Factorial design study of total petroleum contaminated soil treatment using land farming technique

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Abstract

Land farming technique was used to treat hydrocarbon contaminated soil collected from a crude oil spill sites in Edo State, Nigeria. Calibrated standard auger was used to collect soil samples from the site at depth below 30 cm. The samples were characterized and classified. Cow dung and NPK fertilizer were added as additives to complement the nutriments of the soil samples before total petroleum hydrocarbon quantification and remediation procedures. Factorial design was applied to vary the input parameters such as pH, mass of substrate, moisture content and turning times of land farming so to ascertain the optimal conditions for the procedure. The result revealed that the in-situ total petroleum hydrocarbon (TPH) value was 5,000 mg kg -1 on the average and after 90 days of treatment, TPH reduced to 645.907 mg kg -1 . The turning rate, pH, moisture content and mass of substrate had 82.79%, 4.36%, 0.48% and 0.046% contributions respectively to the degradation process using land farming treatment. Numerical optimization techniques applied in the optimum point for land farming input parameters to achieve predicted maximum removal of 98.60% were evaluated as pH, mass of substrate, moisture content and turning rate to be 6.01, 1 kg, 10% and 5 times in a week respectively. TPH removed at this optimum point was 97.83% reducing from 5,000 to 635.907 mg kg -1 . The high coefficient of determination ($r^2 = 0.9865$) as observed in the closeness of predicted and experimental values reflects the reliability of the model and hence, land farming practice with close attention on turning rate as revealed by this study, is recommended for TPH contaminated soil remediation.

1. Introduction

Advancement in technology, continuous urban sprawling and improved standard of living have over the years, caused a corresponding increase on energy demand, which is largely used in powering automobile and other related machines and appliances. Energy from coal, fossil fuel and some renewable sources like solar and biomass have been widely used with fossil fuel being the most utilized among them [1, 2]. Fuel is one of the major products of processed crude oil, rich in hydrocarbon content and is largely sort after for effective running of human daily activities. These activities have in one way or the other hampered the chain procedures of crude oil - drilling, refining, treatment, transportation and utilization which on the long run result in spillage, thus distorting several ecosystems and rendering most lands useless [3]. In Nigeria (especially the Niger Delta region – comprising of nine states), there has been oil spills resulting in soil contamination due to poor operation and management practices [4, 5]. It is reported that about 13 Mt of hydrocarbons are spilled which is caused largely by pipeline vandalism, destructive crude oil theft, operational spills and engineering failure (such as pipeline rupture), and uncivilized refining conditions [6-11]. The severity of damage done to these soils by hydrocarbon spill is a function of diverse factors such as partition coefficient of the soil, permeability, absorption properties and chemical constituents of the hydrocarbon. Another source through which spillage occurs is through natural seeping in locations where hydrocarbon is found in sub-surface deposit to accidental discharge of crude oil onto ground surface and several other points of pollution, but irrespective of this source, once hydrocarbon

spills into the soil, it alters both its physical and chemical properties [12-14], thus becoming harmful to plants, microorganism in the soils and humans.

Effective cleaning-up oil-contaminated soils by adopting some available technologies, is a viable option of remediation process and this is done to degrade hydrocarbon present in the soil. Hydrocarbon degradation is a process that involves the gradual weathering and removal of petroleum constituents especially the non-volatile compounds from the contaminated location by using physical, chemical and biological methods for remediation of contaminated soils [15-17]. For instance, bioremediation which involves the utilization of effective microbes for hydrocarbon degradation has increasingly gained researchers interest in recent decades. The most frequently isolated and utilized hydrocarbon degrading microbes are genus *Pseudomonas* which degrade complex chains of hydrocarbon into smaller and less toxic compound. Also, fungi in the genera of *Fusarium, Rhizopus and Penicillium* have gained acceptance in treating hydrocarbon contaminated soil since Exxon Valdez spillage in 1980 [17, 18]. Land farming has been acknowledged as an effective and low-cost technology for abstraction of total petroleum hydrocarbons (TPHs) from soil [18-20]. It is reckoned to use less energy and it is not harmful to the environment, with reduced residue disposal problems [21]. Land farming treatment is the application of calculated organic and inorganic substrates on contaminated soil in order to mineralize the toxic substances in the soil [22, 23]. Land farming is a concept that entails nutriments addition and replication of microbes, geared towards increasing the number and growth of microorganisms in order to accelerate bioremediation rate [20, 24, 25]. As microbes require sufficient major element like carbon, hydrogen, oxygen, nitrogen, and phosphorous for the development of macromolecules, fertilizer addition provides the bacterial with vital elements to thrive and reproduce. In some cases, sawdusts, animal dungs, and straws may supply bacterial with carbon sources [26]. Land farming techniques has been practiced in some regions of the world to bioremediate crude oil contamination in soils to minimize the health risk on human and the environment at large [27, 28]. It has been used successfully to remove petroleum hydrocarbons at large scale [23, 29], and because of its simplicity in implementation, Niger Delta has also employed it. Unfortunately, with the handful of its application within Nigeria, there is still dearth of information on the efficient practice of land farming treatment for crude oil contaminated soils for effective remediation.

The effectiveness of land farming can be enhanced when environmental circumstances allow the growth of microbes, and this depends on some certain environmental parameters such as pH, moisture content, nutrient availability, among others [23, 30]. Factorial design (FD) is normally used in screening variables (both dependent and independent) and also in optimizing response surfaces. The latter is frequently used for experimental designs involving experimental procedures [31]. FD has been employed in some oil biodegradation studies of constituent's optimization that may induce the microbial debasement phenomenon hereby contributing to the progress of oil spill bioremediation process. Bhattacharya and Biswas [32] investigated the effect of various nutrients added to waste engine oil biodegradation of Bushnell-Haas medium using *Ochrobactrum pseudintermedium* bacterium. The data permit the development of an empirical model ($p < 0.00672$) through the application of a full FD for experimental work thus, describing the connection between dependent and independent variables. Jasmine and

Mukherji [33] also assessed the treatment of refinery oily sludge using 2^n full FD via bioaugmentation and biostimulation processes. FD was also applied in the bioremediation of artificially contaminated soil with weathered bonny light crude oil (WBLCO) using biostimulation and bioaugmentation processes. A statistically significant (p < 0.0001) second-order regression model with a coefficient of determination (R = 0.9996) was ultimately obtained for removal of WBLCO. Numerical optimization process was also carried out based on desirability function to optimize the bioremediation process [34]. Further researches are ongoing to develop and improve on FD methods for minimizing the experiment number and the interactions of their input variables/parameters. This has been achieved by utilizing design experiment procedure to generate information on direct effects, interactive pair effects and effects due to curvilinear variables. Some ample studies have been done on the application of FD in bioremediation of soil contamination using bioaugmentation and biostimulation techniques as presented above. From the resources available and accessible and to the utmost best of our knowledge, there are limited or no information on the optimization of land farming procedure using FD study which plays a major role in the adequate treatment of hydrocarbon contaminated soils. In this study, FD was applied to vary the input parameters such as pH, mass of substrate and moisture content in order to optimize them for best hydrocarbon removal.

2. Materials And Methods

2.1 Site location

The site selected for this project is an oil field located in Ologbo community, Ikpoba Okha Local Government Area of Edo state in Southern Nigeria. Edo state is bounded to the right by Ondo State and to the lower left by Delta (Fig. 1). Ologbo as a major community is one of the oil producing area with multiple petroleum production facilities in Niger-Delta area of Nigeria. The community houses a gas plant operated by the Nigerian National Petroleum Development Corporation (a subsidiary of Nigerian National Petroleum Corporation) and some other petroleum facilities. It lies between longitude $05^0 38'36.44''$ E to $05^0 4'26.56''$ E and latitude $06^0 04'28.17''$ N to $06^0 04'33.79''$ N. It is about 32 km away from the south-western part of Benin-City and over 30 km from Nigeria National Petroleum Development Corporation access road, which is off Benin-Sapele highway. Within this location, crude oil spillage is frequent resulting from vandalism and sabotaging of oil pipes and equipment by militants and oil pilferers, thus leaving the land degraded and contaminated. Figures 1 and 2 give the location map of the study area and one of the contaminated spots in the study area, respectively.

2.2 Preliminary investigation and TPHs quantification procedure

As a vital step towards a successful remediation process, reconnaissance survey was carried out on the contaminated site in order to minimize challenges during sample collection. A calibrated standard auger was used to collect samples at surficial depth not exceeding 30 cm, the samples were sun dried and homogenized (using mortar and pestle) before sieving through a 4 mm sieve. The homogenized samples were store in polythene bags at room temperature to prevent moisturizing. The soil samples were

characterized so as to determine its physical, chemical and microbes' constituents using British Standards BS 5930 (Table 1). The constituents of the soil are seen to fall below the recommended nutrients required for effective biodegradation process. Therefore, NPK fertilizer in ratio 20:10:10 and cow dung was added as additives to complement these nutriments for the remediation procedure. These fertilizers (organic and inorganic) used, have high nitrogen content which makes them suitable for remediation operations. Their compositions are shown in Table 2. Fresh samples from the contaminated site were taken to the laboratory for residual TPH quantification in accordance with USEPA [35] and ASTM [36]. TPHs were extracted from the samples by drying and passing them through a 4 mm sieve aperture size. The samples were placed in 40 mL centrifuge bottle with 25 mL of chloroform added. The samples were tightly closed and kept well in a sonicator bath for 60 min. During the process of extraction, iced deionized water was continuously added to maintain a temperature below 40 °C. On completion of extraction, samples were subjected again to centrifugal force for 11 min at 3000 rpm. The resultant extract was then placed in an Erlenmeyers flask where it was dried to achieve a specific weight. Bathing was done at 65 °C to evaporate volatile chloroform and the extract shows an average contamination concentration of 5,000 mg kg^{-1}. This is equivalent to intervention level according to USEPA, hence the need to remediate the contaminated soil.

2.3 Experimental design and procedure

In the initiation of the treatment, 100 kg of sieve samples were placed in twenty buckets and labeled based on the treatment to be accommodated in the setup in accordance with USEPA [35] and ASTM [36]. The choice of input variables, range of variables and duration of the experiment as stipulated in the USEPA procedure were adopted for this study. Four major input variables were selected namely pH, moisture content, mass of substrate and turning rate and were varied in each of the buckets. Substrate used was cow dung and NPK fertilizer, with its application ranged from 0.6 to 1 kg. In every application, mass of substrate constitutes 50% of cow dung and 50% of NPK fertilizer in any experimental run to make up the total mass of substrate required. The pH and moisture content of each experimental run was adjusted to reflect the value to be used for that particular setup. The pH was adjusted using slaked lime and measured using pH meter while the moisture content was a percentage of the weight of each experimental setup. The batch to batch variation was controlled using the range of input variables presented in Tables 3 and 4. The sorption of hydrocarbon from the soil was carried out using laboratory examination in order to feasibly select factors controlling the biosorption process in land farming treatment. To be able to select the input variables with the highest significant contributions to the remediation process and determine their optimum values, FD of experiment was used for screening. The range and levels of the input variables used in designing the experiment is presented in Table 3. Runs 17−20 were used as control for the study and the treatment was carried out for 90 d after which the samples were taken from each bucket for residual TPH determination. According to USEPA [35] and ASTM [36], FD study of this nature with experimental setup of $2n + 1 < 100$, should have four middle values (control) with the same input variables, hence runs 17−20 were designated as control while all the

input variable had the same range of values as shown in Table 4. Petroleum degrading bacteria was enumerated through Mineral Salt Agar culture following the procedures of Sepahi [37].

2.4 Statistical analysis

The data obtained from the experimental procedures were statistically analyzed using Excel (Microsoft office product version 16), Design-expert and STATISTICA software. The suitability of the FD to screen the variables was carried out by computing the standard error, correlation matrix of regression coefficient and model leverages. Analysis of variance (ANOVA) and goodness of fit were also computed to validate the model significance. The major effects of the four-treatment variable as well as the interactions were interpreted jointly. In every 2^2 factorial designs, the F-tests is enough to reveal the interrelation in combined treatment procedures. It also tells the relationship between all the variables concentrations in the treatment parameters. The result reveals the main variable with the largest effect in the four combined parameters by comparing the means. The F-test procedures employed are shown in Eqs. (1), (2) and (3) respectively.

$$F_{presentation} = \frac{SS_{presentation}/df_{presentation}}{SS_{error}/df_{error}} \tag{1}$$

$$F_{difficulty} = \frac{SS_{difficulty}/df_{difficulty}}{SS_{error}/df_{error}} \tag{2}$$

$$F_{interaction} = \frac{SS_{interaction}/df_{interaction}}{SS_{error}/df_{error}} \tag{3}$$

where $F_{presentation}$ = main effect due to presentation, $F_{difficulty}$ = main effect due to difficulty, and $F_{interaction}$ = main effects due to interaction.

3. Results And Discussion

3.1 TPH biodegradation

The degradation for standard run 17–20 which serve as control for the study was similar having the same combined variables. TPH concentration degraded from 5,000 mg kg^{-1} to between 722–862 mg kg^{-1} in 90 days duration while maintaining 3 d wk^{-1} turning rate. Standard runs 3, 4, 7, 8, 11, 12, 15, and 16; with moisture content of 50% the set-ups had hydrocarbon content floating on the surface. This made the admix semifluid in nature and easy to turn using hand trowel. When turning rate is effective and properly practice, the hydrocarbon contaminants becoming exposed to degrading agents and are therefore either degraded or mineralized [16]. This is attributed to the over 80% TPH reduction recorded in standard run 16 after 90 d treatment.

Substrate addition also enhanced TPH degradation as it serves as energizer for the microbes. This served mainly as catalyst in microbial reproduction processes and consequent consumption of the TPH

contaminants. Although higher concentration of substrate does not guarantee high TPH degradation, but when suitably combined with other parameters such as turning rate, high pH value and average moisture content; then a better degradation result can be obtained [27]. As fertilizer application on crude oil contaminated site was well systemic and well calculated, TPH degradation result was less than 40%, this was mainly due to the low moisture content and high acidic values of the treated samples. Nwilo and Badejo [11] had similar results from their study in which NPK fertilizer was used in the treatment of soil collected from a spill site. TPH degradation was faster in samples with lower moisture content than samples with higher moisture content. The pH of the contaminated soil samples before treatment ranged from 2–5. An increase in pH values was observed as the treatment progress into day 15 to 70, the pH value ranged from 5.7 to 7.1 (neutral). The addition of fertilizer to hydrocarbon polluted soil samples had a catalyst effect on the treatment and the pH value increase from acidic range of 2 to neutral range of 6.8. The substrate applied caused an increase in the total nitrogenous content of the soil but as the treatment days increased from day 50–60, the nitrogen content decreased gradually. This could be linked to the soil bacterial consuming the nitrogen for the hydrocarbon degradation, thus reducing the available nitrogen as treatment time increases [9]. This process utilizes biochemical reduction and it is initiated by denitrifying bacterial in the soil [11]. In all the factorial setups for the hydrocarbon contamination treatment, there was significant TPH degradation and the bacterial population in all the setups increased exponentially. The petroleum degrading bacteria increased from $1.8E+01$ to $3.6E+08$ cfu g^{-1} during the treatment period. This increase confirms the loss of nitrogen which usually accompany degradation procedures [11, 17]. This increment in petroleum degrading bacteria is in tandem with the findings of Oluwatuyi et al. [12] and Okonofua et al. [13]. FD analysis of results was then employed to determine the variable with the most significant contribution in the TPH degradation procedure.

3.2 FD of experiment

The response of TPHs on FD of experiment, used for variable screening hydrocarbon contaminant concentration of 5000 mg kg^{-1} within a period of 90 d is presented in Table 4. The minimum value of TPH is given as 450 mg kg^{-1} while the maximum value is 1393 mg kg^{-1}. The calculated mean value is 921 mg kg^{-1} with the standard deviation of 302 mg kg^{-1}. In assessing the worthiness of FD in screening the input variables based on their fundamental and important contributions, model standard error analysis was used based on Montgomery [38]. Presented in Table 5 are the computed standard errors for the chosen response. From the result, a low model standard error of 0.25 was achieved for both the individual and combine terms and effects. According to Jasmine and Mukherji [33], standard errors must be akin within a coefficient and the lower the value is, the better. Similarly, the error values were lower than the model basic standard deviation (SD) of 1.0 suggesting that the FD was perfect for the screening process. To demonstrate for multicollinearity, the variance inflation factor (VIF) of the analysis was obtained all through as 1.0 representing a superb outcome as a perfect VIF should give 1.0. VIFs closer to 10 or greater are usually cause for concern, and this signifies that coefficients are basely calculated due to multicollinearity [39].

Furthermore, the Ri-squared values also gives zero which perfectly match an ideal Ri-square as high Ri-squared especially values above 1.0 shows that design terms are correlated utimately resulting to poor models. Table 6 presents the correlation matrix of the regression coefficient. It can be seen that, off diagonal matrix, the lower values obtained point out the fact that the model is well fitted and it is strengthened enough to pilot the design space thus adequately optimizing the chosen response variable. Also, the model leveages were computed in order to better understand the influencial effect of individual design points on the model's predicted value. According to Meloun and Militky [40], leverage point indicates the extent of influence of an individual design point on the model's predicted values and it usually varies from 0 to 1. A leverage of 1 indicates that, the predicted value at a specific case will perfectly equal the observed value of the experiment, making the residual to be zero. The addition of leverage values in all cases equals the number of coefficients fit by the model, and the ultimate leverage an experiment can have is determined by 1/m, with m being the number of rounds the experiment was repeated. Leverage of 0.675 calculated in the factorial point indicates that, there is closeness between the predicted values and the experimental values. Hence, less or low residual value approves the sufficiency of the model.

3.3 Strength assessment of factorial model

To assess the strength of the factorial model towards an effective screening and optimization of the input variables, based on their significant contributions, one-way ANOVA was done for the response variable (Table 7). This was used to examine if the model is significant or not and to also measure the important contributions of individual variable. From the analysis in Table 7, the Model F-value of 56 connotes that the model is significant owing to the fact that there is only 0.01% probability that a "Model F-Value" with high value could occur due to noise. When the values of "Prob > F" are < 0.05, it indicate that the model terms are significant while values ⸓ 0.1 indicate the model terms are not significant [41].

Therefore, the terms A, D, AD, BC and CD are all significant model terms. Also, 22 from the "Curvature F-value" means that there exist significant curvature in the design space. This is mostly estimated by the difference between the average of the factorial points and that of the center points, and there is just 0.15% chance that a "Curvature F-value" with high value could occur as noise. Furthermore, 0.60 from the "Lack of Fit F-value" connotes that, it is not significant when compared with the pure error but on the other hand, there is a 71% probability that a "Lack of Fit F-value" could occur due to noise. In Table 8, the goodness of fit statistics was used to formalize the sufficiency of the factorial model regarding its potential to screen the input variables based on their significant contribution. From the statistical analysis, the "Predicted R-Squared" value of 0.9188 is in logical agreement with the "Adj R-Squared" value of 0.9684. According to Singh et al. [42], obtaining an adequate precision shows an adequate signal to noise ratio ⸓ 4 as desirable. Thus, the computed ratio of 20 as shown in Table 8 connotes an adequate signal. This model outcome therefore shows that it can be used to pilot the design space and properly screen the input variables while also determine their optimum value.

3.4 Input parameters and generated equation

The significant contributions of each input variables were determined using pareto chart. Pareto chart is a graphical presentation of input variables in order of their ranking. Statistical tool was used to generate Pareto's chart (Fig. 3) for the selected input variables. The result shows that the variables contributed to the hydrocarbon degradation in varying proportion with turning rate, pH, moisture content and mass of substrate all contributing 83, 4.36, 0.48 and 0.046% respectively. Furthermore, the most fitting equation which depicts both the combine interactions and individual effects of the significant input variables (pH, moisture content, mass of substrate and turning rate) against the mesured response (TPH) is provided based on the coded variables and the actual factors which are shown in Eqs. (4) and (5). Either of these two equations can be used in the estimation of the predicted TPH values which is shown in column 3 of Table 9. The predicted TPH values are then compared with the measured values to obtain the residual and the cook's distance shown in columns 4 and 9 in Table 9. In FD study, only terms without coefficients (zero coefficient) are left out in TPH evaluation using either coded or actual factors, hence the inclusion of AB and BD.

$$TPH = 950.88 - 70.61A - 23.51B + 7.26C - 307.70D - 3.06AB + 30.24AC - 36.78AD +$$
$$52.63BC + 3.01BD - 56.25CD \tag{4}$$

$$TPH = 1930.89 - 65.90A - 11.32B - 541.29C + 29.96D - 0.08AB + 75.59AC - 9.20AD +$$
$$13.16BC + 0.08BD - 140.62CD \tag{5}$$

The symptomatic case statistics show the observed values of the response covariant (TPH) against the predicted values as shown in Table 9. This symptomatic case statistics vividly present a clear and deep understanding into the model strength and the adequacy of the FD model.

3.5 Model validation

To further evaluate the accuracy of the prediction and established the appropriateness of FD of experiment, the observed and predicted values of TPH were presnted via a reliability plot as shown in Fig. 4. The r^2 = 0.9865 which represents the coefficient of determination was utilized in affirming the eligibility of the FD in reducing the TPH. An adequate statistical analysis output must first be used to check the satisfactoriness level of any model before its acceptance. Thus, to examine the statistical properties of the FD model, the normal probability plot of studentized residual shown in Fig. 5 was used to evaluate the regularity of the calculated residuals. The plot of residuals which represent the standard deviation of actual values based on the predicted values was adopted to ascertain if the residuals (observed− predicted) follow a normal distribution pattern. It was depicted that, the computed residuals are normally and approximately distributed which indicates the degree of satisfaction of the developed model. Furthermore, in the analysis, to determine the availability of a possible outlier, cook's distance plot was generated (Fig. 6). This cook's distance is to measure the degree at which the regression can change if

the outlier is excluded from the analysis. A particular point having a high distance value relative to the other points can possibly be an outlier and should therefore be investigated [43]. From Fig. 6, the plot shows an upper bound and lower bound of 1.00 and 0.00. Therefore, experimental values below the lower bound (0.00) or above the upper bounds (1.00) are termed as outliers which must be adequately investigated. Fortunately, the data of this analysis are free of possible outliers thus showing forth the adequacy of the experimental data. A 3D surface response plot was also provided to study the effects of combine input variables on the response (Fig. 7). It can be seen that the plot depicts the connection between the input variables (pH and turning rate) and the response variable (TPH) and also provides a comprehensible concept of the factorial model. In addition, the colour of the surface gets darker towards the turning rate which connotes that a higher turning rate leads to a reduction in TPH. This observation is in tandem with the work of Agarry and Ogunleye [34].

3.6 Numerical optimizaton

The numerical optimization was finally done to be sure of the desirability of the absolute model. Design expert was adopted in the numerical optimization phase in order to minimize the TPH level and determine the optimum pH, moisture content, mass of substrate and the turning rate. The numerical optimization interphase presents the objective function (Fig. S1 of Supplemental Information) with production of twenty (20) optimal solutions (Table 10). From the analysis, turning rate of 5 times a week, with pH of 6.01, moisture content of 10% and substrate mass of 1 kg will result in a minimum TPH value of 636 with a reliability value of 98.6%. The ramp solution showing the graphical representation of the best solution (Fig. S2) while the desirability chart depicting the veracity with which the model can predict the values of the chosen input variables and the similar response is presented in Fig. 8. From the outcome on the chart, it can be inferred that the developed and optimized model using FD and numerical optimization method respectively, predicted the TPH by an accuracy level of 97.83%.

4. Conclusion

This research has studied the remediation of total petroleum hydrocarbon using an environmental friendly method in order to create a clean environment. Factorial design was applied in varying the input parameters (pH, mass of substrate, moisture content and turning) of land farming treatment in order to ascertain the optimal conditions for the procedure. The significant contributions of each input variables which are pH, moisture content, mass of substrate and turning rate associated in the land farming treatment process revealed that, turning rate with 83% was the highest contribution while pH, moisture content and mass of substrate had 4.36, 0.48 and 0.046% contributions, respectively. The numerical optimization done to be sure of the desirability of the absolute model revealed that with initial contamination concentration of 5,000 mg kg^{-1}; turning rate of 5 times weekly, pH of 6.01, moisture content of 10% and substrate mass of 1 kg will achieve a minimum TPH value of 636 mg kg^{-1} with 98.6% reliability thus validating the factorial experimental design established for this study.

Declarations

Availability of data and materials

Not applicable

Competing interests

The authors declare that they have no competing interests

Authors' Contributions

OES conceived and investigated the experiment, and was also a major contributor in writing the manuscript. LKH analyzed data and interpreted the result, and was also a major contributor in writing of the manuscript. AE supervised the research and also edit the manuscript. All authors read and approved the final manuscript."

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Tables

Table 1 Physical and chemical properties of the soil used

Properties	Value
pH (1:1 soil-water)	5.72
Organic carbon (g kg^{-1})	47.8
Nitrogen (mg kg^{-1})	2.83
Phosphorus (mg kg^{-1})	4.73
Exchangeable cations	
Ca^{2+}(mg kg^{-1})	802
Mg^{2+}(mg kg^{-1})	784
Na^{+}(mg kg^{-1})	952
K^{-} (mg kg^{-1})	2,070
Gradation analysis	
Sand (%)	79.4
Silt (%)	14.5
Clay (%)	6.1
Textural class	Well graded Silt with organic content
Specific gravity	2.5

Table 2 Properties of NPK fertilizer and cow dung used

Parameters	Cow dung	NPK fertilizer
pH	8.27	9.62
Organic carbon (%)	14.36	8.06
Total nitrogen (%)	40.65	58.40
Phosphate (mg kg^{-1})	23.68	26.07
Potassium (mg kg^{-1})	17.49	7.83
Magnesium (mg kg^{-1})	5.88	11.35
Calcium (mg kg^{-1})	1.42	37.55
Sodium (mg kg^{-1})	1.94	1.06

Table 3 Ranges and levels of selected input variables

S/No	Input variables	Unit	Lower level	Upper level
1	pH	Nil	6	10
2	Moisture content	%	10	50
3	Mass of substrate	kg	0.6	1.0
4	Turning rate	Times per week	1	5

Table 4 Response of TPH on factorial design of experiment used for variable screening

Std	Run	Type	Factor 1:pH	Factor 2: Moisture content (%)	Factor 3: Mass of substrate (g)	Factor 4: Turning rate (Nil)	TPH response (mg kg^{-1})
17	1	Center	8.0	30	0.8	3	847
18	2	Center	8.0	30	0.8	3	723
19	3	Center	8.0	30	0.8	3	782
20	4	Center	8.0	30	0.8	3	862
1	5	Fact	6.0	10	0.6	1	1346
2	6	Fact	10.0	10	0.6	1	1204
3	7	Fact	6.0	50	0.6	1	1183
4	8	Fact	10.0	50	0.6	1	1048
5	9	Fact	6.0	10	1	1	1248
6	10	Fact	10.0	10	1	1	1344
7	11	Fact	6.0	50	1	1	1394
8	12	Fact	10.0	50	1	1	1304
9	13	Fact	6.0	10	0.6	5	900
10	14	Fact	10.0	10	0.6	5	630
11	15	Fact	6.0	50	0.6	5	749
12	16	Fact	10.0	50	0.6	5	490
13	17	Fact	6.0	10	1	5	675
14	18	Fact	10.0	10	1	5	450
15	19	Fact	6.0	50	1	5	679
16	20	Fact	10.0	50	1	5	573

Table 5 Result of computed standard errors

Term	Std err*	VIF	Ri-squared	0.5 Std dev.	1 Std dev.	2 Std dev.
			Powered at 5% level for effect of			
A	0.25	1.00	0.000	14.6	43.91	94.4
B	0.25	1.00	0.000	14.6	43.91	94.4
C	0.25	1.00	0.000	14.6	43.91	94.4
D	0.25	1.00	0.000	14.6	43.91	94.4
AB	0.25	1.00	0.000	14.6	43.91	94.4
AC	0.25	1.00	0.000	14.6	43.91	94.4
AD	0.25	1.00	0.000	14.6	43.91	94.4
BC	0.25	1.00	0.000	14.6	43.91	94.4
BD	0.25	1.00	0.000	14.6	43.91	94.4
CD	0.25	1.00	0.000	14.6	43.91	94.4

*Basis standard deviation = 1.0, A is the pH, B is the Moisture content, C is the Mass of substrate, D is the Turning rate, VIF is the Variance Inflation Factor

Table 6 Correlation matrix of regression coefficients

| | Correlation matrix of regression coefficients | | | | | | |
	Intercept	A	B	C	D	AB	AC
Intercept	1.000						
A	-0.000	1.000					
B	-0.000	-0.000	1.000				
C	-0.000	-0.000	-0.000	1.000			
D	-0.000	-0.000	-0.000	-0.000	1.000		
AB	-0.000	-0.000	-0.000	-0.000	-0.000	1.000	
AC	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	1.000
AD	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000
BC	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000
BD	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000
CD	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000

Table 7 Analysis of variance table for input variable screening

ANOVA for selected factorial model

Analysis of variance table (partial sum of squares type-III)

Source	Sum of squares	df	Mean square	F-Value	P-Value Prob > F	Comments
Model	1.736E+0.06	10	1.736E+005	56.24	< 0.0001	Significant
A-pH	79778	1	79778	25.85	0.0009	
B-Moisture content	8845	1	8845	2.87	0.1289	
C-Mass of substrate	842	1	843	0.27	0.6155	
D-Turning rate	1.515E+006	1	1.515E+006	490.76	< 0.0001	
AB	150	1	150	0.048	0.8312	
AC	14629	1	14629	4.74	0.0612	
AD	21650	1	21650	7.01	0.0293	
BC	44310	1	44310	14.35	0.0053	
BD	145	1	145	0.047	0.8339	
CD	50623	1	50623	16.40	0.0037	
Curvature	69348	1	69348	22.47	0.0015	Significant
Residual	24694	8	3067			
Lack of fit	12376	5	2475	0.60	0.7107	Non-significant
Pure error	12318	3	4106			

Table 8 Goodness of fit statistics for validating model significance

S/No	ANOVA parameters	Value	ANOVA Parameters	Value
1	Std Dev.	56	R-Squared	0.9860
2	Mean	921	Adj. R-Squared	0.9684
3	C.V. (%)	6	Pred. R-Squared	0.9188
4	PRESS	1.49E+005	Adeq. Precision	20

Note: The 'Pred. R-Squared' of 0.9188 is in reasonable agreement with the 'Adj. R-Squared' of 0.9684.
PRESS = Prediction error sum of squares

Table 9 Diagnostics case statistics report of observed and predicted TPH

Standard order	Actual value	Predicted value	Residual	Leverage	Internally studentized residual	Externally studentized residual	Influence on fitted value	Cook's distance	Run order
1	1346	1335	10.37	0.688	0.334	0.315	0.467	0.020	5
2	1204	1213	-9.51	0.688	-0.306	-0.288	-0.427	0.017	6
3	1183	1183	0.32	0.688	0.010	0.010	0.014	0.000	7
4	1048	1049	-1.18	0.688	-0.038	-0.036	-0.053	0.000	8
5	1248	1297	-48.89	0.688	-1.574	-1.773	-2.63	0.454	9
6	1345	1296	48.03	0.688	1.546	1.728	2.56	0.438	10
7	1393	1355	38.03	0.688	1.230	1.278	1.895	0.277	11
8	1304	1342	-37.34	0.688	-1.202	-1.242	-1.843	0.265	12
9	900	900	0.13	0.688	0.004	0.004	0.006	0.000	13
10	630	631	-0.99	0.688	-0.032	-0.030	-0.044	0.000	14
11	749	760	-10.82	0.688	-0.348	0.328	-0.487	0.022	15
12	490	478	11.68	0.688	0.376	0.355	0.527	0.026	16
13	675	636	38.40	0.688	1.236	1.286	1.907	0.280	17
14	450.43	488	-37.53	0.688	-1.208	-1.250	-1.854	0.268	18
15	679	707	-27.71	0.688	-0.892	-0.879	-1.304	0.146	19
16	573	546	26.84	0.688	0.864	0.849	1.259	0.137	20
17	847	804	43.59	0.250	0.906	0.895	0.517	0.023	1
18	723	804	-80.74	0.250	-1.678	-1.950	-1.126	0.078	2
19	782	804	-21.49	0.250	-0.447	-0.423	-0.244	0.006	3
20	862	804	58.63	0.250	1.219	1.263	0.729	0.041	4

Table 10 Optimal solutions of numerical optimization model

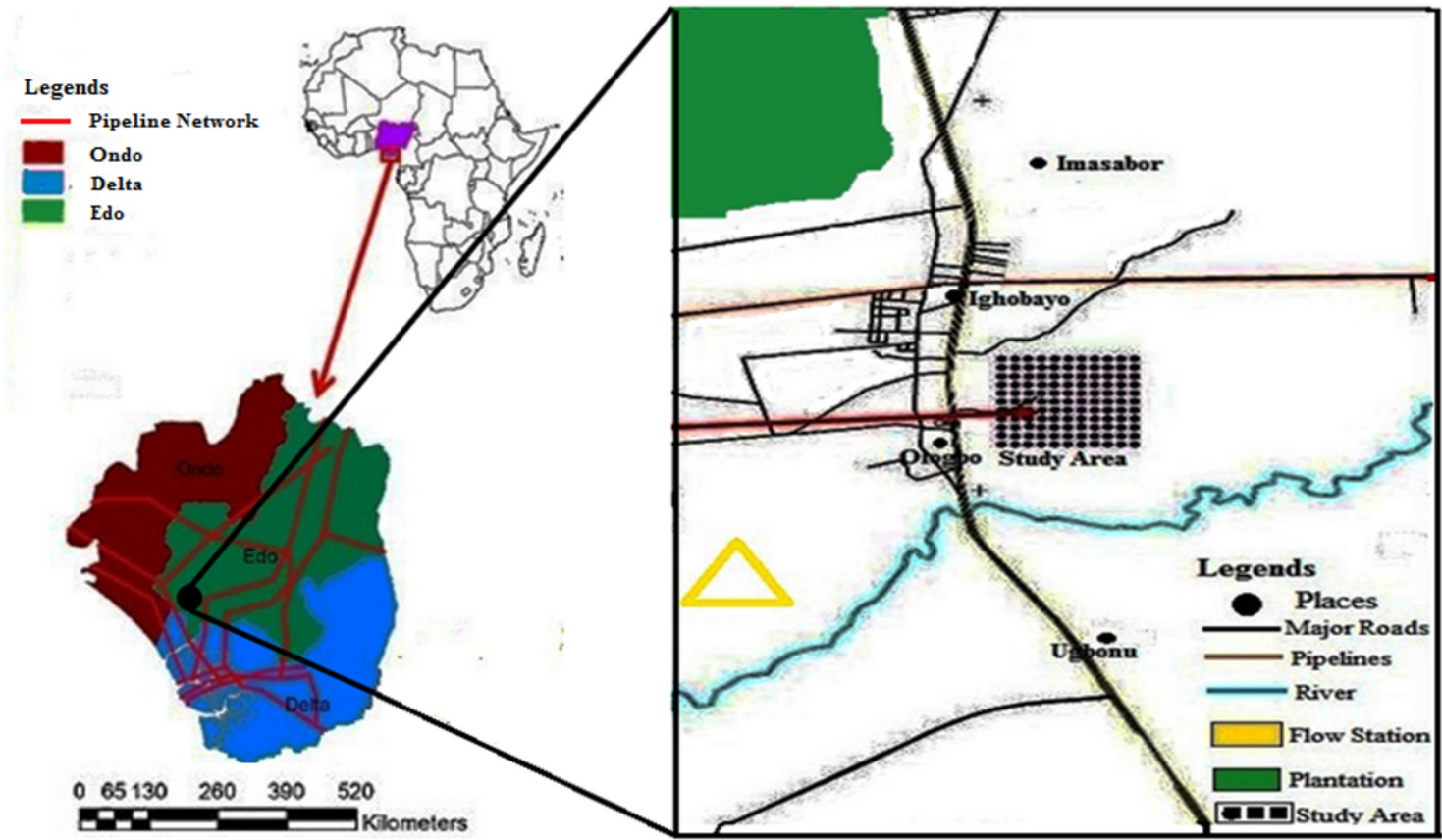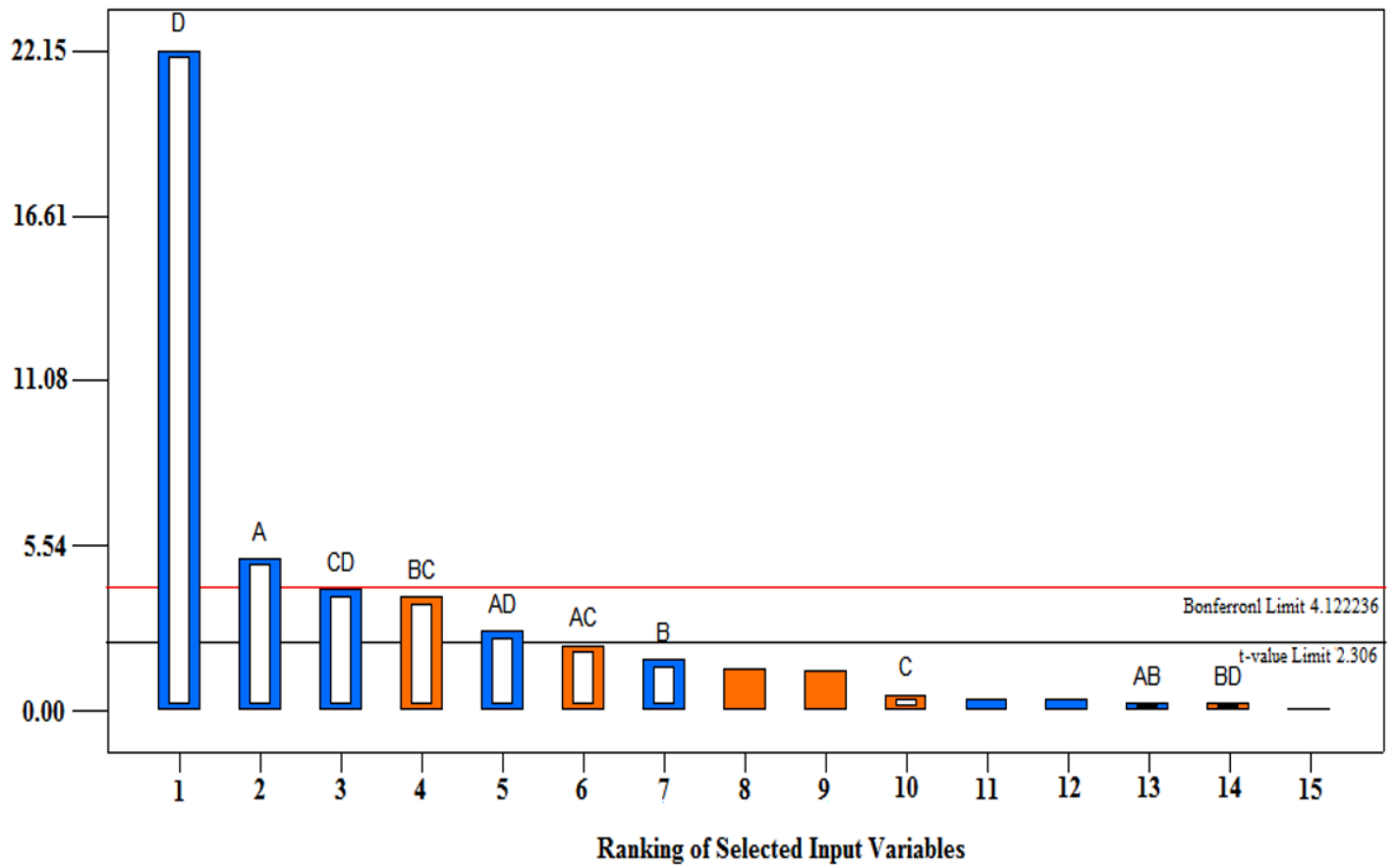| Number	pH	Moisture content	Mass of substrate	Turning rate	TPH	Desirability	
1	6.01	10.00	1.00	5.00	635.907	0.986	Selected
2	6.00	17.44	1.00	4.99	650.986	0.985	
3	6.00	23.73	1.00	5.00	660.319	0.984	
4	6.00	24.32	1.00	5.00	661.415	0.984	
5	6.00	28.81	1.00	5.00	669.695	0.984	
6	6.00	30.84	1.00	5.00	672.851	0.983	
7	6.00	32.26	1.00	5.00	675.421	0.983	
8	6.00	31.47	1.00	4.98	677.410	0.983	
9	6.00	10.00	0.96	4.91	679.292	0.983	
10	6.00	37.28	1.00	5.00	684.185	0.982	
11	6.00	40.14	1.00	5.00	689.686	0.982	
12	6.00	39.45	0.99	5.00	676.788	0.982	
13	6.00	33.53	1.00	5.00	698.162	0.981	
14	6.00	45.15	1.00	5.00	704.886	0.981	
15	6.00	34.21	1.00	4.84	707.500	0.981	
16	6.00	41.29	0.93	5.00	716.346	0.980	
17	6.00	21.70	0.88	5.00	720.118	0.979	
18	6.00	10.00	0.87	5.00	734.523	0.979	
19	6.00	24.54	0.84	5.00	735.764	0.978	
20	6.00	50.00	0.77	5.00	736.972	0.978	

Figures

Figure 1

Map of Project Location

Figure 2

Contaminated Area in the Study Location

Figure 3

Pareto chart showing the ranking of the selected input variables
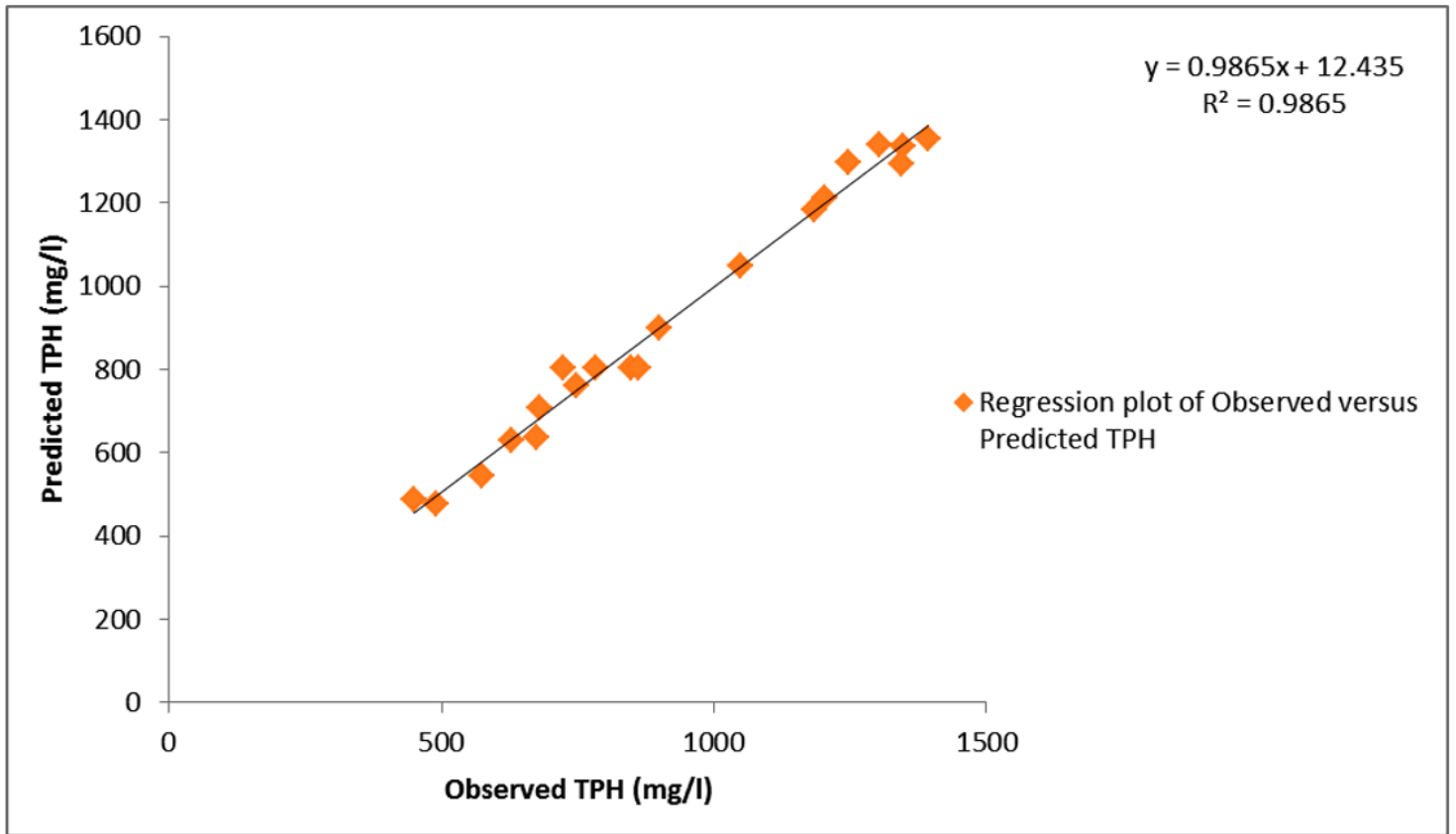
Figure 4

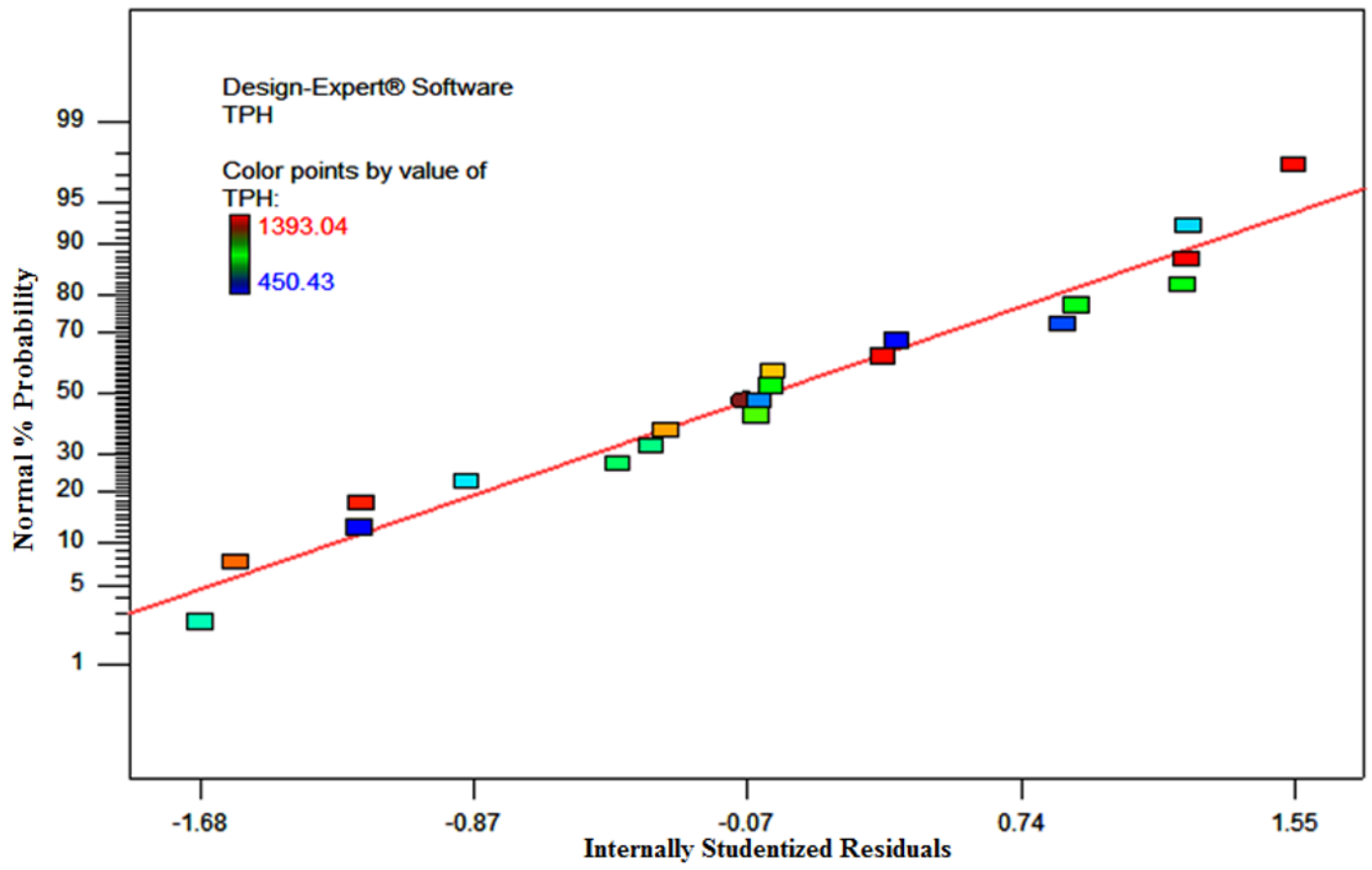Reliability plot of observed versus predicted TPH

Figure 5

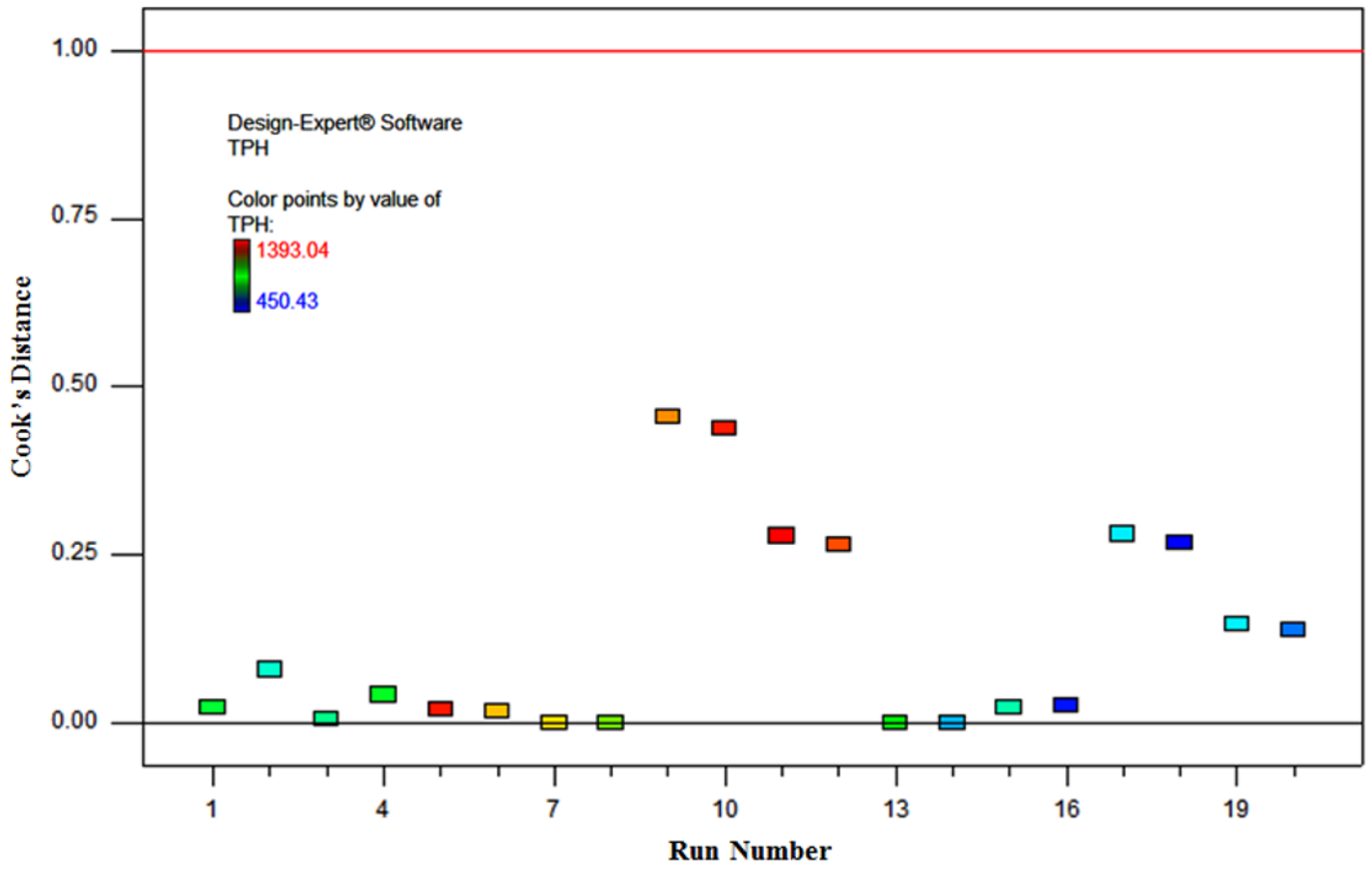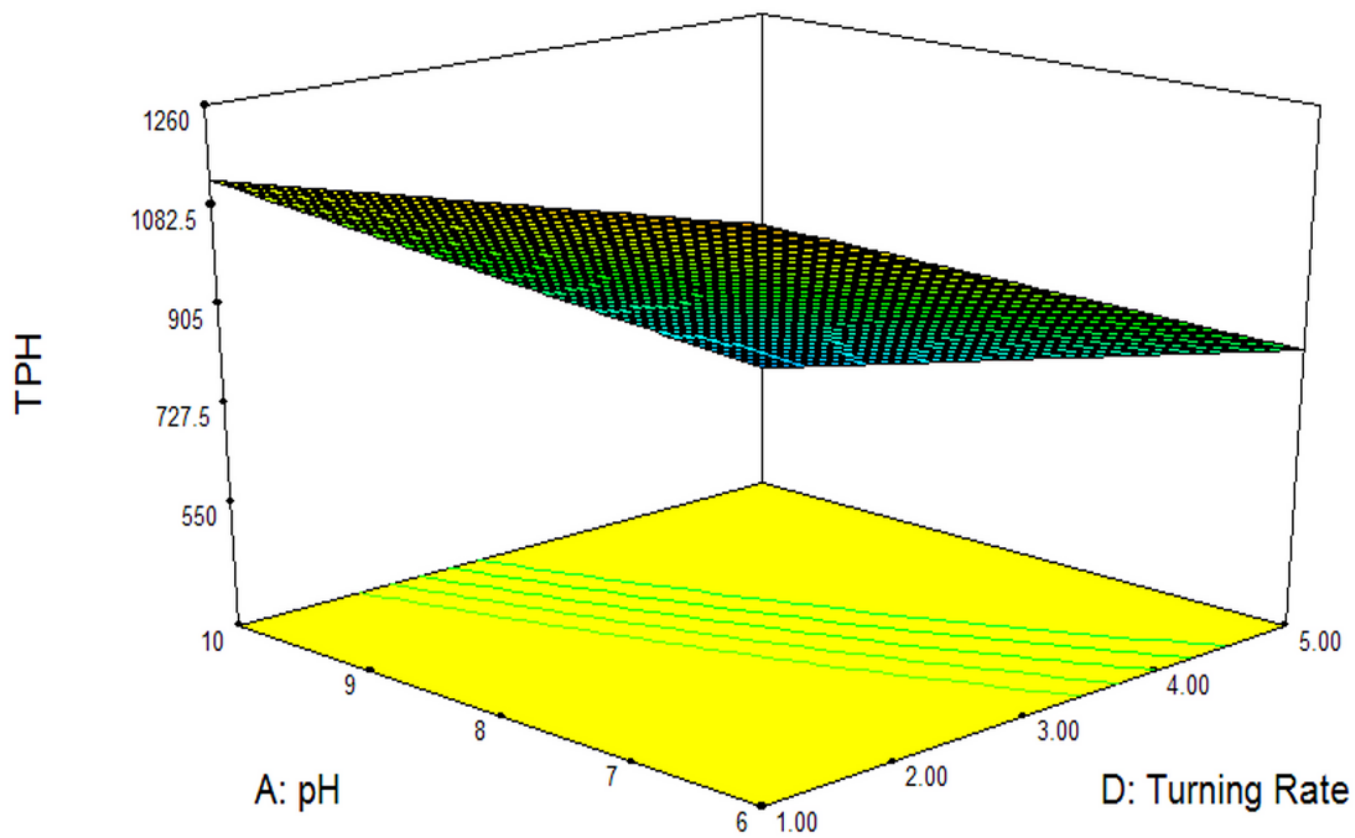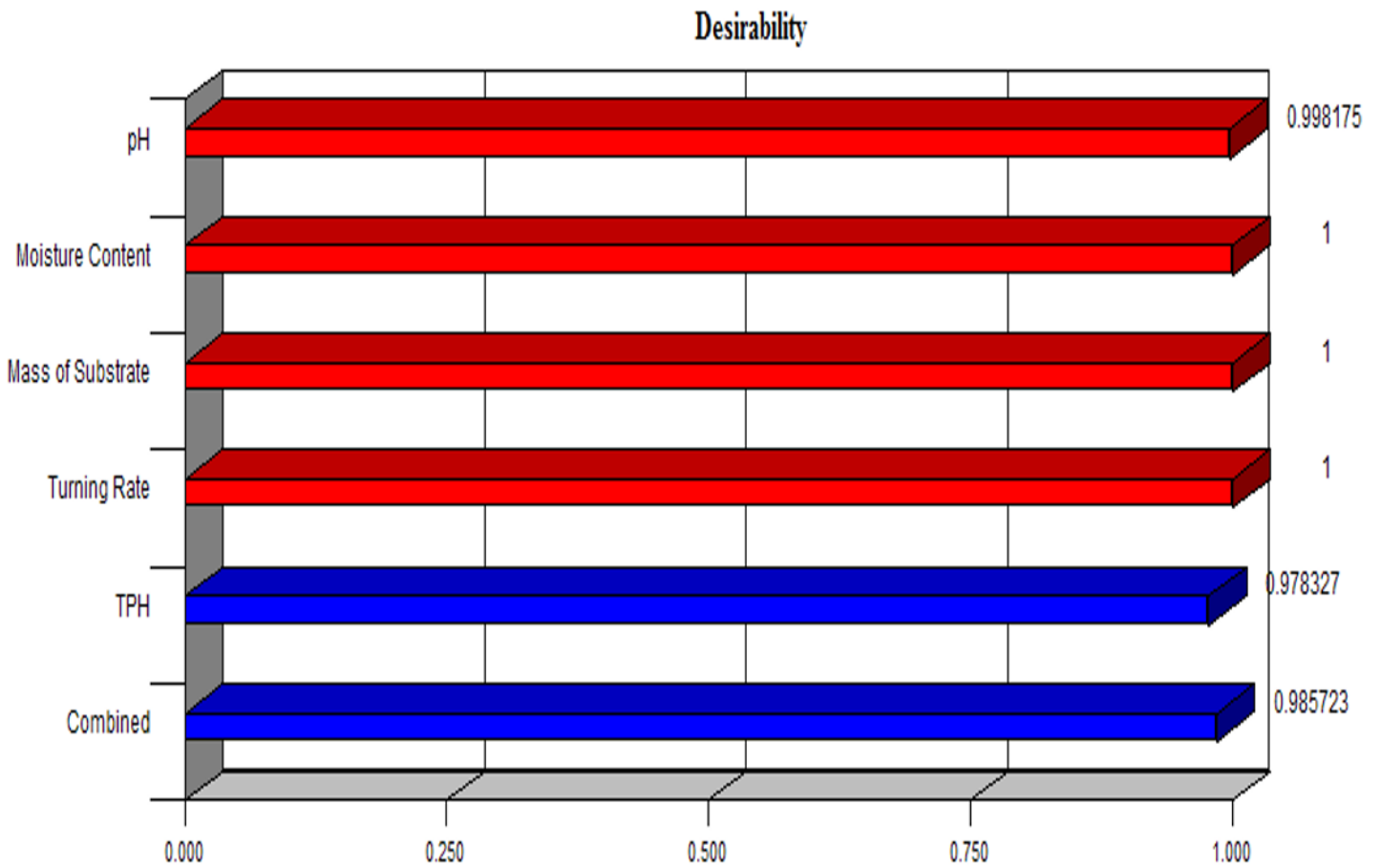Normal probability plot of studentized residuals for TPH

Figure 6

Generated cook's distance for TPH

Figure 7

Effect of pH and turning rate on TPH

Figure 8

Prediction accuracy of numerical optimzation

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