International Journal of
Research in Chemistry and Environment
Available online at: www.ijrce.org
ISSN 2248-9649

Research Paper

Total Hydrocarbon Degradation of Crude Oil Contaminated Soil using Mixture of Poultry Manure and Biochar: Optimization of Amendment Process Variables

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(Received 30th November 2020, Accepted 28th December 2020)

Abstract: *In this work, farmland soil contaminated with crude oil was remediated with a mixed amendment material which comprised of poultry manure and biochar (prepared from corn cob). The soil, poultry manure and biochar were characterized in terms of physico-chemical properties using standard techniques. The amendment experiment was designed employing the central composite design of response surface methodology for three variables at five levels. The process variables considered and their range of values are composition of amendment material (10 – 80% poultry manure), level of application of amendment material (2 – 10%) and duration of amendment (2 – 12 weeks). The values of the physico-chemical properties, particularly the organic matter, nitrogen and phosphorous of the amendment material were markedly higher than in the contaminated soil and suggest their potential to facilitate contaminant degradation. Analysis of total hydrocarbons degradation of the soil after amendment showed that composition of amendment and duration of amendment had significant effects on the total hydrocarbon content of the soil. The optimum total hydrocarbon content degradation of 745.69 $mg.kg^{-1}$ was obtained with amendment composition of 65.8% poultry manure (34.2% biochar), level of application of amendment of 8.4% with respect to the total hydrocarbons content of the contaminated soil and duration of amendment of 10 weeks and corresponded to about 80% total hydrocarbon degradation. The correlation and high regression coefficients of the experimental and predicted values of total hydrocarbon content showed that experimental data are in agreement with the predicted data and suggested that the mixture of poultry manure and biochar have the potential to effectively degrade hydrocarbons present in contaminated soil.*

Keywords: Amendment material; optimization; response surface methods; soil remediation; total hydrocarbon content.

Introduction

More than 65 million barrels of crude oil is extracted per day world-wide to meet the bulk of the world's energy requirements[1]. The Nigerian economy is mainly sustained by the oil industry and at the same time, crude oil is a major source of land pollution in the Niger-Delta region of Nigeria. Crude oil is a potential hazard and can cause severe and lasting damage if it is accidentally discharged into the environment. Despite the close monitoring of the distribution and storage network of crude oil, pollution through accidental discharges are still constantly registered which occurs through blowouts seepages and deliberate flushing activities which leaves a thick layer of crude oil over land, vegetation and water surfaces.

Soil is defined as the layer of minerals and organic matter, in thickness from centimetres to a metre, on the land surface. Its components are rock, mineral and organic matter, water and air [2]. Soils differ in the ratio of these components and hence mechanical properties are largely determined by particle size and strongly

influence the behaviour of polluting agents like hydrocarbons[3]. Soil chemical fertility and quality are significantly impacted by oil spill contamination rendering soil unsuitable for plant growth.
The use of biochar, a solid substance produced by carbonization of biomass is one of the recent and effective biological process for carbon sequestration, soil conditioning and remediation[4,5]. The use of biochar promotes several activities: (a) it facilitates the availability of nutrients in soil, (b) enhances the activity of microbes, (c) enhances the availability of soil organic matter, and (d) promotes water holding and crop production by the soils[6]. While biochar has proven to have a positive conditioning effect on soil, it may be limited as a nutrient supplier alone, because of its relatively low nutrient composition and recalcitrance to biodegradation[7]. A combination of contaminant-degrading microbes and biochar can increase the degradation of PAHs contaminated soil[8,9]. The application of biochar in combination with organic or inorganic fertilizer on crop yield is currently attracting the interest of scientist[6]. Poultry manure is an exceptional source of organic fertilizer which contains high percentage of nitrogen, phosphorus, potassium and other important nutrients readily available for plant uptake as compared to other organic sources[10,11]. It improves the physical characteristics and conditions of the soil and improves the nutrient uptake and crop productivity[12,13].

Response surface methodology (RSM) can be used to evaluate the relative significance of several factors in the presence of complex interactions. RSM answers the question of how to select the levels for the applied factors to obtain the desirable, smallest or largest, value of the response function in a reduced number of experiments[14].

In this study, soil contaminated with crude oil was amended using a combination of biochar and poultry manure. The amendment process was designed employing the central composite design of response surface methodology (RSM).

Materials and Methods

Material collection

Surface soil samples were randomly collected from different locations of a farmland in Iguedaiken, Ekiadolor area of Benin City, Edo State, Nigeria. The samples were mixed to obtain 35 kg of soil and sieved to 3 mm particle size and the air-dried. Crude oil (Escava blend) was obtained from Nigerian National Petroleum Corporation (NNPC) facility in Ologbo, Benin City, Edo State and weathered. Poultry manure (PM) was collected from a local Farm in the Ekiadolor area of Benin and air-dried for 12 days. It was ground to fine particles and sieved to 3 mm particle size. Corn cobs were obtained from a local market at Auchi, Benin City, Edo State Nigeria. It was air-dried for 2 weeks and carbonised using the pit kiln method to obtain corn cob biochar (CCBC). It was again air-dried and milled into fine powder.

Physico-chemical analysis of amendment materials and soil

The physico-chemical properties of the unpolluted soil, poultry manure and biochar were determined using standard methods. The pH and other physico-chemical properties of the soil and amendment material were carried out using methods described by Muche[15]. pH values were determined using Electrical pH meter. Soil organic matter was determined by using titrimetric methods and then its contents were estimated from the total organic carbon content by multiplying with 1.724. Total nitrogen (N) content was determined using the Kjeldahl digestion, distillation and titration method. The available phosphorous content was analysed by 0.5M sodium bicarbonate extraction solution/pH 8.5/method. Exchangeable basic cations (Ca^{2+}, Na^{+}, Mg^{2+}, and K^{+}) were determined by saturating the soil sample and amendment material with 1N NH_4 OAc solution at pH 7. Then, Ca^{2+} and Mg^{2+} were determined from extract by using atomic absorption spectrometry (AAS) (Bulk Scientific model, 210), while exchangeable K^{+} and Na^{+} were measured by flame photometer from the same extract. The heavy metal concentrations (As, Pb, Cd, Cr, Ni, Cu and V) of the soil and amendment materials were determined using AAS techniques. Cation exchange capacity (CEC) was estimated titrimetrically by distillation using ammonium method. Soil texture reflects the amounts of various sized particles (sand, silt, and clay) in the soil. Relative amounts of these particles were used to categorize the soil into textural classes.

Contamination of soil, determination of total hydrocarbon content (THC), Mixing of amendment material

The soil was contaminated in the ratio 1 kg of soil to 10 g of crude oil. A total of 35 kg of soil was contaminated and mixed evenly. The initial total hydrocarbon content of the contaminated soil was determined to be 933.20 $mg.kg^{-1}$ of soil using ultraviolet spectrophotometer (UVS). The amendment material was obtained by mixing poultry manure and biochar to give 100 g or 100% of amendment material according to the amendment composition design of Table 1.

Table 1: CCD experimental conditions for the degradation process

Independent variable	Coding	Levels				
		$-\alpha$	-1	0	+1	$+\alpha$
Composition of amendment (% PM)	A	10	24.19	45	65.81	80
Level of application (%)	B	2	3.62	6	8.38	10
Duration of amendment (weeks)	C	2	4.03	7	9.97	12

Experimental design of degradation of contaminated soil

The crude oil degradation of soil was designed using a three-variable-five-level central composite design of response surface methodology (Design Expert 11, Stat-ease, Inc., Minneapolis, USA). A total of 20 experimental trials that included 8 trials for factorial design, 6 trials for axial points (two for each variable) and 6 trials for replication of the central points were performed. The remediation variables considered are composition of amendment, level of application of amendment and duration of amendment. The composition of amendment was measured in terms of percentage PM and made up to 100% by adding CCBC. The level of application of amendment is the amount of amendment material taking as percentage of the crude oil present in the contaminated soil. The range of values of the degradation variables considered is given in Table 1. Total hydrocarbon content was taken as the response variable.

To predict the optimal conditions and the existence of interaction, experimental data was fitted to a second and polynomial regression model as given by Equation (1) containing three linear, three interaction and three quadratic terms.

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n} \sum_{j>1}^{n} \beta_{ij} x_i x_j \quad \ldots(1)$$

where Y is the response, i.e., x_i and x_j represent the independent variables, β_0 is constant, β_i is linear term coefficient, β_{ii} is the quadratic term coefficient, β_{ij} is cross-term coefficient and 'n' is the number of process variables studied and optimized during the study. The effects of process variables and their possible interaction effects on the maximum THC degradation in the response surface regression procedure was estimated using analysis of variance (ANOVA) in which the level of significance (p-value) of all coefficients was < 0.05. Regression coefficient, R^2 was used to evaluate the goodness and best fit of the model. The response surface and contour plots were obtained using the fitted quadratic polynomial equation generated from regression analysis by keeping one of the independent variables at central value (0) and varying the other two.

Results and Discussion

Physico-chemical properties of amendment materials and soil

Table 2 gives the physico-chemical properties of PM, CCBC and soil. The soil was found to be sandy, acidic, low in organic matter, total N and exchangeable K, high in available P, and adequate in exchangeable Ca and Mg with very low heavy metal concentrations according to the critical levels given Table 2. PM and CCBC were alkaline, PM was higher in organic OM, OC, N, P, K, Na and K micronutrients as compared to CCBC. Both PM and CCBC had low concentrations of heavy metals.

THC degradation

An initial THC degradation value of 933.20 mg.kg^{-1} of soil was obtained before amendment application for remediation of the crude oil contaminated soil. Table 3 gives the experimental design matrix and the actual and predicted values of THC degradation of contaminated soil using amendment materials (PM and CCBC). From the table, minimum THC degradation of 157.15 mg.kg^{-1} (about 17% remediation) was obtained with composition of amendment (45% PM, 55% CCBC) (0) at 6% level of application of amendment (0) for a duration of 2 weeks (-1.68) while the maximum THC degradation of 893.30 mg.kg^{-1} (about 96% remediation) was obtained with composition of amendment (45% PM, 55% CCBC) (0) at 6% level of application of amendment (0) for a duration of 12 weeks (+1.68). This showed there was increase in THC degradation with duration than with composition of amendment material and level of application of amendment.

The actual versus predicted plot of the THC degradation process is given by Figure 1. It can be observed from the plot that there is a strong positive correlation between the actual and predicted values of THC of the contaminated soil. The reasonable agreement of the actual and predicted THC degradation is evident by the high and close predicted and adjusted R^2 values of 0.9417 and 0.9807 respectively as given by the model summary statistics in Table 4. From Table 4, the high R^2 value of 0.9899 of the quadratic model showed that the THC degradation process was better modeled by the quadratic polynomial since the cubic model is aliased.

Table 2: Physico-chemical properties of amendment materials and soil

Parameter(s)	PM	CCBC	Soil
pH	8.17±0.06	9.40±0.00	5.23±0.06
OM (%)	39.90±0.96	36.35±1.14	0.25±0.03
OC (%)	23.20±0.56	21.33±0.67	0.14±0.02
N (%)	1.75±0.07	0.93±0.06	0.06±0.02
P (%)	0.17±0.02	0.11±0.02	11.32±0.31
Ca (%)	8.29±0.44	9.56±0.26	0.71±0.08
Mg (%)	0.72±0.09	1.91±0.09	0.42±0.09
Na (%)	0.13± 0.01	0.06±0.02	0.03±0.01
K (%)	11.00±0.20	3.14±0.15	0.05±0.02
As (ppm)	0.03±0.01	0.02±0.00	0.00±0.00
Pb (ppm)	0.02±0.01	0.02±0.01	0.00±0.00
Cd (ppm)	0.02±0.01	0.01±0.00	0.00±0.00
Cr (ppm)	0.05± 0.02	0.03±0.01	0.00±0.00
Ni (ppm)	0.04±0.01	0.03±0.01	0.01±0.00
Cu (ppm)	4.30±0.17	3.67±0.11	2.41±0.07
V (ppm)	0.02±0.01	0.02±0.00	0.01±0.01
CEC (meq/100g)	-	-	1.21±0.12
Clay (%)	-	-	4.13±0.15
Silt (%)	-	-	2.83±0.06
Sand (%)	-	-	93.03±0.15

Table 3: Experimental design matrix and values of THC degradation

Run order	Coded factors			Actual factors			Response	
				Composition of Amendment	Level of Application	Duration	THC degradation ($mg.kg^{-1}$)	
	A	B	C	(%PM)	(%)	(weeks)	Actual	Predicted
1	0	-1.68	0	45	2	7	453.65	467.34
2	1	-1	1	65.81	3.62	9.97	736.70	734.07
3	0	0	0	45	6	7	455.10	450.27
4	0	0	0	45	6	7	454.70	450.27
5	0	1.68	0	45	10	7	466.75	493.01
6	0	0	0	45	6	7	412.30	450.27
7	1	-1	-1	65.81	3.62	4.03	298.00	287.77
8	1.68	0	0	80	6	7	493.40	501.36
9	-1	1	1	24.19	8.38	9.97	717.55	699.53
10	0	0	1.68	45	6	12	893.30	906.91
11	0	0	-1.68	45	6	2	157.15	183.49
12	1	1	1	65.81	8.38	9.97	755.85	745.69
13	-1	-1	-1	24.19	3.62	4.03	284.70	266.61
14	0	0	0	45	6	7	465.90	450.27
15	0	0	0	45	6	7	458.80	450.27
16	-1	-1	1	24.19	3.62	9.97	705.85	690.86
17	-1	1	-1	24.19	8.38	4.03	311.15	285.53
18	-1.68	0	0	10	6	7	412.75	444.75
19	1	1	-1	65.81	8.38	4.03	322.90	309.64
20	0	0	0	45	6	7	461.67	450.27

Table 4: Model summary statistics of THC degradation

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	38.92	0.9633	0.9564	0.9424	38053.94	
2FI	42.91	0.9638	0.9470	0.8713	84991.45	
Quadratic	**25.88**	**0.9899**	**0.9807**	**0.9412**	**38860.31**	**Suggested**
Cubic	31.42	0.9910	0.9716	-0.3384	8.842E+05	Aliased

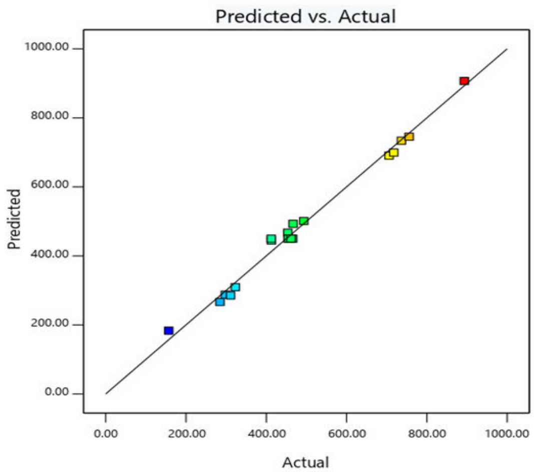


Figure 1: Actual vs. predicted plot of THC degradation by amendment material

Table 5 gives the analysis of variance (ANOVA) of the THC degradation of contaminated soil at the 5% significant level (probability of error, 0.05). P-values less than 0.05 indicate model terms/factors are significant i.e. change in the factor leads to a corresponding change in THC degradation of the soil at a significant level of 5%. From Table 5, high F-value of 108.46 and very low p-value of <0.0001 (<0.05) indicate model term is highly significant. Among the main/linear factors, the composition of amendment (A) and duration of amendment (C) with p-values < 0.05 were found to have significant effects on the THC degradation of soil while the level of application of amendment (B) was found to be insignificant. All interaction factors (AB, AC and BC) were found to be insignificant on THC degradation by the amendment material. Among the quadratic factors, only C^2 was significant on the THC degradation of contaminated soil. The insignificant lack of fit (17.05%) showed that the model reasonably fits the THC degradation process.

Table 5: ANOVA of THC degradation of contaminated soil

Source	Sum of squares	df	Mean squares	F-value	P-value
Model	6.54E+05	9	72659.39	108.46	< 0.0001*
A-Composition of amendment	3868.01	1	3868.01	5.77	0.0371*
B-Level of application	795.51	1	795.51	1.19	0.3014
C-Duration	6.32E+05	1	6.32E+05	943.01	< 0.0001*
AB	4.35	1	4.35	0.0065	0.9374
AC	243.1	1	243.1	0.3629	0.5603
BC	52.53	1	52.53	0.0784	0.7852
A^2	935.02	1	935.02	1.4	0.2648
B^2	1611.3	1	1611.3	2.41	0.1520
C^2	16234.69	1	16234.69	24.23	0.0006*
Residual	6699.09	10	669.91		
Lack of Fit	4775.22	5	955.04	2.48	0.1705
Pure Error	1923.87	5	384.77		
Cor. Total	6.61E+05	19			

***=significant**

Equation (2) gives the empirical relationship between the degradation process variables considered and the THC degradation of the contaminated soil in coded terms.

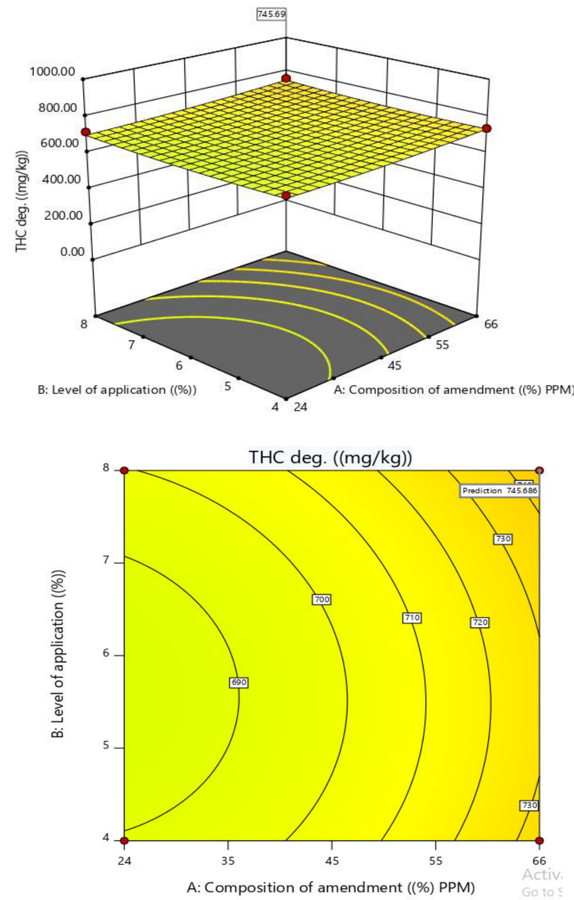
$$THC\ deg. = 450.27 + 16.83A + 7.63B + 215.08C + 0.74AB + 5.51AC - 2.56BC + 8.05A^2 + 10.57B^2 + 33.56C^2 \quad \text{..................................(2)}$$

In a regression equation, when an independent variable has a positive sign, it means that an increase in the variable will cause an increase in the response while a negative sign will result in a decrease in the response [16,17]. From the Equation (2) all (main, interaction and quadratic) factors except the interaction of level of application and duration of amendment (factor BC) had positive effect on the THC degradation of the contaminated soil by amendment material. Among the main/linear factors, the duration of amendment had the highest significant effect on THC degradation while level of application of amendment produced the least effect. From the Fit Statistics (Table 6), the coefficient of regression R^2 was used to validate the fitness of the model equation. Table 6 gives an R^2 of a high value of 0.9899, showing that about 99% of the variability in the THC degradation of the contaminated soil can be explained by the model. The **Predicted R^2** of 0.9412 is in reasonable agreement with the **Adjusted R^2** of 0.9807; i.e. the difference is less than 0.2 and showed that the model reasonably predicted the THC degradation process using a quadratic polynomial.

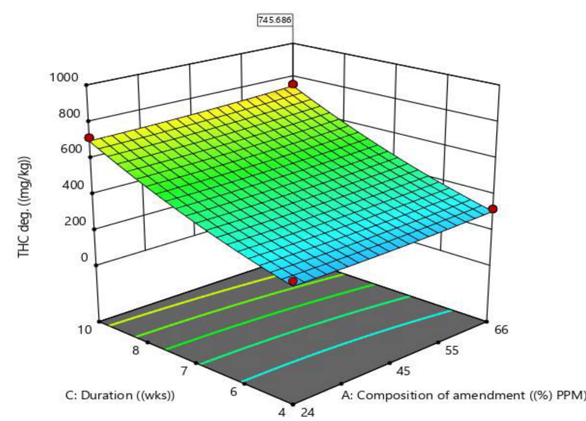
Table 6: Fit Statistics

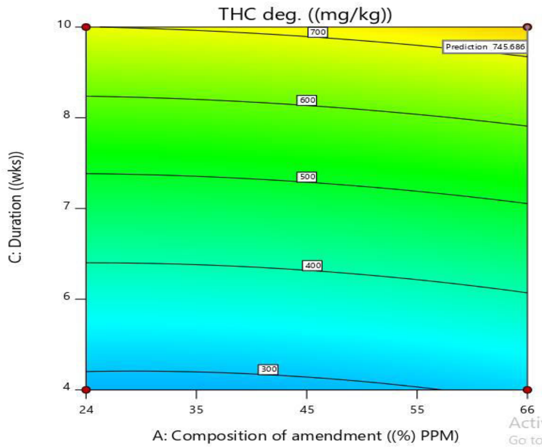
Standard Deviation ($mg.kg^{-1}$)	25.88	Adjusted R^2	0.9807
Mean ($mg.kg^{-1}$)	485.91	Predicted R^2	0.9412
CV (%)	5.33	Adequate precision	39.5276
R^2	0.9899		

Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 39.528 indicates an adequate signal. This model can be used to navigate the design space. Coefficient of variation (CV) of 5.33 is within acceptable range, since CV is a measure of expressing standard deviation as a percentage of the mean, small values of CV gives better reproducibility. In general, a high CV indicates that variation in the mean value is high and does not satisfactorily develop an adequate response model[18,19,20].

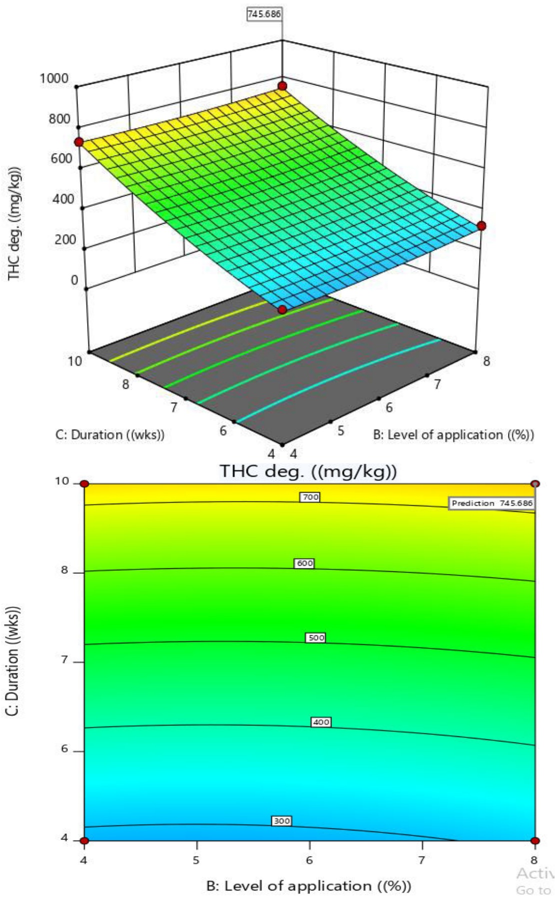


(a)





(b)



(c)

Figure 2: Effects of interaction of variables on THC degradation of contaminated soil (a) interaction effect of composition of amendment and level of application of amendment (AB), (b) interaction effect of composition of amendment and duration of application of amendment (AC) and (c) level of application and duration of application of amendment (BC).

Figure 2 shows response surface and contour plots showing the interaction effects of the remediation variables on THC degradation of contaminated soil by the amendment materials. Figure 2 (a) gives the effect of interaction of composition of amendment and level of application of amendment (AB) on THC degradation. From the plot, it can be seen that THC degradation increased slightly with the simultaneous increase in the interaction of composition of amendment and level of application. At constant composition of amendment, increase in the level of application increased the THC degradation of contaminated soil. At constant level of application, increase in composition of amendment also increased THC degradation. Composition of amendment produced a slightly more effect on THC degradation than the level of application. Figure 2 (b) gives the effect of interaction of composition of amendment and duration of amendment (AC) on THC degradation. It can be observed that the concurrent increase in composition of amendment and duration of amendment lead to a corresponding increase in the THC degradation of the contaminated soil with duration of amendment producing more dominant effect. Figure 2 (c) gives the effect of level of application of amendment and duration of amendment (BC) on THC degradation. It can be observed that the concurrent increase in the level of application of amendment and duration of amendment lead to a decrease in the THC degradation of contaminated soil with duration of amendment producing a more dominant effect than the level of application of amendment.

Numerical optimization of the THC degradation of contaminated soil gave maximum desirability of 0.758 which means that there is about 76% possibility to reach maximum THC degradation of the contaminated soil. The maximum THC degradation value of 745.69 mg.kg^{-1} was obtained at amendment composition of (65.8% PM, 34.2% CCBC), level of application of amendment of 8.4% and duration of amendment of about 10 weeks.

Conclusion

Crude oil pollution is known to significantly impact detrimentally on soil leading to poor soil health and quality for plant growth. In this work, soil contaminated with crude oil was treated with a mixture of poultry manure and biochar. The amendment process was designed, analyzed and optimized using response surface methodology. Data obtained from the analysis of total hydrocarbons content of the contaminated soil after amendment showed that duration of amendment is the most significant factor in total hydrocarbons degradation of soil. The predicted optimal conditions showed that maximum total hydrocarbons degradation of 745.69 mg.kg^{-1} (80% degradation) was attained at a composition of amendment of 65.8% poultry manure, 8.4% level of application of amendment and duration of amendment of about 10 weeks. These data showed that the mixtures of biochar and poultry manure are effective for amendment of soils contaminated with crude oil.

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