Mathematical Modelling of insitu-Bioremediation of Crude Oil Polluted Soil

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Abstract

A bioremediation model was developed for the bioremediation of a crude oil polluted soil. The developed mathematical model considers a batch process. The model was designed to predict the quantity of crude oil remaining per time in crude oil contaminated areas during in-situ bioremediation. The model can be used to monitor the progress of soil bioremediation by monitoring crude oil residual concentration per time. Comparing the results of the simulations of the derived model to the results of an existing model, shows that the new model is valid and reliable for monitoring the progress of any batch bioremediation process of crude oil polluted soils.

Keywords: Mathematical modelling; bioremediation; crude oil; batch process; derived model.

1. Introduction

Upstream production and transportation of crude oil is more often recently discussed with emphasis on petroleum contamination of soils resulting from unsuitable operations and pipeline leakages. Contaminated soils pose severe threats to the environment and must be taken care of in order to preserve aquatic or plant life and soil nutrients. Methods for cleaning up contaminated sites include incineration, solidification/stabilization, soil vapour extraction, soil washing, bioremediation etc. Some currently used physical and chemical methods as pollution control measures have their disadvantages because of the release of toxins which are harmful to plant and animal life. These methods are relatively expensive hence the need for cheaper alternatives, cost effective and very effective means of control [19]. Bioremediation is preferred over the aforementioned methods but long term tolerance studies need to be carried out for their consideration in large scale applications [11].

Recently, bioremediation has become one of the most promising technologies [18] with growing demand for resuscitating petroleum invaded soils because pollutants can be removed by the establishment of microbial colonies in such soils. The method makes use of inoculated/naturally occurring microbes which are spatially distributed in the subsurface of soils; its disadvantage is the inadequate spatial distribution of the much

needed nutrients to the microorganisms within the subsurface of the soil [8] which may also result in excessive competition or death of some starved microbes while in some cases, it is possible that the products of the microbial metabolic activities may be toxic. Also, the oil may mix with other contaminants such as radionuclides, heavy metals and some chlorinated salts that are non-biodegradable [5]. The continued demand for crude oil products has led to an increase in the number of recorded pipe leakages, poor management of refinery wastes and accidents while transporting crude oil and its products hence, the need for better ways of tackling the problem. A recent study revealed that Nigerian crude oil may be hemotoxic/hepatotoxic, and can cause infertility and cancer in man. Besides the dangers inherent in oil spills, the dispersants used to remediate polluted environments are also capable of endangering human health because they can disrupt both bacterial and human cell membranes which may subsequently lead to cancer and eventual death [12]. In [9], the hazardous effects of crude oil intrusion in soils was discussed as having great potentials in reducing plant life and animal growth because of the toxins and other harmful constituents which contaminate the soils and poison the nutrients. According to [7], bioremediation of crude oil polluted soils may result in complete mineralization of organic contaminants giving products such as carbon dioxide, water, inorganic compounds, cell protein or other simple organic compounds. Agamuthu et al. [3] reported that traditional soil bioremediation is one of the world's most expensive methods of soil treatment and is preferred over other

existing methods based on its effectiveness in removing numerous pollutants from polluted sites. The investigation identifies potential organic wastes in enhancing the biodegradation of used lubricating oil in a contaminated soil. Sewage sludge and cow dung were added to the used-lubricant-contaminated-soil to serve as nutrients for the microbes and samples of the soil were taken for periodic sampling. Results from the experiment indicate that the Cow dung amended set-ups gave the best bioremediation performance. Bioremediation of soil polluted with used lube oil amended with brewery spent grain (BSG), banana skin, and spent mushroom compost was investigated by Abioye et al. [1] for a period of 84 days. The highest percentage of hydrocarbon consumed during the bioremediation process was recorded in the soil polluted with used lubricating oil and blended with BSG. Results of the applied first order kinetic model revealed that soil amended with BSG gave the best result. The findings also showed that BSG is a potential substrate for enhancing bioremediation of low concentrations hydrocarbon contaminated soils. Nwogu et al. [15] carried out an investigation on the use of *Acinetobacter*, *Achromobacter*, *Bacillus*, *Flavobacterium*, *Klebsiella*, *Micrococcus*, *Pseudomonas*, and *Staphylococcus* in the bioremediation of a soil artificially contaminated with hydrocarbon and having mixed portions of goat manure. The results obtained show that the applied manure is a good biostimulant which helped to improve the remediation ability of the microbe. Adekunle et al. [2] carried out bioremediation studies of a crude oil polluted soil using a locally formulated remediating agent. The process kinetics was aimed at understanding the effect of the formulated agent (Ecorem) on the soil conductivity, soil status and salinity. Based on the findings, they recommended marginal negative errors of 9% and positive errors of 2 to 17% for planned bioremediation project execution for soils contaminated with spent engine and crude oils. In [21], a kinetic study on ex-situ bioremediation of a crude oil polluted soil was carried out using *Baccilus Mycoides*. GC mass spectrometer was used to analyze the contents of the soil samples. The results from the analytical method employed show that the TPH of the soil decreased over time with the bioremediation process showing a first-order-kinetic behavior. Also, an investigation of the bioremediation of a crude oil polluted soil supplemented with organic manure such as poultry droppings and goat dung, NPK and saw dust was carried out in [6]. The soil under investigation was polluted with Bonny Light crude oil. The relative effectiveness of the soil additives was monitored for 112 days and it was observed that the soil-crude oil sample with NPK gave the least total hydrocarbon relative to other supplements. Similarly, a first-order kinetic model was used to explain the remediation of crude oil contaminated arable soil for several concentrations of crude oil spill biostimulated with inorganic fertilizer (NPK), cow dung, and palm kernel shell ash; the additives were applied as single amenders and in combined forms [16]. Based on their results, the setup comprising the combination of inorganic fertilizer and cow dung gave the best results. Yelebe et al. [20] also developed a kinetic model for the bioremediation of a petroleum polluted soil using palm bunch ash and wood ash, which they found to be replaceable alternatives for NPK. Their studies also revealed that, natural degradation of the petroleum can also take place over time without any soil amendment. In the bioremediation study carried out in [14], hydrocarbon degradation rate and halve

lives were determined and compared for three bioremediation strategies which include natural attenuation, biostimulation and bioaugmentation, for some weathered crude oil (WCO) contaminated sediment samples at varying concentrations. The kinetic evaluations were for a period of 90 days, after which the oil contaminated sediments were found to have lower crude oil concentrations with time. After two weeks of commencing the exercise, natural attenuation showed constant remediation rate while the highest oil removal was recorded during bioaugumentation. The results show that first order kinetics can be used to describe the bioremediation of sediments polluted with crude oil. Biostimulation and bioaugumentation study of a Bonny light crude oil polluted soil was carried out in order to determine the effects of NPK fertilizer, tween 80 and mixed culture during decontamination of the soil sample [4]. Response surface method was employed in the experimental design and the remediation process was optimized in order to obtain optimum values of soil amendment required for maximum removal of the pollutant. A simulation approach to the bioremediation of diesel oil polluted soil was carried out by Olu-Arotiowa et al. [17] where single and multiple *Pseudomonas Aeruginosa* catalyzed bioremediation reactions were modeled and validated with experimental data. Aside the simple nature of bioremediation, the routine operation is quite laborious and could be somewhat expensive. However, a previously established bioremediation model, such as that of Kompala et al. [13], an experimental evaluation of cybernetic models for bacterial growth on mixed substrates, which has its origin in the monod's model was used as a basis for developing the new model described in this paper hence, a Monod-based-mathematical model for describing the bioremediation process of crude oil polluted soils was attempted in this work in order to reduce the high cost implications arising from bioremediation activities by simply determining the initial contaminant concentration. This will further help to curb the excesses involved in deploying microbes with the intention of controlling wastes or excess spent microbes by estimating the required microbial cells for a particular operation i.e. the model is to serve as a predictive tool, thus making it easier to determine the initial concentration of oil pollutant and the time involvement of the bioremediation process of a petroleum oil contaminated site.

2 Kinetic Model

The model was developed based on some assumptions.

2.1 Model Assumptions

The process is considered a batch process i.e. there is no flow of materials in and out of the reactor as soon as substrate and scavengers are charged into the reactor. Since the process is assumed a batch process, it follows that there is no accumulation within the system at any time. The only components of the reactor are soil sample from site, substrate and a suitable microbe. Thus the microorganisms consume the crude oil as the substrate. The rate of consumption of the substrate for cell growth is significant. The concentration of substrate is steady with respect to position. The crude oil and soil samples were well mixed so as to completely simulate an upstream contaminated soil.

2.2 Model Development

The mathematical description of the consumption of crude oil within a typical soil in a batch reactor can be obtained based on the following physical principles

- Law of conservation of mass

- Monod's kinetics.

The law of conservation of mass states that matter can neither be created nor destroyed in a process but may change from one form to another while the total mass remains constant. However, no crude oil is generated in the process, rather, consumption of the oil takes place.

Continuity equation:

The rate of flow of oil into a soil layer −
rate of oil flow out of the soil layer −
rate of consumption of oil by microbes =
rate of oil accumulation in the soil   (1)

Monod's kinetics:

This is a simple mathematical model which relates the specific growth rate of the microorganism to its soil nutrient concentration. The monods equation considers the limiting nutrient. It is an empirical equation which assumes the form of Michaelis-menten equation.

Monod's equation is:

$$\mu = \frac{\mu_{max} \cdot s}{k_s + s} \qquad (2)$$

μ = specific growth rate constant (h^{-1})

μ_{max} = maximum specific growth rate constant

k_s = "half − velocity constant"— the value of S when $\mu/\mu max = 0.5$ (gL^{-1})

s = concentration of limiting substrate   (gL^{-1})

Continuity equation:

rate of flow in − rate of flow out −
rate of consumption = accumulation   (3)

The process is a batch process and reduces the equation to:

−rate of consumption = accumulation   (4)

$$\frac{-\mu x}{Y_{x/s}} = \frac{ds}{dt} \qquad (5)$$

Introducing (6) and substituting for x,

$$Y_{x/s} = \frac{x - x_0}{s_0 - s} \qquad (6)$$

$$x - x_0 = Y_{x/s}(s_0 - s) \qquad (7)$$

Putting (7) in (5)

$$\frac{-\mu[Y_{x/s}(s_0 - s) + x_0]}{Y_{x/s}} = \frac{ds}{dt} \qquad (8)$$

Introducing Monod's equation,

$$\mu = \frac{\mu_{max} \cdot s}{k_s + s} \qquad (9)$$

$$\frac{-\mu_{max} \cdot s[Y_{x/s}(s_0 - s) + x_0]}{(K_s + s)Y_{x/s}} = \frac{ds}{dt} \qquad (10)$$

$$\left[\frac{\mu_{max}Y_{x/s}s^2 - \mu_{max}s_0 Y_{x/s}s - \mu_{max}x_0 s}{Y_{x/s}k_s + Y_{x/s}s}\right] = \frac{ds}{dt} \qquad (11)$$

2.3 Discretization of the Model

The model obtained was evaluated using the Euler's numerical method. The model was discretized as given by the Euler formulae below (i.e. Equations 12-17):

$$\frac{s_{n+1} - s_n}{h} = \frac{ds}{dt} \qquad (12)$$

$$\left[\frac{\mu_{max}Y_{x/s}s^2 - \mu_{max}s_0 Y_{x/s}s - \mu_{max}x_0 s}{Y_{x/s}k_s + Y_{x/s}s}\right] = \frac{ds}{dt} \qquad (13)$$

$$\frac{s_{n+1} - s_n}{h} = \left[\frac{\mu_{max}Y_{x/s}s^2 - \mu_{max}s_0 Y_{x/s}s - \mu_{max}x_0 s}{Y_{x/s}k_s + Y_{x/s}s}\right] \qquad (14)$$

$$s_{n+1} = s_n + h\left[\frac{\mu_{max}Y_{x/s}s_n^2 - \mu_{max}s_0 Y_{x/s}s_n - \mu_{max}x_0 s_n}{Y_{x/s}k_s + Y_{x/s}s_n}\right] \qquad (15)$$

The discretized form of the model was solved using MATLAB and the results obtained are presented and discussed in the following sections.

2.4. Model Validation

The new model was calibrated in order to establish the values of some constants and the model was compared with the Kompala et al. [13] model based on the simulated data for TPH estimation in order to determine the model's accuracy.

3. Results and Discussion

Table 1: Monod's parameters for the model

Parameter	Value
Maximum specific growth rate constant, μ_{max} (hr^{-1})	0.33
Initial cell concentration, x_0, (g/L)	1
Initial crude oil concentration s_0 (g/L)	250
Yield, $Y_{x/s}$	0.08
Saturation constant, k_s (g/L)	1.7

The model obtained was used to obtain plots of bioremediation time against the total petroleum hydrocarbon (TPH) content of the crude oil in the soil. The data and model parameters were obtained from [10]; see Table 1.

From Figure 1, it could be seen that the total petroleum hydrocarbon content within the soil decreased with increasing time. This is because, as time increases, the oil consumption by the microbes increases thus reducing the total petroleum hydrocarbon content of the soil. The plot reveals that at 9.4 hours, the TPH content of the soil would have been totally depleted.
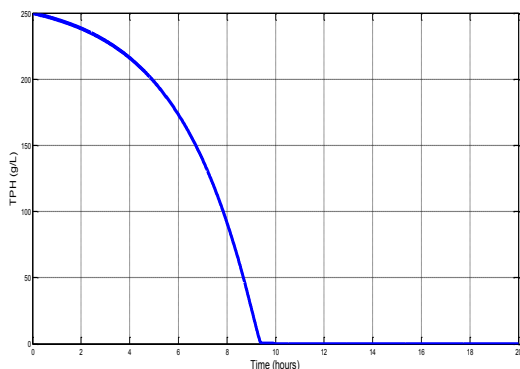
Figure 1: Variation of total petroleum hydrocarbon of the soil with time

The model obtained was also used to make a plot of total petroleum hydrocarbon against time using data obtained from [13]. The model results were plotted on the same graph as shown in Figure 2.

Table 2: Selected Monod's parameters for the model

Parameter	Value
Maximum specific growth rate constant, μ_{max} (hr^{-1})	0.9
Initial cell concentration, x_0, (g/L)	0.00083
Initial crude oil concentration s_0 (g/L)	4
Yield, $Y_{x/s}$	0.004
Saturation constant, k_s (g/L)	0.1

Source: [13]

The derived model was used to generate data for the total residual petroleum hydrocarbon in the soil at different times. The results obtained from the new model and the model in [13] were plotted on the same graph as shown in Figure 2. It could be seen that the hydrocarbon content of the soil dropped from 4 to 0.2 gL^{-1} and 0 gL^{-1} for both models respectively. For the new model, the residual oil concentration remained constant at 3.5 hrs while the TPH of the oil was zero at 3.6 hrs for the Kompala model. However, the new model agrees with the Kompala et al [13] model in terms of TPH estimation until after 3.5 hours where there seems to be slight deviation down to the 8th hour.
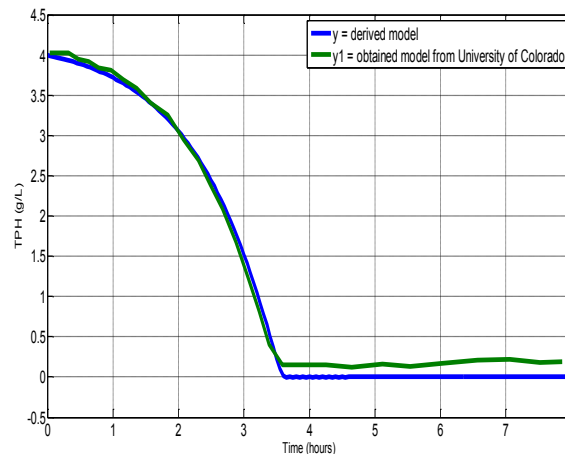

Figure 2: Total residual petroleum hydrocarbon in the soil vs time

Effect of Yield, Initial Substrate and Cell Mass Concentrations on Bioremediation Time

The model was used to study the variations in yield, initial substrate concentration, initial cell /mass concentration.

Effect of yield

By arbitrarily increasing the yield (cell growth) from 0.08 to 0.3, it was observed that the time required for complete depletion of the TPH within the soil also increased i.e. the bioremediation time increased from 9.4 hours to 13.2 hours; see Figure 3. Also, decreasing the yield from 0.08 to 0.02 shows that the bioremediation time is 5.4 hours for complete depletion of the TPH content in the soil; see Figure 4.

Figure 5 shows a graphical relationship between the biomass yield and the time required for complete deletion of the TPH within the soil..
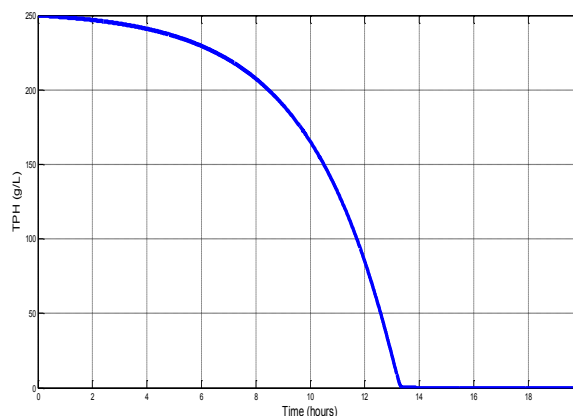

Figure 3: Profile of total hydrocarbon content with time for increased yield

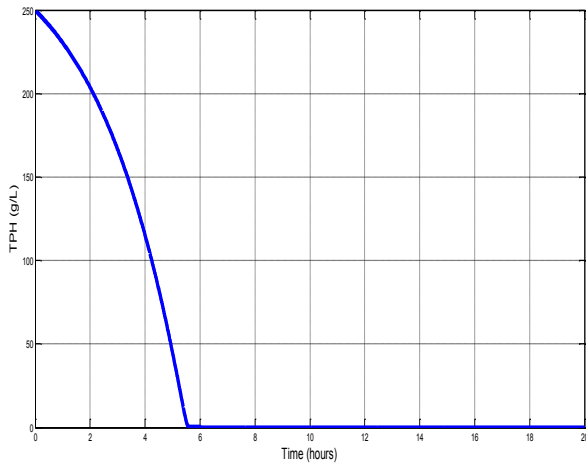consumption of the crude oil in the soil decreased from 9.4 hours to 8.2 hours; see Figure 8.

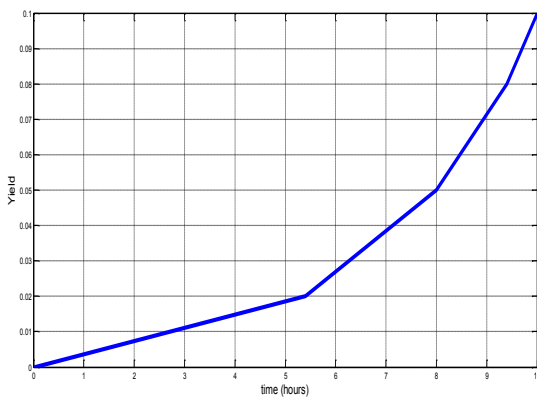Figure 4: Variation of time with total petroleum hydrocarbon content for decreasing yield

Figure 5: Variation of Biomass yield with time

Different values of yield were fixed in order to determine the time required for complete consumption of the crude oil content within the soil and the results from the new model are as shown below

Variation of initial crude oil concentration

For a constant yield, while maintaining the same initial substrate concentration of 250 g/L, the initial cell concentration was varied to determine its effect on the bioremediation time. As shown in Figure 6, an increase in the initial crude oil concentration shows that the time required to completely consume the crude oil will drop to 12.1 hours. However, as the initial crude oil concentration was decreased from 250 g/L to 100 g/L, the time required for total depletion of the substrate within the soil decreased to 7 hours; see Figure 7.

Effect of initial cell concentration on bioremediation time

While maintaining the yield of biomass at 0.08 and the initial crude oil concentration at 250 g/L, the initial cell concentration was varied. When the initial cell concentration was increased from 1 g/L to 1.5 g/L, the time required for complete
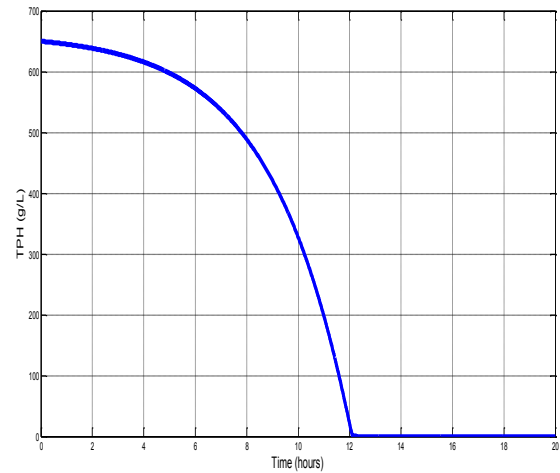

Figure 6: Variation of TPH with time for increased initial substrate concentration (650 g/L)
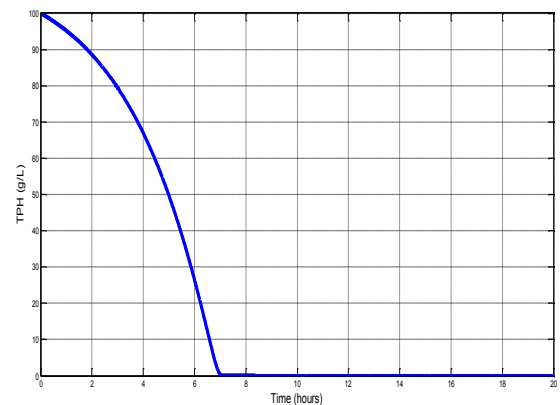

Figure 7: Variation of TPH with time for change in initial substrate concentration (250 -100 g/L)
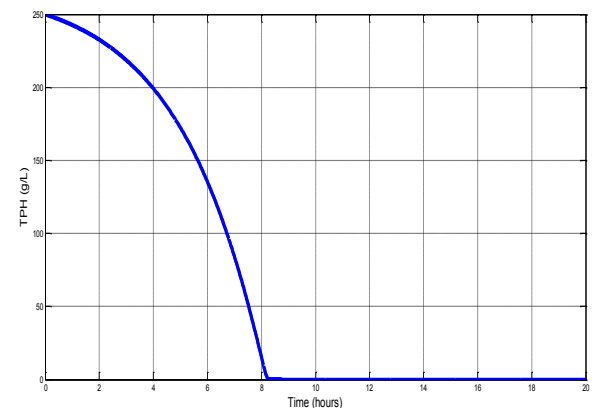

Figure 8: Variation of TPH with time for initial cell mass concentration of (1 - 1.5 g/L)
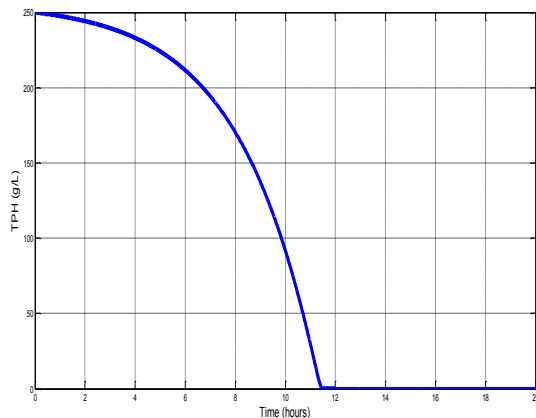
Figure 9: Effect of time on TPH for decrease in initial cell mass concentration (1 to 0.5 g/L)

Furthermore, Figure 9 is the graphical presentation of the situation that arises when there is a decrease in initial cell mass from 1 g/L to 0.5 g/L; here, the total time for complete consumption of the oil in the soil increased from 9.4 hours to 11.6 hours.

Conclusion

A new model has been developed for in-situ bioremediation of a crude oil contaminated soil. The model can be used to predict the total residual petroleum hydrocarbon present in soils at different times. The model results are in agreement with the results of the Kompala et al. [13] model. Increasing the initial cell mass concentration decreases the bioremediation time while decreasing the initial cell mass concentration, increases the bioremediation time when all other parameters are invariable. Also, from the results obtained, one could infer that, increasing the initial substrate (crude oil) concentration increases the bioremediation time while decreasing the initial substrate concentration decreases the bioremediation time.

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