Mathematical Modeling of Bioremediation of Soil Contaminated With Spent Motor Oil

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Abstract
A study was carried out on mathematical modeling of soil contaminated with spent motor oil. This research work is important for the prediction of bioremediation times of hydrocarbon contaminated soil. Mathematical model for a typical soil contaminated with spent motor oil was derived from basic principles. The Oil and Grease (O&G) content and carbon dioxide (CO₂) released from bioremediation experiments were used as indicators for monitoring bioremediation. The model developed was based on CO₂ evolutions and it was evaluated using kinetic data, and compared with experimental results. Results obtained from this study revealed a goodness of fit between the experimental and predicted values. In addition, at 95% confidence level there was no significant difference between the experimental and predicted cumulative CO₂ generation using the Chi-square (χ²) statistical tool. It was observed that the profile obtained from the evaluated model concurred with the shifting order kinetics (1-0). Therefore, the developed model can be used for the prediction of bioremediation.

Keywords: bioremediation; CO₂ evolution; basic principles; experimental values; predicted values; significant difference.

INTRODUCTION
Bioremediation is a cleaning technology used from time immemorial to detoxify or reduce pollutant levels of harmful chemicals such as hydrocarbons, heavy metals, etc to acceptable level by the regulatory authorities by the action of micro-organisms. Its use as a treatment option was unpopular until recently when attention has shifted to the area of biotechnology. Economic advantage, environmental friendliness and ease of application were in no doubt factors that make this remediation technology popular in recent times. Bioremediation is not a pinnacle but meant to complement existing remediation options such as the thermal treatment, dig and dump method, chemical method, separation techniques and stabilization/solidification technology with can be broadly classified as the physicochemical technologies. In addition, these technologies have their limitations such as high cost to implement at full scale, complexity in technology, destruction of soil texture and characteristics, and above all, most of them are not environmentally friendly (Less and Senior, 1995; Vidali, 2001). More so, the physicochemical technologies do not always result in complete neutralization of pollutants (Yerushalmi et al., 2003).

From the aforementioned, there is no doubt that bioremediation option is gaining more acceptability over other treatment options where ever it can be applied. Great deals of literature have reported that bioremediation technologies are alternatives and or supplements to the physicochemical technologies, some of these literatures include; Less and Senior (1995); Vidali (2001); Yerushalmi et al. (2003). In addition, most of the works carried out on bioremediation were basic proof of concepts, practical oriented but not geared towards modeling and simulation or process development. Some of the works done on modeling of bioremediation processes were mainly on in-situ processes (Yaghmaei, 2002).

The dig and dump method currently used in disposing oil contaminated with spent motor oil polluted lands is expensive and only transfer the contamination from one place to another. This disposal technique is very prominent in the developing countries, where there were no strict enforcement on environmental regulatory policies. In no doubt, the dig and dump practice has lead to the contamination of millions of other sites remote from their place of initial contamination and therefore, urgent actions need to be taken for environmental safety in general and of importance public health.

In Nigeria, oil spills at auto-mechanic workshops have been left uncared for over the years and its continuous accumulation is of serious environmental concern because of the hazard associated with them. For instance, used motor oil disposed of improperly contains potentially toxic substances; such as benzene...
(carcinogen), lead, arsenic, zinc and cadmium, which can seep into the water table and contaminate ground water (Http. 2). In addition, one gallon of used motor oil can contaminate one million gallons of fresh water (Http.1; Http. 2) and render four-acre of soil unusable for planting for decades (Http. 2).

In recent times, aerobic fixed bed bioreactor is the most frequently used solid-phase bioreactor for the treatment of sites polluted with minor oil spills. However, the various types of aerobic fixed bed bioreactor currently in use are lacking in safety factor such as the containment of volatile organic compounds (VOC). For instance, Croft et al. (1995) and Baptista et al. (2005) carried out bioremediation experiments in aerobic fixed bed bioreactors but their experimental designs were lacking in the containment for volatile organic compounds.

Furthermore, in the last few years a great deal of work has been done on several aspects of bioremediation mainly because of its environmental friendliness, cost effectiveness and simplicity in technology (Admon and Avnimelech, 2001; Odukuma and Dickson, 2003; Baptista et al., 2005). However, most of the works carried out were basic proof of concepts, practical oriented and not geared towards modeling and simulation or process development.

Aim and objectives of this research work are to develop a safe, robust and economical treatment technology for the rehabilitation of soil contaminated with used motor oil using bioremediation technique and to develop a mathematical model for the prediction of bioremediation of soil contaminated with used motor oil.

The problem of soil contamination arising from spills of used motor oil needs to be given priority attention because of the hazard associated with them, hence the need to address this problem for human and environmental safety. In addition, a realistic model will enable us to predict the time required to detoxify a contaminated site.

MATERIALS AND METHODS

These biodegradation investigations were carried out in six aerobic fixed bed bioreactors (TR1 to TR6), as presented in Fig. 1. Each bioreactor contained 1.5 kg of contaminated soil; this included, where appropriate, the various additives at room temperature. The bioreactors were completely closed in order to avoid CO₂ leakage to the environment before passing into the CO₂ traps. The moisture content in all the six treatments was set at 20% of the total weight of the soil at the initiation of bioremediation. The airflow rate was maintained in all cases at an average rate of 10 L/h using a flow meter for fourteen (14) hours daily for the period of investigation.

At the beginning of this investigation the contaminated soil was tested in order to provide the baseline data for the study. The physicochemical and microbiological integrities of the soil were tested using standard methods well detailed in Abdulsalam (2011a). In addition, the following physicochemical and microbiological tests were also carried out on all the treatments on weekly basis: oil and grease content (O&G), moisture content, pH, temperature. More so, carbon dioxide (CO₂) respiration rate was monitored every 48 h throughout the duration of the experimental work. Methods of analyses are also detailed in Abdulsalam (2011a).

RESULTS AND DISCUSSION

Oil and Grease Biodegradation

The levels of reduction in the oil and grease content at different periods during the course of this study were shown in Fig. 2. From this figure, the percentage O&G content removal increased with time, which is typical of any degradation process. The process was characterized by a period of fast decrease in hydrocarbon concentrations during the first five weeks (40, 45, 51, 40, 59 and 63% for TR1, TR2, TR3, TR4, TR5 and TR6 respectively), followed by a period of slower activity (past Week 5). The degradation pattern followed shifting order (1-0) degradation (Okpokwasili and Nweke, 2005).

At the initiation of bioremediation (at time zero), the concentrations of O&G contents in bioreactors TR1, TR2, TR3, TR4, TR5, and TR6 were 29 010, 37 966, 35 519, 33 746, 32 027 and 38 592 mg/kg dry weight respectively. After 70 days, their concentrations reduced to 14 439, 14 088, 12 085, 14 438 10 115 and 9 830 mg/kg dry weight, which translate to 50, 63, 66, 57, 68 and 75% losses in O&G contents.

Of the six treatments employed in this study, TR6 in which the indigenous microorganisms were stimulated with NPK (20:10:10) and KH₂PO₄ resulted in the maximum bioremediation response of 75% reduction in the initial O&G content. This observation is in line with the literature that biostimulation strive well in aged contaminated sites (Kosteck and Calabrese, 1991).
Based on the results obtained for the O&G content and CO₂ generation, treatment option 6 (TR6), the sample stimulated with NPK (20:10:10) and KH₂PO₄ gave the best result. Therefore, TR6 could be used to develop a safe, robust, and economical full-scale treatment technology for soils contaminated with used motor oil. Since treatment option six (TR6) gave the best result in this study, the parameters obtained from it was employed in analyzing mathematical model developed.

**MATHEMATICAL MODEL FOR PREDICTION OF BIOREMEDIATION**

**Model Formulation**

In this study, mathematical model for the prediction of the cumulative rate of carbon dioxide (CO₂) generation for the treatment technology (TR6) was developed from basic principles. The model formulation is as follow:

\[
\frac{dCO_2}{dt} = \alpha \mu + \beta
\]

where \( \alpha \) and \( \beta \) are the growth-related product formation coefficient and non-growth-related product formation coefficient, respectively.

**CO₂ Generation in Bioreactors**

CO₂ evolution was also used as an indicator of bacteria respiration (a product of bioremediation process). The CO₂ evolution was monitored on 48-hourly basis and this enables us to compute the cumulative CO₂ generation presented in Fig. 3. From this figure, all the treatment (TR1 to TR6) appears to show a trend of adaptation period (1 to 10 days), maximum oil degrading period (25 to 55 days) and a decaying rate of oil degradation period (past 60 days). The cumulative CO₂ generation in each bioreactor increased with pollutant or oil degradation. The cumulative CO₂ generation for TR1, TR2, TR3, TR4, TR5 and TR6 were 4 276, 5 226, 5 493, 5 279, 5 667 and 6 249 mg/kg respectively for this study. Treatment option 6 (TR6), gave the best CO₂ generation, which corresponds to the best O&G content (75%) removals. The control (TR1), showed the least CO₂ generation, which also corresponds to the least O&G removals of 50%.

**Selection of a Treatment Technology**

Considering the schematic diagram of an aerobic fixed bed bioreactor as indicated in Fig. 4. Material balance around the bioreactor system is express as:

\[
\text{Rate of flow of material into bioreactor} = \text{Rate of flow of material out of bioreactor} + \text{Rate of accumulation of material within the bioreactor}
\]

Taking CO₂ balance around the bioreactor:

Since CO₂ is not supplied into the bioreactor, the first term of Equation (1) equals to zero. Therefore, we have:

\[
\text{Rate of formation of } CO_2 \text{ by biochemical reaction in bioreactor} = \text{Rate of flow of } CO_2 \text{ out of bioreactor}
\]

Mathematically, equation (2) can be express as:

\[
\left( \alpha \mu + \beta \right) x V = F \cdot CO_2 \frac{dCO_2}{dt} = V \frac{dCO_2}{dt}
\]

Where: \( \left( \alpha \mu + \beta \right) \) is the specific rate of product (CO₂) formation (Leudeking and Piret, 1959)

- \( \alpha \) is growth-related product formation coefficient and \( \beta \) is non-growth-related product formation coefficient.
- Both \( \alpha \) and \( \beta \) are dependent on the treatment option employed or bioremediation approach used.
\( \mu \) is the specific growth rate of microorganisms
\( x \) is the cell concentration
\( V \) is the active or effective volume of bioreactor
\( F \) is the volumetric feed flow rate

Dividing equation (3) by \( V \) and assuming that the rate of generation of CO\(_2\) in the bioreactor is equal to the rate of CO\(_2\) leaving the system. Therefore, equation (3) reduces to:

\[
(\alpha \mu + \beta) x = D.CO_2
\]

where: \( D \) is the dilution factor

However, we know that:

\[
x = \frac{dx}{d\mu}
\]

In addition, \( \mu \) could be represented by the popular microbial growth equation (i.e. the Monod’s equation), given by:

\[
\mu = \frac{\mu_{\text{max}}x}{k_s + x}
\]

where: \( \mu_{\text{max}} \) is the maximum specific growth rate
\( k_s \) is the substrate saturation constant or Monod’s constant

Substituting equations (5) and (6) in (4), we have:

\[
\alpha + \frac{\beta}{\frac{\mu_{\text{max}}x}{k_s + x}} \frac{dx}{dt} = D.CO_2
\]

Nevertheless, the substrate concentration (\( s \)) is a function of cell mass (\( x \)) and the relationship between them is given by equation (8):

\[
\frac{dx}{dt} = Y_{\mu} \frac{ds}{dt}
\]

or

\[
Y_{\mu} = \frac{x - x_0}{s_0 - s}
\]

Substituting equation (8b) in (7) and rearranging gives:

\[
\left[ \frac{\beta Y_{\mu} k_s + Y_{\mu} x_0 + x - x_0}{Y_{\mu} k_s} \right] \frac{dx}{dt} = D.CO_2
\]

Further rearranging equation (9) and integrating gives:

\[
\alpha + \beta \frac{\mu_{\text{max}}}{\ln \left(\frac{Y_{\mu} x_0 + x - x_0}{Y_{\mu} k_s}\right)} \frac{dx}{dt} = D.CO_2 t
\]

Evaluating gives:

\[
[CQ] = \frac{1}{D t} \left[ \left( \alpha + \frac{\beta}{\mu_{\text{max}}} \right) x - x_0 \right] + \frac{\beta}{\mu_{\text{max}}} \ln \left( \frac{Y_{\mu} x_0 + x - x_0}{Y_{\mu} k_s} \right)
\]

Equation (11) is the model equation for the prediction of cumulative rate of carbon dioxide (CO\(_2\)) generation in an aerobic fixed bed bioreactor.

In terms of substrate concentration, equation (11) becomes:

\[
[CQ] = \frac{1}{D t} \left[ \left( \alpha + \frac{\beta}{\mu_{\text{max}}} \right) Y_{\mu} (s_0 - s) \right] + \frac{\beta}{\mu_{\text{max}}} \ln \left( \frac{2s_0 - s}{s_0} \right)
\]

**Model Validation**

The mathematical model developed (Eqn. 12) was tested for the prediction of CO\(_2\) generation. Results obtained indicate a good fit between the experimental and predicted values (Fig. 5). In addition, a goodness-of-Fit test was carried out between the experimental and predicted cumulative CO\(_2\) generated using the Chi-square (\( \chi^2 \)) statistical tool. Results obtained also, indicate that there was no significant difference between the experimental and predicted values at 95% confidence level. Therefore, the developed model can be used for the prediction of bioremediation. The model parameters \( \alpha \) and \( \beta \) (Table 1) were obtained by iterative method using Microsoft Excel.

![Cumulative CO2 generated by the treatment technology](image)

**Table 1: Summary of Model Parameters for TR6**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>2.067527 - 1.7569Z + 0.35 for Z = 0 - 6, ( R^2 = 0.9989 )</td>
</tr>
<tr>
<td>( \beta )</td>
<td>157.27Ln (Z) - 218.12 for Z = 6-10, ( R^2 = 0.9998 )</td>
</tr>
<tr>
<td>( Z )</td>
<td>time interval</td>
</tr>
</tbody>
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It should be noted that \( \alpha \) is dependent on the time interval (\( Z \)) from the starting point since it is a growth dependent coefficient (the first time interval takes the value of 1; the second, 2; the third, 3 and so on) and in addition, the values of \( \alpha \) and \( \beta \) depend on the treatment option employed.
Physical Significance of Model Parameters (α and β)
The growth dependent constant, α increased with increasing cumulative \( \text{CO}_2 \) generation. At high substrate concentration, \( \alpha \) is directly proportional to the cumulative \( \text{CO}_2 \) generation and can be represented by a first order reaction, neglecting the lag phase (i.e. between Weeks 2 and 6). At low substrate concentration (past Week 6), \( \alpha \) is characterized by slow increased in cumulative \( \text{CO}_2 \) generation and hence, the profile approached a plateau, which is best described by zero order phenomena (Fig. 3). From these observations, it can be concluded that the predicted model followed a similar pattern as the kinetic profile (Abdulsalam, 2011b).

Limitations of Mathematical Model
Haven identified how representative the developed model was in predicting bioremediation; the following limitations were also identified;
1) The model cannot predict accurately the experimental data at the start of bioremediation (i.e. between weeks “0” and “2”).
2) The model parameter, \( \alpha \) (i.e. the variable parameter) was represented by two equations (i.e. at low and high values of \( \text{CO}_2 \)).

CONCLUSIONS AND RECOMMENDATIONS
Conclusions
From the results obtained in this study, the following can be concluded;
1) The hydrocarbon removal efficiency can reach 75% in an aerobic fixed bed bioreactor within the experimental data used over a period of seventy days.
2) The bio-stimulation option can gave the best hydrocarbon removal efficiency in this study (75% removal of the initial oil and grease content in 70 days) and hence can be employed to develop a realistic pilot plant for the treatment of soil contaminated with spent motor oil.
3) The mathematical model developed was effective in the prediction of bioremediation.

RECOMMENDATION
I wish to recommend that the result of this investigation should be used to size a pilot plant for the treatment of hydrocarbon contaminated soil and also the model developed should be employed for the prediction of bioremediation.

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REFERENCES


Figure 1: Process flow diagram of an experimental rig for bioremediation studies (Source: Abdulsalam, 2011a)