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MODELLING KINETICS OF SELECTED ORGANIC AMENDMENTS ON BIOSTIMULATION OF CRUDE OIL CONTAMINATED SOIL

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ABSTRACT

Crude oil polluted soils are very common in the Niger Delta region of Nigeria due to oil spillage, theft and activities of artisanal refiners. Though, the Nigerian government have put in place different measures to checkmate further contaminations, but the already contaminated soils are adversely affecting the livelihood of residents. The Niger Delta region being known for its numerous creeks and rivers is also affected by the presence of aquatic weed, water hyacinths in many ways. Hence, the research investigated the possibility of utilizing water hyacinth (WH) blended with poultry droppings (PD) as biostimulants for the remediation of a non-recent crude oil contaminated site. This was achieved by treating the contaminated soil for a period of 91 days in different bioreactors labelled A to F with varied proportions of WH and PD. Results showed that the selected site had a concentration of 1309 mg/kg of total petroleum hydrocarbons (TPH) prior to the experiment. However, the best amendment among the six bioreactors recorded a half-life of 44 days with kinetics rate constant of 0.0157 day^{-1} *as well as percentage degradation and biostimulant efficiency of 76.17% and 65.09% respectively, after 91 days. Reliable predictive model equations were developed for the various amendments and it was concluded that both water hyacinth and poultry droppings could be effectively used in remediating crude oil contaminated soils especially when blended at ratio 3:1 of WH:PD, thereafter, necessary recommendations were made.*

Keywords: Amendment, Bioremediation, Efficiency, kpo-Fire, Michaelis-Menten

1. INTRODUCTION

The Niger Delta region of Nigeria is blessed with abundant crude oil nevertheless, the pump price of petroleum product such as diesel, kerosine and petrol in filling stations are still not affordable by most citizens in the country. One of the reasons is because none of the certified crude oil refineries in Nigeria is functional at the moment hence the Nigerian government export its crude oil to foreign countries and import the petroleum products. Apart from the high price per litre of these petroleum products, there were certain periods of the year (especially December) when they became scarce due to hoarding and other factors thus, crumbling most transportation businesses. Hence, artisanal refiners seize the opportunity to augment the supply of the petroleum products by refining the crude oil using local techniques, which actually relief the scarcity and high price of petroleum products. However, the artisanal refining of crude oil has adversely affected the ecosystem due to the introduction of certain chemicals to the environment including polynuclear aromatic hydrocarbons (Obenade and Amangabara, 2014; Ogbuagu *et al.,* 2011). In fact, the Nigerian Government tagged the persons involved in the practice as illegal refiners as the raw material (crude oil) being used in such refineries are stolen from pipelines. Hence the sites of such refineries are usually hidden in bushes within the Niger Delta region especially in Rivers, Bayelsa and Delta states.

Although, the artisanal crude oil refining in Nigeria, popularly known as "kpo-fire" has drastically reduced as the Nigerian Government vowed to deal with people involved in such practices nevertheless, the ripple effects are still alarming. For instance, several research including Sibe and Onwugbuta (2023) have shown that soils within these refining sites are heavily contaminated with petroleum hydrocarbons even years after stopping the refining operations. Besides, these refining sites are mostly located within mangrove forests or bushes (Plate 1) in riverine communities having minimal landmass for farming. Hence the contaminated soil of the little available lands by activities of the artisanal refiners has seriously impaired the usual farming of arable crops in the host communities since soils contaminated with petroleum hydrocarbons adversely affects crop growth and yield (Ugochukwu, 2023; Odiyi *et al.,* 2020; Oyedeji *et al.,* 2012). This consequently increase the cost of living (especially foodstuff) incurred by residents in such communities. Besides, there are numerous adverse health impacts including carcinogenic and neurological diseases, on prolong exposure to petroleum hydrocarbons hence there is need to remediate the contaminated soil.

Plate 1: Abandoned artisanal crude oil refining site in Niger Delta region

Bioremediation has been identified to be the best method for clean-up of crude oil contaminated sites in terms of eco-friendly and cost effective (Yu *et al.,* 2022). Among the various techniques employed in bioremediation of contaminated soil, bioaugmentation and biostimulation are most widely used. However, bioaugmentation have the setback of inefficient degradation of old contaminated sites since a great proportion of the volatile components of the crude oil would have evaporated, leaving weathered petroleum hydrocarbons that mostly resist degradation by microbes (Mishra and Kumar, 2015; Zhang *et al.,* 2015). Hence biostimulation is a better option for remediating lands in which the crude oil contamination is not recent (Abed *et al.,* 2014; Abdulsalam *et al.*, 2011). Besides, biostimulation add nutrients into the soil apart from remediating the contaminated soil. Nutrients used as biostimulants can either be organic or inorganic fertilizers however, organic nutrients have been found to be more ecologically safer and beneficial to the degrading microbes than inorganic fertilizers (Talha *et al.,* 2022; Zhao *et al.,* 2021; Liu *et al.,* 2017; Macci *et al.,* 2016). A good source of organic nutrient is water hyacinth (*Eichhornia crassipes*) due to its recorded high nutritional contents (Enyi *et al.,* 2020; Adeyemi and Osubor, 2016).

Water hyacinth (*Eichhornia crassipes*) being an aquatic weed is readily available in the freshwater creeks within the Niger Delta region and its presence has caused numerous environmental challenges to residents within the riverine communities of the region. These includes obstruction of boats and canoes movement, deterioration of water quality leading to loss of aquatic biodiversity as well as affecting fishing and recreational activities in the concerned creeks and rivers. In fact, water hyacinth is considered as the worst aquatic weed in the world due to its rapid growth.

The adverse impacts of the water hyacinth on the waterways especially in terms of fishing activities have made most of the fishermen to go into poultry farming. It is well known that poultry droppings being wastes (faeces) generated from poultries usually produce foul smell, though, they are known to be good source of organic nutrients (Uwadiae and Obasi, 2021). Some researchers have earlier identified the advantages of water hyacinth in remediating simulated contaminated environments (Gonzalez-Tavares *et al.,* 2023; Singh and Balomajumder, 2021; Ogbozige and Nwobu, 2021) notwithstanding, the blending of water hyacinth and poultry droppings as amendment in remediating aged contaminated site with crude oil has not been investigated yet. Hence, it will be necessary to investigate the potentials of the blends of these organic wastes (water hyacinth and poultry droppings) as biostimulants in remediating the non-recent crude oil contaminated soils available in the Niger Delta Region of Nigeria. Thus, proffering solutions to different environmental challenges at same time.

2. MATERIALS AND METHODS

2.1 Collection of Soil Sample

Crude-oil contaminated loamy soil samples were obtained at an abandoned artesian crude-oil refining site in Ahoada-West Local Government Area of Rivers State, Nigeria using a sterile soil auger from a depth of 0 – 50 cm. The soil samples were transported to the laboratory through sterile polyethylene bags, sieved through sterile 2 mm mesh then stored in a refrigerator before usage.

2.2 Preparation of Remediating Agents

Water hyacinth (*Eichhornia crassipes*) were harvested at Oxbow-Lake in Bayelsa State, Nigeria. Thereafter, it washed, sundried for 7 days, pulverised by means of a laboratory-grinding machine (EcoMet 30) and sieved through a 2 mm mesh. Similarly, poultry droppings were collected from a poultry in Azikoro town in Bayelsa State, Nigeria and were sundried for 7 days and pulverised. However, both prepared water hyacinth and chicken droppings were autoclaved for 20 minutes at 121°C. This was done to ensure that external bacteria or microbes did not participate in the treatment process (bioaugmentation) so that the remediation will be strictly biostimualation. Thereafter the pulverised remediating agents were separately stored in sterile airtight containers and properly labelled as WH and PD, representing water hyacinth and poultry droppings respectively.

2.3 Treatment and Analysis

Six sterile beakers of 1000 mL capacity were labelled as A, B, C, D, E and F and 500 g of the contaminated soil sample were weight into each of the labelled beaker. The first beaker labelled A, served as a control hence the soil sample in it was not enriched with nutrient. Conversely, the soil samples in the remaining beakers were enriched with composite of the selected organic nutrients (water hyacinth and poultry droppings) at varying concentrations. The considered proportions of water hyacinth to poultry droppings in the composite organic nutrient are 100 g, 0 g for sample B; 75 g, 25 g for sample C; 50 g, 50 g for D; 25 g, 75 g for sample E; and 0 g, 100 g for sample F. The added organic nutrients were thoroughly mixed with the soil samples to ensure uniform distribution of the nutrients or biostimaulants withing the soil masses thereafter, the bioremediation process in each of the bioreactor (beaker) was conducted for a period of 91 days. However, the concentration of total petroleum hydrocarbon (TPH) in the soil sample was analysed just before the commencement of the bioremediation process (i.e., at day 0) using standard methods (APHA, 20212) thereafter, sampling and analysis of TPH was done at a frequency of 7 days intervals in each of the labelled bioreactor. Nevertheless, the moisture content of the soil in each of the bioreactor was adjusted to 30% of the soil weight (USEPA, 2006) using sterile and de-ionised water on weekly basis.

2.4 Kinetics Studies

The degradation percentage (D) of total petroleum hydrocarbon in the contaminated soil during treatment was determine through Equation (1).

$$D = \left(\frac{TPH_0 - TPH_t}{TPH_0}\right) 100\% \qquad (1)$$

Where: TPH_0 is the concentration of total petroleum hydrocarbon in the contaminated soil prior to treatment (i.e. at time $t = 0$) while TPH_t is the concentration of total petroleum hydrocarbon remaining in the soil at any time t (in days) from the beginning of treatment. However, the time rate of change (r) of petroleum hydrocarbon during biodegradation can be represented using the general expression for rate of reaction as given in Equation (2) as:

$$r = \frac{d[C]}{dt} = -k[C]^n \qquad (2)$$

Where: $[C]$ is the concentration of reactants (petroleum hydrocarbon in mg/kg of soil mass) remaining at any time t (in days) from commencement of the remediation, k and n are the rate constant and order of reaction respectively while the negative sign $(-)$ indicates that the concentration of reactants reduces with time. Since degradation of petroleum hydrocarbon during bioremediation follows first order reaction (Xin-Gen *et al.,* 2021; Ozyurek and Bilkay, 2020; Al-Hawash *et al.,* 2018), it implies, Equation (2) can be written as shown in Equation (3).

$$r = \frac{d[C]}{dt} = -k[C] \tag{3}$$

The Michaelis-Menten kinetics, presented in Equation (4) was applied to model the bacterial reaction rate and substrate (petroleum hydrocarbon) utilisation at different concentrations.

$$r = \frac{R_{max}[C]}{K_m + [C]} \tag{4}$$

Where r is degradation rate of petroleum hydrocarbon during bioremediation (day^{-1}), R_{max} is the maximum achievable reaction rate (day^{-1}) when the bacteria present in the soil sample are saturated with substrate (petroleum hydrocarbon), $[C]$ is the concentration of substrate in soil (petroleum hydrocarbon, mg/kg) while K_m is Michaelis constant which is the concentration of substrate (petroleum hydrocarbon) corresponding to 50% of R_{max}). However, at low concentration of substrates, $[C]$ is much less than K_m (Srinivasan, 2022; Rodriguez and Towns, 2020; Sundaram, 1978) thus, implying that $K_m + [C] \cong K_m$ hence Equation (4) reduced to Equation (5) as follows:

$$r = \frac{R_{max}[C]}{K_m} \tag{5}$$

In Equation (5), the ratio $\frac{R_{max}}{K_m}$ is known as biodegradation first-order rate constant and it is denoted as k_1 hence, Equation (5) was reduced to Equation (6) as;

$$r = -k_1[C] \tag{6}$$

Where the negative sign $(-)$ signifies that the concentration of petroleum hydrocarbon remaining to be biodegraded reduces with time. Hence, Equations (3) and (6) were equated to form Equation (7) which also led to the formation of Equation (8).

$$\frac{d[C]}{dt} = -k_1[C] \tag{7}$$

$$\frac{d[C]}{[C]} = -k_1 dt \tag{8}$$

Equation (8) was integrated between the boundaries $[C] = [C_0]$ to $[C] = [C_t]$ and $t = 0$ to $t = t$ as follows to yield Equation (9).

$$\int_{[C_0]}^{[C_t]} \frac{d[C]}{[C]} = \int_0^t -k_1 dt$$

$$\int_{[C_0]}^{[C_t]} \frac{1}{[C]} d[C] = -k_1 \int_0^t dt$$

$$[\ln[C]]_{[C_0]}^{[C_t]} = -k_1[t]_0^{[t]}$$

$$\ln[C_t] - \ln[C_0] = -k_1 t$$

$$\ln\frac{[C_t]}{[C_0]} = -k_1 t$$

$$t = \frac{\ln\frac{[C_t]}{[C_0]}}{-k_1}$$

$$t = -\frac{\ln\frac{[C_t]}{[C_0]}}{k_1}$$

$$t = \frac{\ln\frac{[C_0]}{[C_t]}}{k_1} \tag{9}$$

Where $[C_0]$ is the concentrations of the substrate (petroleum hydrocarbon) before the commencement of treatment (bioremediation), $[C_t]$ is the concentration of substrate at time t from the commencement of treatment. In other words, $[C_0]$ and $[C_t]$ respectively have same meaning with the earlier defined TPH_0 and TPH_t hence, Equation (9) was rewritten as shown in Equation (10).

$$t = \frac{\ln\frac{[TPH_0]}{[TPH_t]}}{k_1} \tag{10}$$

Since the half-life $(t_{1/2})$ of a degradable matter is defined as the time required for half of the original quantity or concentration to decompose, the half-life ($t_{1/2}$) of the petroleum hydrocarbon during the bioremediation was therefore obtained as follows.

At $t = t_{1/2}$, $[TPH_t] = 0.5[TPH_0]$ hence Equation (10) was rewritten and simplified to generate Equation (11) as:

$$t_{1/2} = \frac{\ln\frac{[TPH_0]}{0.5[TPH_0]}}{k_1}$$

$$t_{1/2} = \frac{\ln\left(\frac{1}{0.5}\right)}{k_1}$$

$$t_{1/2} = \frac{\ln(2)}{k_1} \qquad (11)$$

The first-order rate constant (k_1) of the biodegradation was gotten by linearising Equation (10) to generate Equation (12) as follows.

$$k_1 t = \ln\frac{[TPH_0]}{[TPH_t]}$$

$$k_1 t = \ln[TPH_0] - \ln[TPH_t]$$

$$\ln[TPH_t] = -k_1 t + \ln[TPH_0] \qquad (12)$$

Equation (12) was applied by plotting $\ln[TPH_t]$ against time t in a linear graph and the associated gradient (slope) was taken as the first-order rate constant (k_1). Also, the model for determining the concentration of petroleum hydrocarbon remaining in the soil sample at any time t after the start of the treatment process was known by making $[TPH_t]$ the subject of formula of Equation (10) which led to Equation (13). That is;

$$k_1 t = \ln\frac{[TPH_0]}{[TPH_t]}$$

$$e^{k_1 t} = \frac{[TPH_0]}{[TPH_t]}$$

$$[TPH_t] = \frac{[TPH_0]}{e^{k_1 t}}$$

$$[TPH_t] = [TPH_0]e^{-k_1 t} \qquad (13)$$

The observed values of $[TPH_t]$ determined in the laboratory were plotted against their corresponding values obtained from the developed Equation (13) to certain the validity of the developed model.

The efficiency of the various biostimulant amendments at required time (E_{bt}) were calculated using Equation (14).

$$E_{bt} = \frac{[TPH_{ut}] - [TPH_{at}]}{[TPH_0]} \times 100\% \qquad (14)$$

Where $[TPH_{ut}]$ is the concentration of total petroleum hydrocarbon in unamended soil (i.e. control) at time t, $[TPH_{at}]$ is the concentration of total petroleum hydrocarbon in amended soil with biostimulant at the corresponding time t, while $[TPH_0]$ is the concentration of total petroleum hydrocarbon in soil before commencement of bioremediation (i.e. at time, $t = 0$).

3. RESULTS AND DISCUSSION

The results of the analysed total petroleum hydrocarbon in all the labelled bioreactors during the bioremediation period are presented in Figure 1 to 6 while the calculation for half-life, kinetics model, percentage degradation and biostimulant efficiency is summarized in Table 1.

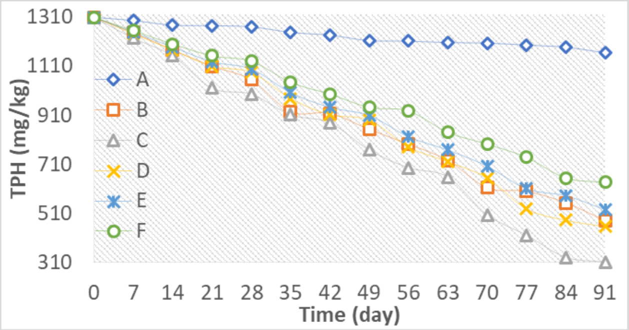

Figure 1: Biodegradation of petroleum hydrocarbon at varying amendments of biostimulants

The information in Figure 1 revealed that the concentration of petroleum hydrocarbon in the contaminated site just before the remediation process (i.e. at day zero) was 1309 mg/kg. This is above the permissible limit of 500 mg/kg, set by both the Nigerian Department of Petroleum Resources (DPR) and the US Agency for Toxic Substances and Disease Registry (ATSDR). However, the initial TPH concentration of 1309 mg/kg reduces to 1164, 480, 312, 456, 525 and 637 mg/kg for samples A (control), B, C, D, E and F respectively, after 91 days. However, the graphical illustration for the determination of the first – order rate constants $(-k_1)$ based on Equation (12) are presented in Figure 2 to 5 while the summary of calculations is presented in Table 1.

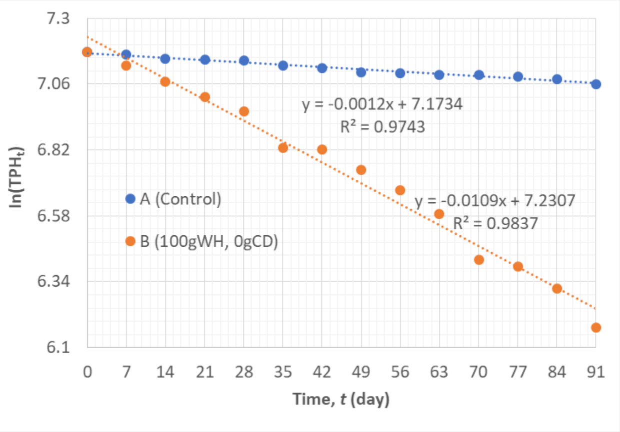

Figure 2: Graph for determining 1st-Order rate constant for sample *B* compared with control

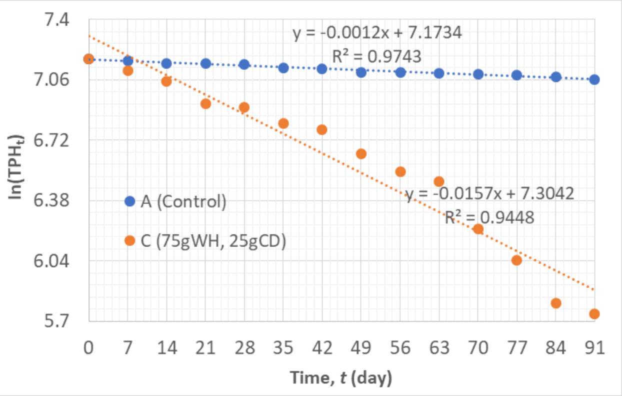

Figure 3: Graph for determining 1st-Order rate constant for sample *C* compared with control

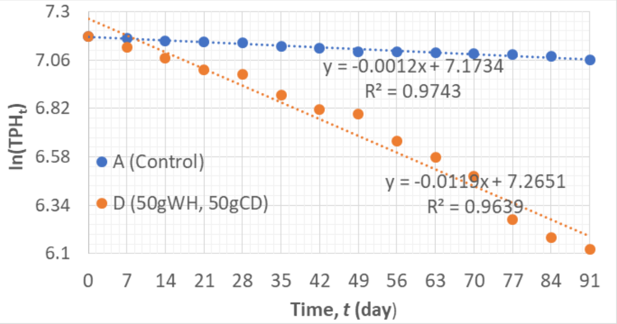

Figure 4: Graph for determining 1st-Order rate constant for sample *D* compared with control

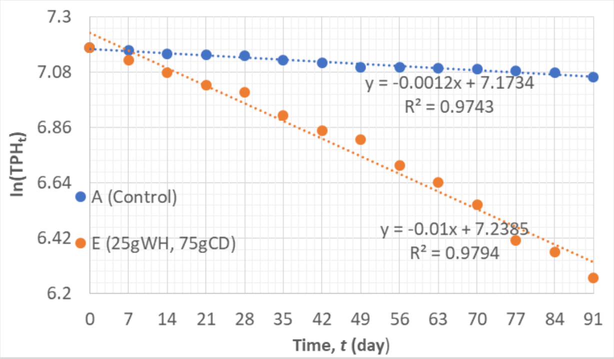

Figure 5: Graph for determining 1st-Order rate constant for sample *E* compared with control

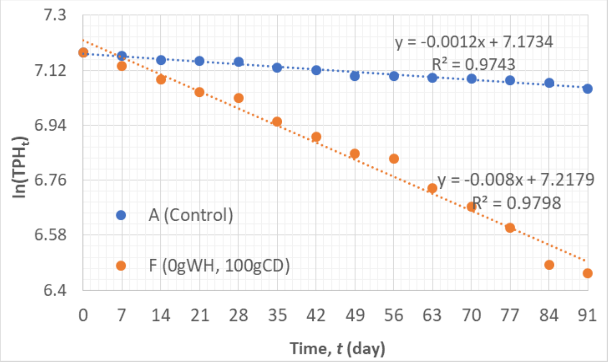

Figure 6: Graph for determining 1st-Order rate constant for sample *F* compared with control

Table 1: Summary of calculations

Sample	1st Order Rate constant, k_1 (day^{-1})	Half-Life, $t_{\frac{1}{2}} = \frac{\ln 2}{k_1}$ (days)	Conc. at time $t = 0$ $[TPH_0]$, (mg/kg)	Model for Conc. at any time *t-days* $[TPH_t] = [TPH_0]e^{-k_1 t}$	Conc. at $t = 91days$, $[TPH_{91}]$ (mg/kg)	Percentage Degradation at 91days $= \left[\frac{TPH_0 - TPH_{91}}{TPH_0}\right]100\%$	Efficiency of Biostimulant at 91days, $E_{b91} = \left[\frac{TPH_{u91} - TPH_{a91}}{TPH_0}\right]100\%$
A	0.0012	578	1309	$[TPH_t] = 1309e^{-0.0012t}$	1164	11.08%	–
B	0.0109	64	1309	$[TPH_t] = 1309e^{-0.0109t}$	480	63.33%	52.25%
C	0.0157	44	1309	$[TPH_t] = 1309e^{-0.0157t}$	312	76.17%	65.09%
D	0.0119	58	1309	$[TPH_t] = 1309e^{-0.0119t}$	456	65.16%	54.09%
E	0.01	69	1309	$[TPH_t] = 1309e^{-0.01t}$	525	59.89%	48.82%
F	0.008	87	1309	$[TPH_t] = 1309e^{-0.008t}$	637	51.34%	40.26%

Note: Conc. = concentration, 〖TPH〗_u91= total petroleum hydrocarbon in unamended soil (i.e. control) after 91days, 〖TPH〗_a91= total petroleum hydrocarbon in amended soil with biostimulant after 91days, Sample A (control – no amendment), Sample B (100gWH, 0gPD), Sample C (75gWH, 25gPD), Sample D (50gWH, 50gPD), Sample E (25gWH, 75gPD), Sample F (0gWH, 100gPD), WH = water hyacinth, PD = poultry droppings

The gradients of the graphs in Figure 2 to 5 were taken as the half-lives, k_1 of the associated amendments (based on equation 12). The exponential value of the various y-intercepts which obviously represent the concentration of total petroleum hydrocarbon at day zero [TPH$_0$] ranges between 1304 – 1487 mg/kg however, the actual value of [TPH$_0$] obtain in the field was 1309 mg/kg. The deviations from the actual value could be attributed to experimental errors beyond control, emanated from different factors including variation in the ambient temperature. Table 1 revealed that sample C which has 75 g of water hyacinth and 25 g of poultry droppings performed best in remediating the crude oil contaminated site, as it recorded the least half-life of 44 days together with highest rate constant of 0.0157 day^{-1} as well as highest percentage of degradation (76.17%) and highest biostimulant efficiency (65.09%). Table 1 also informed that there was self-remediation of the soil since the control sample *A* which has no amendment or biostimulant also recorded lesser concentration of petroleum hydrocarbon days after the commencement of the remediation process. This agrees with similar reports conducted by Ali *et al.,* (2023); Ambaye (2022), and Jumbo *et al.,* (2022). However, its biodegradation performance was the poorest since it recorded the longest half-life of 578 days and least kinetic rate constant of 0.0012 day^{-1} as well as least percentage of degradation being 11.08%. The performance by the various samples in remediating the soil is of the order: C > D > B > E > F > A but only samples C, D and B were able to record allowable limit of TPH ($\leq$ 500 mg/kg) within the 91 days of the experiment.

The reliability of the kinetic model equations in the fifth column of Table 1 are presented in Figure 7 to 12 and was noted that the biodegradation rate in the predictive models were slightly lesser than the observed values apart from sample A (control) notwithstanding, the values of determination coefficients (R^2) in all cases were very high, ranging from 0.9492 to 0.9843.

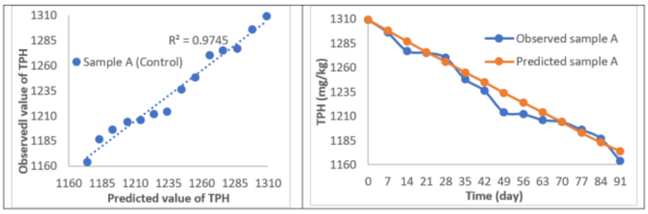

Figure 7: Comparison of observed and predicted results for sample A

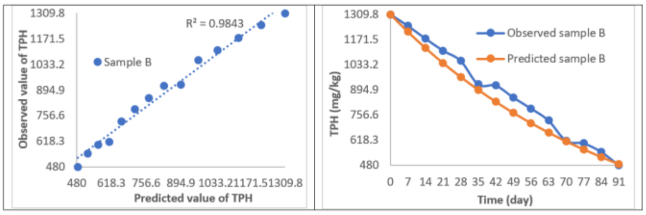

Figure 8: Comparison of observed and predicted results for sample B

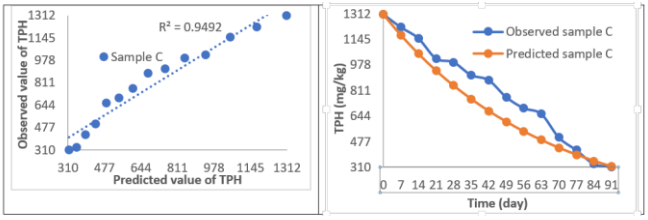

Figure 9: Comparison of observed and predicted results for sample C

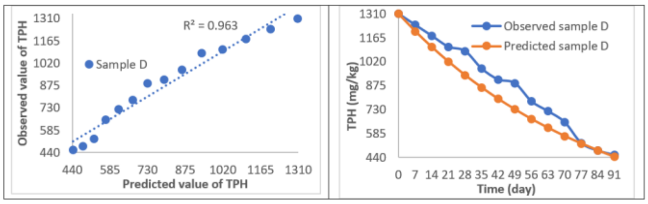

Figure 10: Comparison of observed and predicted results for sample D

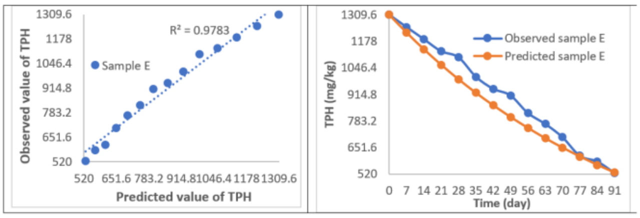

Figure 11: Comparison of observed and predicted results for sample E

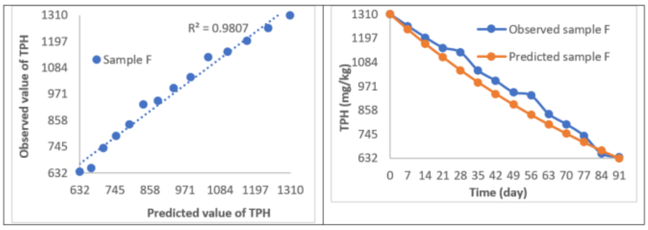

Figure 12: Comparison of observed and predicted results for sample F

4. CONCLUSION AND RECOMMENDATIONS

The research has revealed that the soil at the abandoned artisanal crude oil refining site located at Okarki town in Ahoada-West Local Government of Rivers State, Nigeria is polluted with petroleum hydrocarbon at 161.8% higher than the permissible limit. Both water hyacinth (WH) and poultry droppings (PD) can be effectively used as biostimulants in remediating crude oil contaminated soils but blending water hyacinth and poultry droppings at ratio 3:1 (i.e. 75 g of WH and 25 of PD) as biostimulant will produce better result compared to either of them. Nevertheless, reliable predictive models have been developed in forecasting the period of remediation to a given concentration of TPH with respect to the various considered amendments or biostimulants.

It is hereby recommended that other abandoned artisanal crude oil refining sites especially within the Niger Delta region of Nigeria should be investigated by the relevant regulatory authorities to ascertain the level of contamination with TPH. Thereafter, the developed biostimulant amendment (water hyacinth and poultry droppings blend at higher quantity of the former) should be used in remediating the site thus, solving different environmental challenges at same time on the principle of waste to wealth.

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