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Modelling the Remediation of Diesel Contaminated Soil Using Palm Bunch Ash

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ABSTRACT

The adoption of petroleum and its derivative such as diesel in all transport forms hasamplified its pollution dangers to the soil. This research is aimed at modelling the remediation of diesel contaminated soil by palm bunch ash. A plot of land measuring 4.8m^2 was divided into nine equal cells of 0.36m^2 with a furrow of 0.2m created between cells. The cells were randomly contaminated with diesel and treated with 0.0kg, 0.1kg and 0.2kg of palm bunch ash. After eight weeks, it was observed that the 0.2kg palm bunch ashreduced the soil total hydrocarbon content by 76%, while the 0.1kg and 0.0kg palm bunch ash gave reductions of 70% and 20%, respectively.Three models, namely zero, first and second order models, were developed and tested. The first order model gave the best description of the remediation of the diesel contaminated soilby palm bunch ash compared to the zero and second order models. Therefore, it was concluded that palm bunch ash can serve as a good remediating material for a diesel contaminated soil, and that a first order model can suitably predict the remediation.

Keywords: Palm bunch ash, diesel, pollution, soil, remediation.

1. INTRODUCTION

Petroleum has been commercially explored since the 19th century and was used for the purposes of illumination and lubrication (Chorom et al., 2010). The adoption of petroleum and its derivatives in most transport industries increased its demand, storage, and production. The world consumption of petroleum and its by-product in 2003 was over thirteen billion litres per day (Jain et al., 2011). Petroleum is a mixture of several components that are separated by fractional distillation. The separated components include diesel, gasoline, jet fuel, liquefied petroleum gas, etc.

The solubility of diesel in water at 20^{o}C is about 5mg/L, the colour ranges between colourless and brown, and the logarithm of the octanol-water partition coefficient (Log K_{ow}) ranges from 3.3 to 7.06 (ATSDR, 1995). Diesel is a medium-weight petroleum fuel with a boiling point range of 175^{o}C to 355^{o}C (Brady, 2001). It is composed of about two hundred hydrocarbons having molecular weight between C_{10} – C_{28} alkanes (Riffaldi et al., 2006). The composition of diesel is about thirty percent alkanes, forty-five percent cyclic alkanes and twenty-four percent aromatics (Zytner et al., 2001). Therefore, diesel can be said to be a complex mixture of saturated and aromatic hydrocarbons that is partially soluble in water. Thus, its release to the environment could constitute a major source of soil, water and air contamination.

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Generally, diesel pollutes the environment through leaks from wrecks of tankers carrying it, cleaning of tanks, ship ruptures, accidents, power plants and automobile mechanics (Hill and Moxey, 1980).In Nigeria, large spillages of diesel are usually associated with accidental discharge or wilful sabotage. Apart from benzene, the United States Environmental Protection Agency stated that diesel is the second most frequently remediated contaminants (Zytner et al., 2001). When diesel spills on the ground, it penetrates easily to the depth of 10 - 20cm, a depth range usually considered vital for agricultural activities (Nikejah et al., 2014). As spillages occur on soil, it affects soil properties as well as the response of soil to plants' need, which results to poor yield (Akpan and Udoh, 2013). The presence of diesel in soil could also cause long term groundwater contamination. Given these consequences, there is need to remediate the diesel contaminated land and to predict the extent of remediation. Although different materials have been used for remediation of soil contaminated with diesel, the application of palm bunch ash is new.

In Nigeria, oil palm is widely known for its economic value. After the extraction of the nuts, the empty bunches are thrown away thereby constituting nuisance to the environment. Since palm bunch ash is a good source of sodium and potassium (Onyelucheya et al., 2010), it can be exploited in remediation of contaminated soil. Therefore, this study aims at investigating the effectiveness of palm bunch ash in remediating a diesel contaminated soil as well as developing models for predicting the rate of the remediation.

2. MATERIALS AND METHODS

2.1 Experimental Design

A plot of land measuring 4.8m^2 was divided into nine equal cells of 0.36m^2 with a furrow of 0.2m created between cells. The furrow prevented runoff of rain water from one cell to another. The diagram of the design is shown in Figure 1. The random replication block design was adopted. Three treatments consisting of 0.0 kg, 0.1 kg and 0.2kg remediating materials were applied to the cells. The palm bunch ash used for the study was produced from waste empty palm bunches dried for 90 min. in an oven at a temperature of 200^{o}C. The dried palm bunches were crushed and sieved with 0.297 mm sieve to obtain the ash.

The soil in each cell was first tilled before been contaminated with 250 ml of diesel. The diesel was uniformly distributed over the surface of the soil, after which the soil was left undisturbed for three days to allow infiltration of the diesel into the soil. The area-volume ratio method of contaminants distribution as proposed by Jonathan et al. (2014) was adopted. The palm bunch ash was applied after the third day of contamination.

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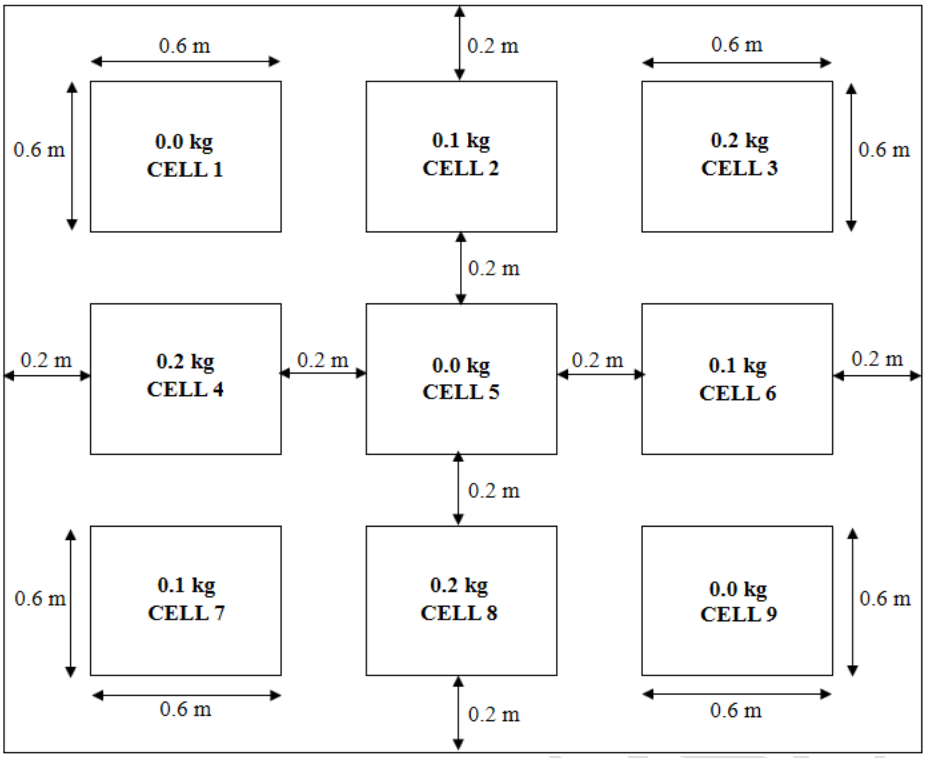

Figure 1: Schematic of plots used for experiment.

The palm bunch ash was analysed for the following parameters: pH, total nitrogen, organic carbon, organic matter, available phosphorus, potassium and calciumas shown in Table 1. Particle size analysis of soil used in the experiment was done using the United State Department of Agriculture (USDA) method and the result shown in Table 2. From the universal soil classification method, the soil was classed as sandy loam soil.

Table 1: Physico-chemical properties of the palm bunch ash used for the remediation process

Parameter	Quantity
pH	8.50
Total nitrogen (%)	1.10
Organic carbon (%)	7.88
Organic matter (%)	8.21
Available phosphorus (mg/kg)	241.94
Potassium (cmol/kg)	440.64
Calcium (cmol/kg)	68.00

Table 2: Particle size of the soil used

Soil particle	Quantity
Silt (%)	14
Clay (%)	24

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Sand (%)	62

2.2 Soil Sample Collection and Analysis

Three days after contamination, soil samples were taken at a depth of 0.2m for analysis. During the remediation process, soil samples were collected every two weeks for analysis until the eighth week. The parameters analysed include pH, organic matter, organic carbon, total nitrogen, total hydrocarbon content (THC), total heterotrophic bacteria (THB), available phosphorus, potassium and calcium.

The pH of the soil samples was ascertained using the U-10 Series multi-parameter meter (Hanna Instruments, model HI 9828). Walkey and Black (1934) technique was adopted for the determination of organic carbon and organic matter. The Persulfate technique (D'Elia et al., 1977) was adopted in ascertaining the total nitrogen. The available phosphorus of the soil was ascertained through Bray technique (Bray and Kurtz, 1945). The total hydrocarbon content of the soil samples was determined using toluene cold extraction method (ASTM D1157-91, 2014). The American Society for Testing and Materials (ASTM) D-4373-14 method was used in the determination of calcium in the soil samples. Potassium was determined using the spectrophotometer method (John, 2010). The soil hydrocarbon utilizing bacteria for the different soil samples were determined using the spread plate techniques (Gradi, 1985). The total bacterial count was obtained using Equation (1).

$$Total\ count = \frac{Colony\ count}{Volume\ inoculated} \times Dilution\ \ factor \qquad (1)$$

2.3 Development of Model

Zero, first and second order models were developed and tested to ascertain the model that best describe the remediation process. The remediation rate was compared using the reaction rate constant for the three modified kinetic models as presented in the equations below.

The zero-order model was derived as shown in Equations (2a) – (2f):

$$\frac{dQ}{dt} = -AQ^0 \qquad (2a)$$

$$\frac{dQ}{dt} = -A \qquad (2b)$$

$$\int dQ = -A\int dt \qquad (2c)$$

$$Q_t = -At \qquad (2d)$$

After calibrating the model with data obtained from the experiment, the model was improved to be:

$$Q_t = -At + Q_0\, d_\xi \qquad (2e)$$

$$d_\xi = 1/(n-1) \qquad (2f)$$

The first order model was derived as shown in Equations (3a) – (3h):

$$\frac{dQ}{dt} = -AQ \qquad (3a)$$

$$\int dQ/Q = -A\int dt \quad (3b)$$
$$InQ_t - InQ_o = -At \quad (3c)$$
$$In\left(\frac{Q_t}{Q_o}\right) = -At \quad (3d)$$
$$\frac{Q_t}{Q_o} = e^{-At} \quad (3e)$$
$$Q_t = Q_o e^{-At} \quad (3f)$$

After calibrating the model with data obtained from the experiment, the model was improved to be:

$$Q_t = Q_o e^{-At} - \xi \quad (3g)$$
$$\xi = 0.1M + 2nt \quad (3h)$$

The second order model was derived as shown in Equations (4a) – (4h).

$$\frac{dQ}{dt} = -AQ^2 \quad (4a)$$
$$\int dQ/Q^2 = -A\int dt \quad (4b)$$
$$-\left(\frac{1}{Q_t} - \frac{1}{Q_0}\right) = -At \quad (4c)$$
$$-\left(\frac{1}{Q_t}\right) = \frac{-AQ_0 t - 1}{Q_0} \quad (4d)$$
$$Q_t = \frac{Q_0}{(AQ_0 t + 1)} \quad (4e)$$

After calibrating the model with data obtained from the experiment, the model was improved to be:

$$Q_t = \left(\frac{Q_0}{(AQ_0 t + 1)}\right) - \xi_0 \quad (4f)$$
$$\xi_0 = 0.1M \quad (4g)$$
$$t\left(\frac{1}{2}\right) = \frac{0.6932}{A} \quad (4h)$$

where A is the biodegradation rate (graphically A= 0.0181755 mg/kg/day), M is the quantity of remediating material applied (kg), t is the remediation period (days), n is an arbitrary constant ranging from 0 to 3, ξ, d_ξ and ξ_0 are error terms,and t(½) is the half-life of the contaminant.

3. RESULTS AND DISCUSSION

3.1 Changes in Soil Properties

The results of the changes in soil properties before, during and after the remediation process is shown in Table 3.The total hydrocarbon content (THC) increased from 12.06 mg/kg before contamination to 1245.87 mg/kg after contamination. Without any treatment (0.0 kg remediating material), the THC decreased at a slower average rate of 4.4 mg/kg/day for the eight weeks of observation due to natural attenuation. However, with 0.1 kg and 0.2 kg remediating material treatment, the THC decreased at a higher average rate of 15.6 mg/kg/day and 16.9 mg/kg/day, respectively. With these rates of decrease, it will take forty-one weeks for the diesel to be completely removed from the soil by natural attenuation while it will take only twelve weeks and eleven weeks with 0.1 kg and 0.2 kg remediating material treatment, respectively.Overall, after the eight weeks of monitoring, the Control (0.0kg palm

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bunch ash) reduced the THC by only 20%, while the 0.1kg and 0.2 kg palm bunch ash treatment reduced the THC by 76% and 70%, respectively.

The count on heterotrophic bacteria in the soil dropped from $0.5*10^{-6}$cfu/g before contamination to $0.3*10^{-6}$cfu/g after contamination, probably due to the adverse effect of the diesel. However, after two weeks the bacteria population of the soil became $0.41*10^{-6}$, $1.8*10^{-6}$ and $2.1*10^{-6}$cfu/g for the 0.0 kg, 0.1 kg and 0.2 kg treatment, respectively and increased until the eighth week with values of $1.21*10^{-6}$, $3.42*10^{-6}$ and $4.98*10^{-6}$ cfu/g for 0.0 kg, 0.1 kg and 0.2 kg treatment, respectively. Possibly, after the initial adverse effect of the diesel, the surviving bacterial population utilised the diesel as a source of carbon for their metabolic activities. This is reflected in the decreasing trend associated with the THC at the end of eighth week. This increment which is more with the palm bunch ash treatment improved the usefulness of the soil for agricultural purposes.

The soil pH which was originally acidic (pH: 5.5) and more acidic after contamination (pH: 4.9) was raised close to neutrality by the palm bunch ash. With 0.2 kg and 0.1 kg treatment,the pH was raised to 6.91 and 6.30 respectively, while with the Control (0.0 kg) pHremained relatively at the original acidic level (pH: 5.6)after the eight weeks of monitoring.This increase in pH observed during the remediation process may be due to the high pH (8.5) of the palm bunch ash.

Similarly, the available phosphorus (AP) and calcium (Ca) of the soil were reduced from 22.05 to 8.98 mg/kg and from 0.15 to 0.13 cmol/kg, respectively after contamination. Without any treatment, it took the soil eight weeks to attain its original AP concentration while with 0.1 kg and 0.2 kg remediating material treatment, the AP concentration was already increased by approximately 3 and 4 times, respectively after two weeks and by approximately 4 and 5 times, respectively after eight weeks. Without any treatment, it took the soil two weeks to attain just the original Ca concentration but with 0.1 kg and 0.2 kg remediating material treatment, the Ca concentration was already increased by approximately 102 and 187 times, respectively after two weeks. Since AP and Ca are essential plant nutrients, the use of palm bunch ash for soil remediation is likely to result in the enrichment of the soil with vital nutrients.

The soil organic carbon (OC)increased from 1.96% before contamination to 4.57% after contamination, due to the carbon content of the diesel. Without any treatment, the OC further increased to 5.21% after eight weeks of contamination. However, with 0.1 kg and 0.2kg remediating material treatment, the OC increased to 5.81% and 6.01%, respectively after eight weeks of remediation. This result agreeswith the findings of Adjei and Boahen (2013) on the effect of palm bunch ash on various soils where it was reported that OC of soils increased with application ofpalm bunch ash. Similar trend of increase with 0.1 kg and 0.2kg remediating material treatment was observed for the soil organic matter (OM), total nitrogen (TN) and potassium (K), indicating improvement in soil fertility (Udoetok, 2012).

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Table 3: Changes in soil properties during 8-week period of remediation

Parameters	**U Soil**	**3-DAC**	**2wks after remediation of soil**			**4wks after remediation of soil**			**6wks after remediation of soil**			**8wks after remediation of soil**		
			0.0kg RM	**0.1kg RM**	**0.2kg RM**	**0.0kg RM**	**0.1kg RM**	**0.2kg RM**	**0.0kg RM**	**0.1kg RM**	**0.2kg RM**	**0.0kg RM**	**0.1kg RM**	**0.2kg RM**
THC (mg/kg)	12.06	1245.87	1236.8	1011.4	989.79	1124.2	819.6	614.81	1001.6	531.8	324.1	999.8	372.2	296.8
THB (cfu/g)	$0.5*10^{-6}$	$0.3*10^{-6}$	$0.41*10^{-6}$	$1.8*10^{-6}$	$2.1*10^{-6}$	$0.76*10^{-6}$	$2.72*10^{-6}$	$3.8*10^{-6}$	$0.98*10^{-6}$	$3.2*10^{-6}$	$4.1*10^{-6}$	$1.21*10^{-6}$	$3.42*10^{-6}$	$4.98*10^{-6}$
pH(1:2:5)	5.5	4.9	5	5.5	5.8	5.2	5.8	6.3	5.5	6.1	6.8	5.6	6.3	6.91
OC (%)	1.96	4.57	4.98	4.99	5.2	4.99	5.29	5.4	5.01	5.47	5.99	5.21	5.81	6.27
OM (%)	3.05	5.05	5.1	5.27	5.67	5.18	5.31	5.71	5.29	5.44	5.83	5.34	5.71	6.01
TN (%)	0.2	0.3	0.33	0.39	0.44	0.35	0.42	0.51	0.41	0.47	0.59	0.49	0.51	0.66
AP (mg/kg)	22.05	8.98	11.14	65.8	94.2	16.91	79.8	103.6	19.3	83.4	105.3	22.1	88.6	109.8
K (cmol/kg)	1.05	2.05	2.08	49.89	99.07	2.96	76.76	101.2	3.78	88.3	109.8	4.28	91.8	221.7
Ca (cmol/kg)	0.15	0.13	0.15	15.33	28	0.19	19.1	31	0.22	21	33.1	0.28	23.2	36.2

THC = Total hydrocarbon content; THB = Total heterotrophic bacteria; OC = Organic carbon;OM = Organic matter; TN = Total nitrogen; AP = Available phosphorus; K = Potassium; Ca = Calcium; U Soil = Uncontaminated soil; 3-DAC = 3 days after contamination; RM = Remediating material

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3.2 Comparison of Developed Models and Measured Data

The comparison of the developed models and thedata from the 0.0 kg, 0.1 kg and 0.2 kg remediating materialexperiments are shown in Figures 2, 3 and 4, respectively.The data of the Control (0.0 kg remediating material) experiment was best predicted by the zero-order model with an average deviation of only 28.4% compared with the first and second order model with an average deviation of 31.9% and 69.3%, respectively. The data of the 0.1 kg and 0.2 kg remediating material experiments were best predicted by the first order model with an average deviation of only 14.3% and 2.6%, respectively compared with the zero and second order model with an average deviation of 40.2% and 39.2% and 59.2% and 58.8%, respectively. Overall, the first order model best predicted the remediation of diesel contaminated soil using palm bunch ash while the zero-order model is best suited for the prediction of natural attenuation of diesel contaminated soil.

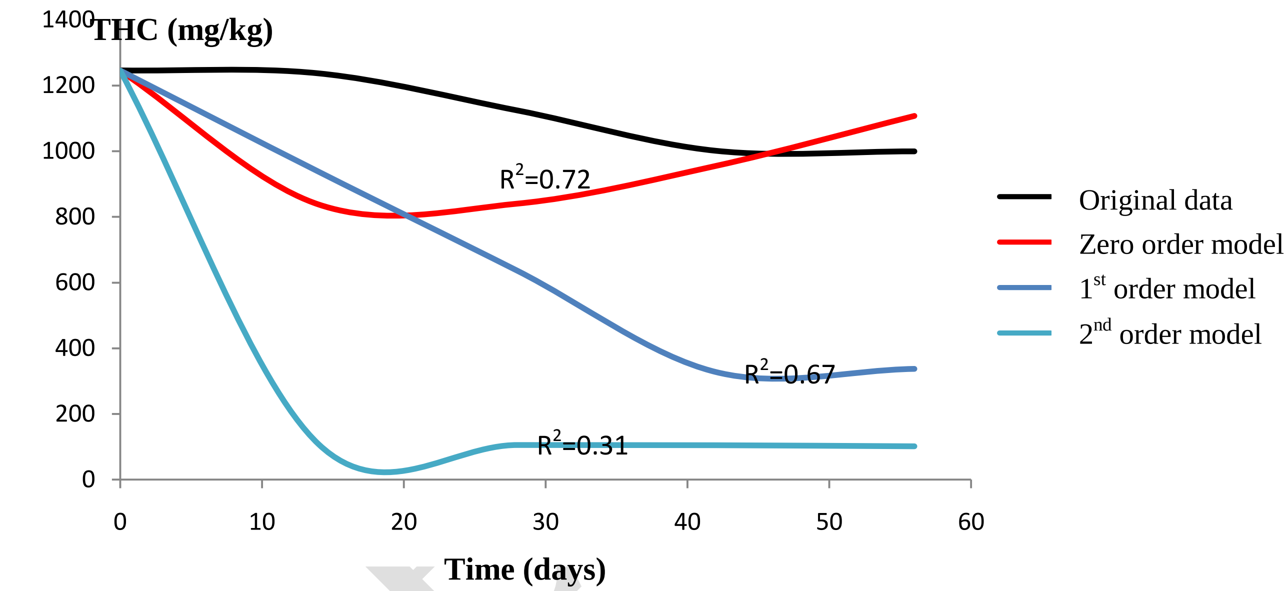

Figure 2: Comparison of models and 0.0 kg experimental data.

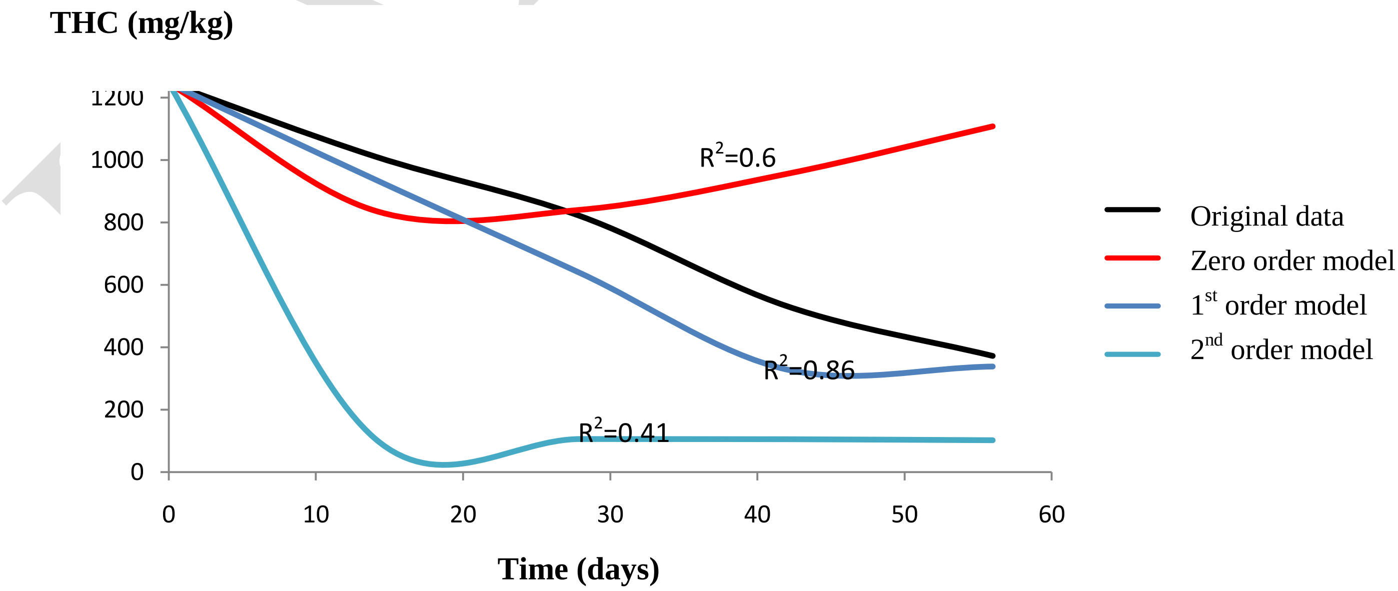

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Figure 3: Comparison of models and 0.1 kg experimental data.

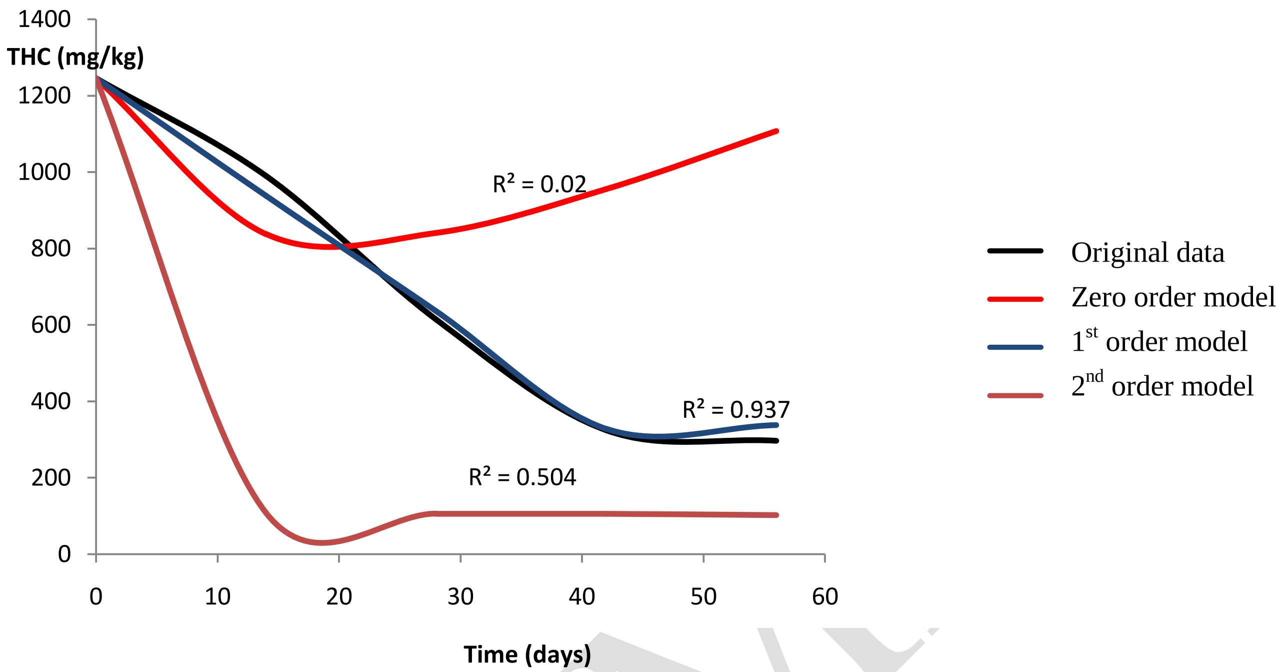

Figure 4: Comparison of models and 0.2 kg experimental data.

4. CONCLUSIONS

The remediation of diesel contaminated soil using palm bunch ash has been studied. After eight weeks of remediation, it was concluded that palm bunch ash showed a high-level performance as a remediating material for the reduction of total hydrocarbon content in the diesel contaminated soil. This performance increased with increasing quantity of the palm bunch ash. The characterisation of the palm bunch ash revealed that it would make a good source of nutrient for soil improvement especially for agricultural purposes. The study also revealed that time affected the soil remediation positively. Among the developed models, the first order model predicted the remediation of the diesel contaminated soil using palm bunch ash better than the second and zero order models.

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