPH]}$

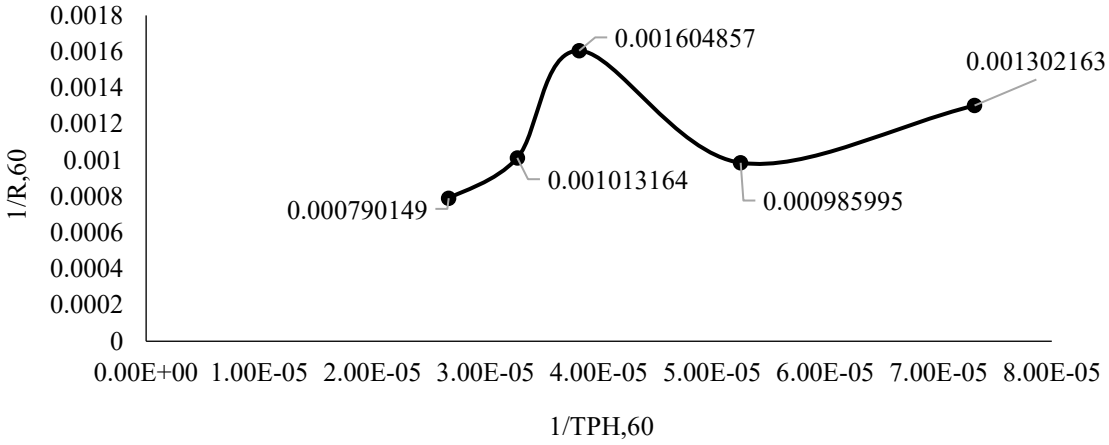

Figure 3. Dosage 60 g of reciprocal of specific rate of TPH against reciprocal of TPH degradation for nutrient sample application of POPWW.

Figure 3 illustrates the correlation of the $^1/_R60$ g with $\left(\frac{1}{TPH}\right)_{60\ g}$ and the process revealed the regression equation of Y_{60} = 10.884X + 0.0005 with value of R_{60}^2 = 0.9611. The percentage acceptability of reliability shows 96.11% of accuracy in the process. However, this research shows that the 60 g dosage of contaminated soil with fermented palm fruit processed wastewater is a good biostimulant due to the available nutrient that is contained in it. The determination of the Michaelis–Menten constant parameter reveals the following that $V_{max} = \left(\frac{1}{intercept}\right)$ and $K_{TPH} = (slope)(V_{max})$

Therefore, $V_{60} = \frac{V_{max}\,[TPH]}{K_{TPH} + [TPH]}$

where: $V_{max} = \frac{1}{0.005} = 2000\ (\text{ppm/day})^{-1}$ and $K_{TPH} = 2000\ (10.884) = 21768\ (\text{ppm})^{-1}$.

Hence: $V_{60} = \frac{2000\,[TPH]}{21768 + [TPH]}$.

Figure 4 demonstrates the plot of $^1/_R$ against $^1/_{TPH}$ for TPH remediation using 90g dosage of FPFPWW. The equation of regression obtained is $Y_{90} = 4.4511X + 0.0008$ with, $R_{90}^2 = 0.925$, which further revealed the reliability value of 92.5%. The Lineweaver–Burk-plot parameters were determined by establishing the slope as 4.4511 and intercept as 0.0008.

The Michaelis–Menten model of $V_{90} = \frac{V_{max}\,[TPH]}{K_{TPH} + [TPH]}$

where:
slope = $\frac{K_{TPH}}{V_{max}}$ and intercept = $\frac{1}{V_{max}}$ = 1250 (ppm/day^{-1} and = K_{TPH} = V_{max} (slope) = 1250 (4.4511) = 5563.875 (ppm)$^{-1}$.

$$V_{90} = \frac{1250\ [TPH]}{5563.5\ +\ [TPH)}$$

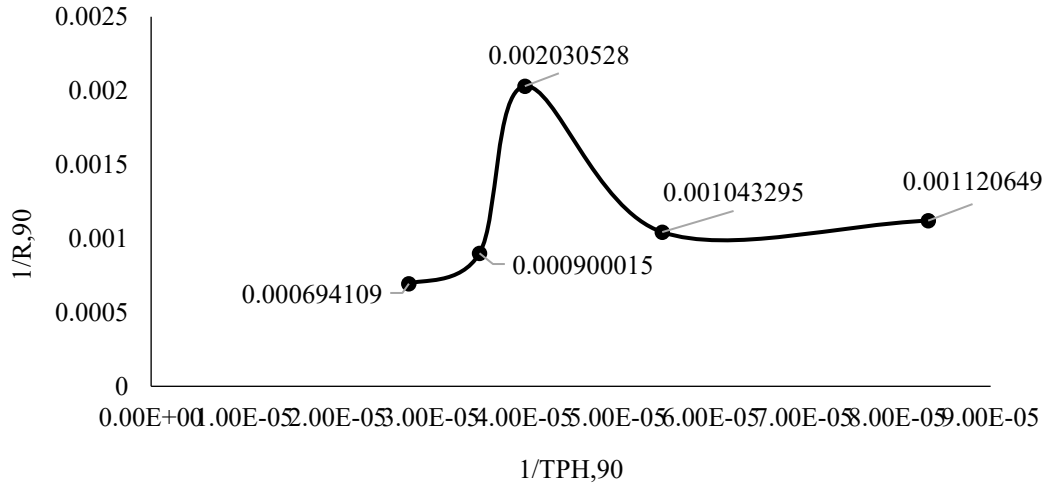

Figure 4. Dosage 90 g of reciprocal of specific rate of TPH against reciprocal of TPH degradation for nutrient sample application of POPWW.

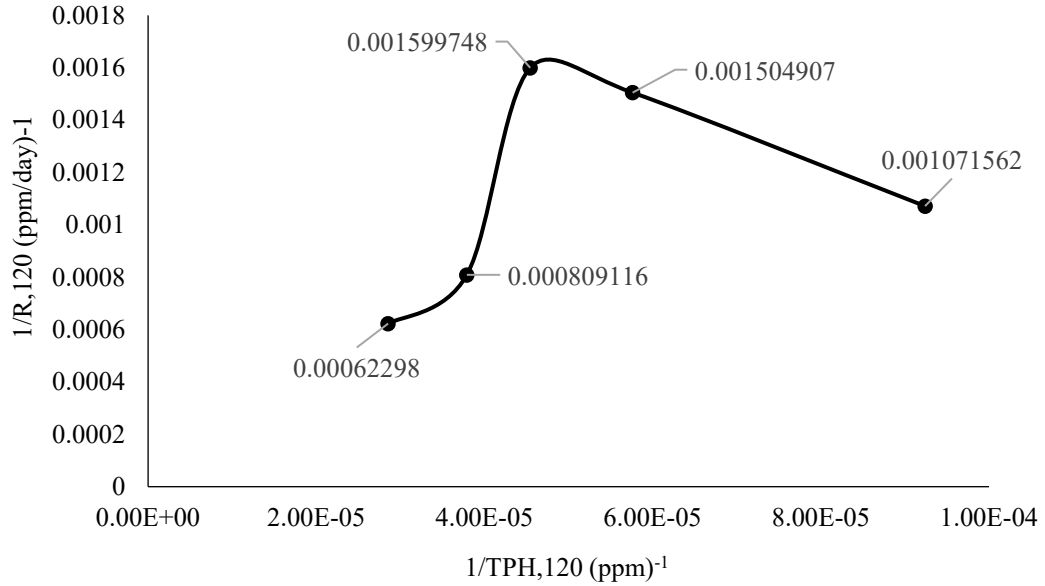

Figure 5. Dosage 120 g of reciprocal of specific rate of against reciprocal of TPH degradation for nutrient sample application of POPWW.

Figure 5 shows the relationship between 1/R and 1/TPH of 120 g dosage of biostimulant and the regression equation of $Y_{120} = 11.516X + 0.0021$ with $R^2_{120} = 0.9931$ was obtained, which demonstrates the reliability value of 99.31% acceptability. However, the rate of degradation of TPH was determined using the concept of Michaelis–Menten model.

Thus, slope = $\frac{K_{TPH}}{V_{max}}$ and intercept = $\frac{1}{V_{max}}$, hence

$V_{max} = \frac{1}{0.0021}$ = 476.19 day/ppm and

K_{TPH} = 476.19 (11.516) = 5483.81 $(ppm)^{-1}$.

Therefore:

$$V_{120} = \frac{476.19\ [TPH]}{5483.81 + TPH}$$

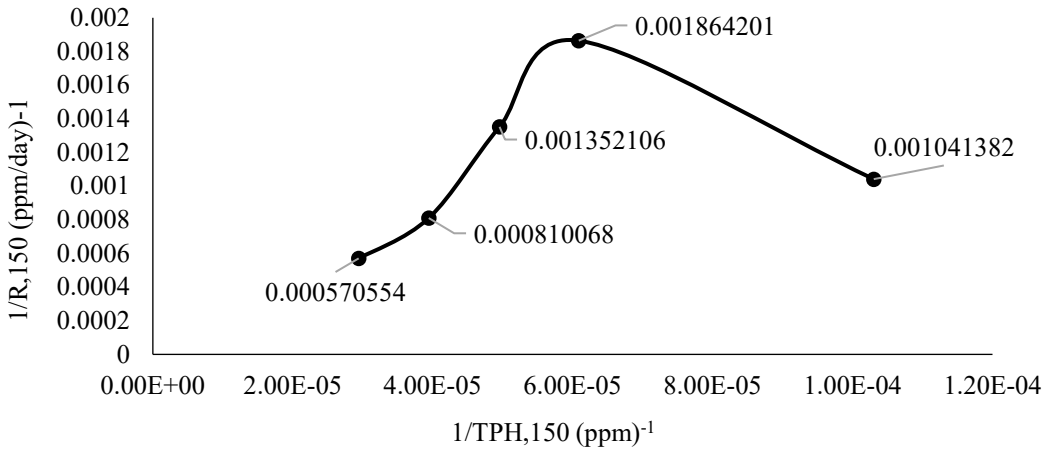

Figure 6. Dosage of 150g of Reciprocal of Specific Rate of TPH against Reciprocal of TPH Degradation for nutrient sample application of POPWW.

Figure 6 demonstrates the plot of Lineweaver–Burk-Plot adopted from Michaelis–Menten Equation. Indeed, the regression equation is given as Y_{150} = 49.089 x 0.0011 with R^2_{150} = 0.9976, which predict that the reliability value of 99.76% showing the acceptability of the process as well as has more effective biostimulant. The slope value is 49.089 and intercept value is 0.0011, however, inputting the values with the Michaelis–Menten model shows the following expression, thus:

$$V_{max} = -\frac{1}{0.0011} = -909.09\ (ppm/day)^{-1}$$

and = $K_{TPH} = V_{max}\ (slope)$ = 909.09 (49.089) = –44626.36 (ppm)$^{-1}$

Therefore, $V_{150g} = \frac{909.09\ [TPH]}{44626.36 + [TPH]}$

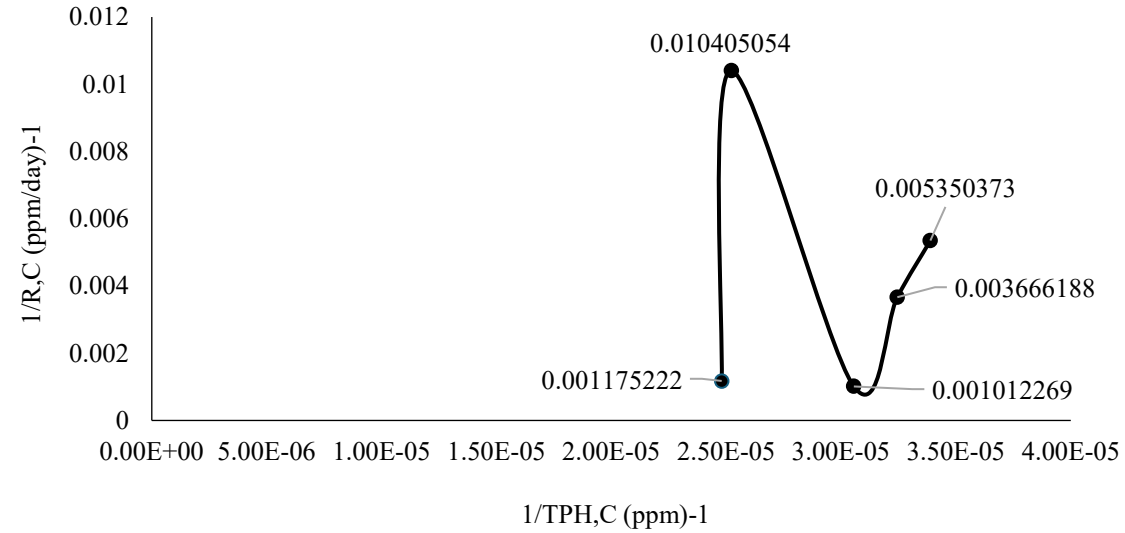

Figure 7. Control of reciprocal of specific rate of TPH against reciprocal of TPH degradation for control.

Figure 7 shows the plot of Lineweaver–Burk-Plot of the control sample and the regression equation reveals that Y_{con} = 13.07.1X – 0.00389 with R^2_{con} = 0.9975, and this showcase, the reliability value of 99.75%. The Michaelis–Menten Equation and expression is evaluated as detailed below:

Intercept = –0389 and $V_{max} = -\frac{1}{0.0389}$ = –25.71 (ppm/day) and

$K_{TPH} = V_{max}\,(slope) = -25.71\,(1307.1)$ = –33601.54 $(ppm)^{-1}$.

Therefore, $V_{con} = \frac{25.71\,[TPH]}{33601.54 + [TPH]}$

CONCLUSION

This research has demonstrated that the palm oil processed wastewater is useful in cleaning polluted regions, thereby restoring the loss glory of the contaminated soil by crude oil. However, this research has demonstrated that the palm oil processed wastewater possesses the characteristics of the required nutrient to catalyze and biostimulate the microbes in enhancing bioremediation process.

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