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Removal of Total Petroleum Hydrocarbons (TPHs) and Polycyclic Aromatic Hydrocarbons (PAHs) in Spent Synthetic-Based Drilling Mud Using Organic Fertilizer

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Authors' contributions

This work was carried out in collaboration between all authors. Author FO designed the study & wrote the protocol which was approved by his supervisors. Authors ILN, OA, GOA and FO equally collected field samples and carried out laboratory analyses. Authors OA and GOA guided the laboratory studies. Author ILN guided the statistical analysis and the draft report. All authors read and approved the finial manuscript.

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ABSTRACT

Treatment and disposal of spent (used) drilling mud have become an important environmental challenge in the oil and gas industry. Total Petroleum Hydrocarbons (TPHs) and Polycyclic Aromatic Hydrocarbons (PAHs) constitute the major contaminants in spent drilling mud. In this study, five spent synthetic-based drilling mud samples were collected from five oil fields in the Niger Delta. Samples collected on day 0 were analyzed for TPHs and PAHs. Concentrations

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higher than the permissible regulatory limits were recorded. The efficacy of urea fertilizer in the remediation of TPH-and PAH-impacted mud was investigated. Six sub-samples and six control sub-samples were tested bi-weekly for 12 weeks with 20 g, 25 g, and 30 g doses of urea fertilizer per 20 L of spent mud for each of the five samples representing each individual oil field (marked A through E). Removal of TPHs and PAHs with urea fertilizer treatment proved to be fast and efficient. In 6 weeks, with a dose of 1.5 g/L, over 98% removal of TPHs was recorded, and more than 94% of PAHs, and in 12 weeks, more than 99.5% removal was recorded for both. The residual levels of TPHs and PAHs met Department of Petroleum Resources (DPR: Nigeria) and US EPA limits for land disposal. Mathematical models with a goodness of fit (R^2) of 0.999, were developed to predict the rate of the degradation processes.

Keywords: *Spent drilling mud; Niger Delta; total petroleum hydrocarbons; and polycyclic aromatic hydrocarbons; biodegradation; urea fertilizer; mathematical model.*

1. INTRODUCTION

Drilling is one of the major chemical intensive operations in oilfields that generates wastes, which can impact the environment. [1-5]. In drilling operations, two main types of wastes are generated, drill cuttings and spent drilling mud [6-9].Drilling fluids, including synthetic base fluids (SBFs), play important roles in drilling operations by providing relatively better shale inhibition, lubricity, and thermal stablity characteristics [4,10,11]. Other SBF functions include lifting of drill cuttings from the well and controlling hydraulic pressure [12,13].

Total Petroleum Hydrocarbons (TPHs) and Polycyclic Aromatic Hydrocarbons (PAHs) are some of the major contaminants of the spent drilling mud and they impact adversely on the environment if carelessly disposed of [14,15]. Studies have shown that plant growth is affected when petroleum hydrocarbon-impacted spent drilling mud is released on land [16]. Levels of spent drilling mud above a few percentages in soil (by weight) have been shown to degrade plant growth [17,18] Improper disposal of spent drilling mud into water bodies endanger marine life [19]. Safe disposal of spent drillng mud after drilling is a major problem in the oil and gas industry [20-22]. Most of the existing methods of treatment like fixation,and thermal methods,have disadvantages ranging from high risk to personnel to huge costs because of the high energy demands due to high temperature requirements [23,24]. Some of these existing methods of treatment require expensive and sophisticated equipment with high capital and operating costs [5,24,25].

Bioremediation is the biological breakdown or biodegradation of contaminants [26]. It involves the microbial breakdown of organic compounds into less complex compounds, mostly water, and carbon dioxide and sometimes methane [26]. The rate and extent of biodegradation depends on the population and type of microorganisms, the environment, and the chemical structure of the contaminant [28]. Most organic compounds are biodegraded under aerobic conditions [29]. Biodegradation of some organic compounds has also occurred under anaerobic conditions, although at rates not as rapid as under aerobic conditions [30]. Intrinsic bioremediation or natural attenuation is the biodegradation of a target contaminant without intervention under an appropriate environmental condition, available nutrients (mostly phosphate, nitrogen and sulfur), and microorganisms [31]. However, from regulatory point of view, the rate of intrinsic bioremediation is slow because of time limits [32]. As a result, enhanced (engineered) bioremediation is required most of the time [33,34]. In engineered bioremediation, the rate of bioremediation is increased in two ways: biostimulation and bioaugmentation [33,35]. Biostimulation was deployed in this study by use of urea fertilizer, as a source of nutrient to the indigenous microorganisms, to biodegrade TPHs and PAHs in impacted, spent synthetic based mud.

Urea is one concentrated source of available nitrogen. It is widely used in agriculture as a fertilizer and animal feed additive. Urea fertilizer is the most important nitrogenous fertilizer. It is called the King of Fertilizers because of its high nitrogen content (about 46 percent). It is a white crystalline organic chemical compound. It is neutral and can adapt to almost all the land. It is a waste product formed naturally by metabolizing protein in humans as well as other mammals, amphibians and some fish. The main function of urea fertilizer is to provide the plants with nitrogen to promote green leafy

growth. It can make the plants look lush, and it is necessary for the photosynthesis of plants. Nitrogen is an important nutrient required for microbial growth. Urea fertilizer is widely used in biostimulation because of its high nitrogen content.

Advantages of urea fertilizer include: high nitrogen content (this percentage is much higher than in other available nitrogenous fertilizers), low cost of production, no storage risk (not subject to fire or explosion hazards), and wide application-urea fertilizer can be used for all types of crops and soils and does not harm the soil. However, it is very soluble in water and hygroscopic, and requires better packaging quality.

Mathematical models help to predict the expected outcome of experiments. This saves time and cost for future jobs. More often the field and laboratory data are used to calibrate multi-purpose regression models of linear and/or higher order equivalence. The statistical approach was adopted in this study for model development.

2. METHODOLOGY

2.1 Area of Case Study

This study was carried out with spent, synthetic based mud (SBM) from five oilfields in the Niger Delta. The Niger Delta is located at an elevation of 96m above mean sea level. It lies between Longitude 5° and 8° East and Latitude 3° and 6° North.Samples A, B, C, D and E were taken at Longitude 5°9'40.58" East and Latitude 5°19'17.71"North, Longitude 6°47'4.912" East and Latitude 3°11'37.644" North, Longitude 6°16'41.972" East and Latitude 4°11'42.948" North, Longitude 6°21'20.38" East and Latitude 4°54'28.648" North, Longitude 6°42'12.077" East and Latitude 4°59'30.057" North, respectively. (Fig. 1).The region has a population of 30 million people [36]. Over 90% of Nigeria's proven oil and gas reserves are located in the region [37]. The Niger Delta covers a coastline of 560 km^2, and it is formed primarily by sediment deposition [38]. It's a rich mangrove swamp covering over 20,000km^2 within wetlands of 70,000km^2 [39]. Oil was first discovered in the delta by Royal Dutch Shell (Shell Nigeria), formerly Shell-BP, in 1957 at Oloibiri, and production began in 1958. The oil and gas industry play significant role in Nigeria's economy, accounting for about 90% of its gross income [40]. Fig. 1 shows the map of Niger Delta and drilling mud sample locations.

2.2 Data Collection

Adequate quantities of the spent drilling mud from five oil fields were sampled from well-agitated mud tanks and transported to the laboratory as quickly as possible to ensure that the parameters of the mud did not change before testing. Convenience sampling method was used because of low drilling activities in Nigeria, at the time of this study. In the laboratory, the samples were again thoroughly agitated with sample mixers to ensure proper mixing. The samples were marked MUD-A to E and tested for baseline values of the physicochemical parameters (Table 2). For each sample, 25 (twenty-five) sub samples of 20L each were created: (i) One sub-sample for baseline studies; (ii) Eighteen (18) sub-samples for bioremediation treatment for Total Petroleum Hydrocarbons (TPHs) and PAHs with urea fertilizer (6 sub-samples each for 20 g, 25 g, and 30 g doses); (iii) Six (6) sub-samples for control. The control samples were the original spent drilling mud without treatment. Urea

Table 1. Analytical methods employed in the study

Parameter	Analytical Method	Standard
TPHs and PAHs	GC/FID (Agilent 7890A GC systems)	ASTM D 3921
THB and HUB	Total Plate Count	ASTM D5465-16
Total Nitrogen	Kjeldahl	ASTM D8001-16e1
Temperature	Meter reading	ASTM E2251-14
pH	Meter reading	ASTM D1293-18
Moisture Content	Gravimetric method	ASTM D2216-98
CO_2	Standard method for dissolved carbon dioxide in liquid	ASTM D513-16
DO	Standard method for dissolved oxygen in liquid	ASTM D888-12e1
Phosphorous	Total phosphorous-EPA method	EPA 365.1
TOC	Standard test method for total carbon and organic carbon in liquid by ultraviolet and infrared dictation	ASTM D4839-03(2017)

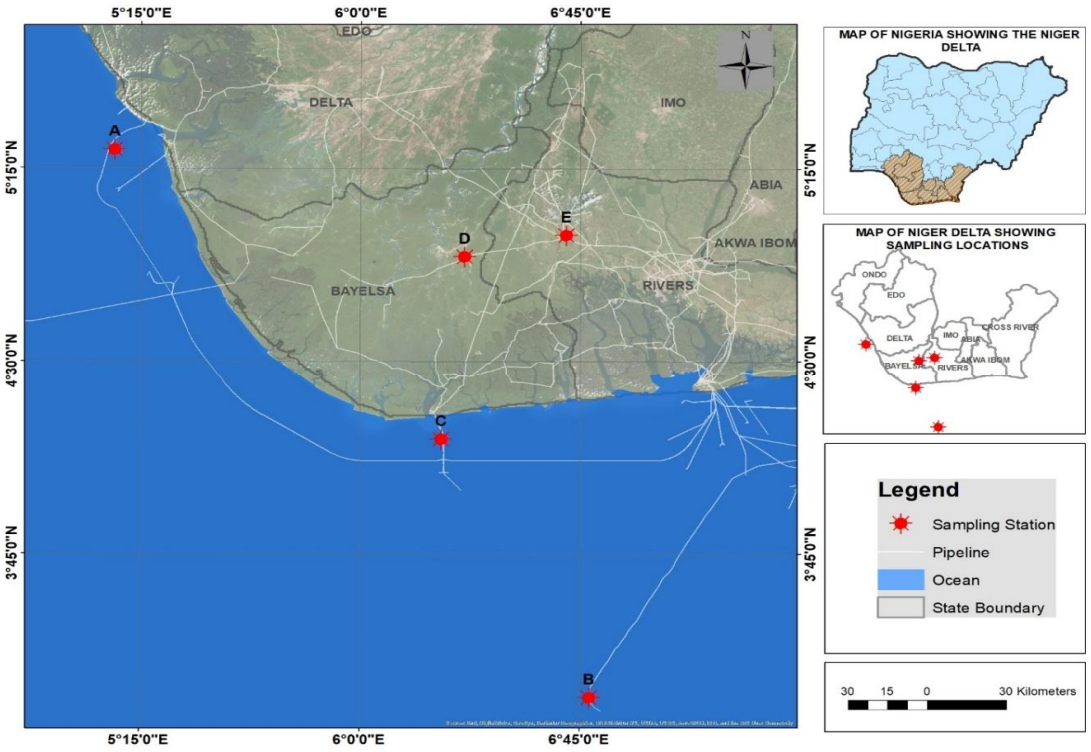

Fig. 1. Location map of study area

fertilizer was used as a source of nutrients for the hydrocarbon utilizing bacteria (HUB) for the remediation of the mud impacted with Total Petroleum Hydrocarbons and PAHs. Both the treated and control samples were tested bi-weekly for 12 weeks. The tests conducted and methods used are shown in Table 1.

2.3 Predictive Model

Nonlinear regression analyses were applied in modeling the duration of the effective biological treatment of the spent drilling mud. XLSTAT 2018 was the statistical tool employed as an aid for the model development [41,42].

3. RESULTS AND DISCUSSION

3.1 Results

3.1.1 Baseline physicochemical parameters of spent drilling mud samples

The baseline values of the physicochemical parameters of the spent drilling mud are shown in Table 2. Nigerian and US EPA effluent limits for TPHs and PAHs are also shown in Table 3. It can be seen that spent drilling mud from different oil wells have varying concentrations of the contaminants.

3.1.2 TPHs and PAHs biodegradation

The laboratory test results for biodegradation of TPHs and microbial growth (HUB and THB) for sample-A of the drilling mud impacted with Total Petroleum Hydrocarbons and Polycyclic Aromatic Hydrocarbons using 20 g, 25 g, and 30 g doses of urea fertilizer are presented in Figs. 2 through 5. The population of the microorganisms varied from sample to sample. When stimulated by the addition of nutrients, the microbial population count of the indigenous heterotrophic bacteria increased. On amendment with 30g urea fertilizer, the total heterotrophic bacteria (THB) grew from 9.40×10^5 CFU/ml and peaked in week 6 with a population of 6.27×10^8 CFU/ml before dropping to 3.79×10^8 in week 12. The hydrocarbon utilizing bacteria (HUB) grew from 4.30×10^5 CFU/ml peaking in week 6 to 4.52×10^5 CFU/ml. After reaching this peak, the HUB started dropping gradually to 2.63×10^8 in week 12. The same trend was observed with treatment using 20g, and 25g of urea fertilizer. This is represented in Figs. 2 through 5. It is this growth that can lead to the metabolizing of the hydrocarbons.

Table 2. Physico-chemical parameters of the spent drilling muds

S/no	Parameters	Sample				
		A	B	C	D	E
1	pH	7.5 ± 0.01^{b}	7.3 ± 0.01^{a}	7.8 ± 0.00^{c}	7.4 ± 0.09^{a}	7.9 ± 0.00^{c}
2	Temperature(^{o}C)	28 ± 0.00^{a}	28.3 ± 0.10^{b}	28.7 ± 0.05^{c}	29.0 ± 0.00^{d}	28.5 ± 0.10^{bc}
3	Nitrogen (mg/L)	0.06 ± 0.004^{b}	0.08 ± 0.005^{d}	0.06 ± 0.004^{b}	0.04 ± 0.002^{a}	0.05 ± 0.003^{ab}
4	Potassium (mg/L)	2.0 ± 0.3^{ab}	2.7 ± 0.3^{d}	1.7 ± 0.2^{a}	2.2 ± 0.1^{ab}	2.0 ± 0.2^{ab}
5	Sodium (mg/L)	2.4 ± 0.03^{b}	1.7 ± 0.02^{a}	2.3 ± 0.03^{b}	1.7 ± 0.10^{a}	2.4 ± 0.10^{b}
6	Calcium (mg/L)	13.4 ± 0.2^{a}	16.3 ± 0.2^{c}	17.4 ± 0.00^{d}	14.7 ± 0.10^{b}	19.10 ± 0.2^{e}
7	Phosphate(mg/L)	2.3 ± 0.03^{a}	7.4 ± 0.03^{d}	7.6 ± 0.05^{e}	5.8 ± 0.03^{c}	3.8 ± 0.04^{b}
8	Conductivity	2.58 ± 0.02^{a}	2.68 ± 0.02^{b}	2.84 ± 0.03^{c}	2.62 ± 0.02^{ab}	2.86 ± 0.02^{c}
9	Chlorides (mg/L)	18.8 ± 0.2^{a}	22.2 ± 0.4^{b}	23.3 ± 0.43^{c}	19.64 ± 0.04^{a}	25.47 ± 0.03^{d}
10	TOC (%)	1.4 ± 0.2^{a}	1.8 ± 0.2^{a}	1.95 ± 0.3^{a}	2.0 ± 0.3^{a}	1.6 ± 0.3^{a}
11	DO (mg/L)	7.1 ± 0.3^{a}	7.95 ± 0.45^{a}	10.4 ± 0.4^{b}	8.4 ± 0.5^{a}	7.2 ± 0.4^{a}
12	Moisture Content (%)	8.9 ± 0.6^{bc}	9.2 ± 0.4^{bc}	7.6 ± 0.3^{ab}	10.3 ± 0.3^{c}	6.8 ± 0.5^{a}
13	CO_2 (mg/L)	1.6 ± 0.1^{a}	1.8 ± 0.1^{a}	2.2 ± 0.2^{a}	1.7 ± 0.3^{a}	2.1 ± 0.4^{a}
14	TPHs (mg/L)	6211 ± 10^{a}	8591 ± 8^{c}	9474 ± 10^{d}	10110 ± 10^{e}	7482 ± 8^{b}
15	PAHs(mg/L)	82.0 ± 0.5^{a}	94.6 ± 0.4^{d}	84.7 ± 0.3^{b}	86.25 ± 0.55^{b}	92.6 ± 0.4^{c}
16	THB (CFU/ml)	$9.4 \pm 0.1\times10^{5e}$	$7.6 \pm 0.02\times10^{5a}$	$8.4 \pm 0.01\times10^{4b}$	$9.3 \pm 0.0\times10^{5d}$	$8.9 \pm 0.05\times10^{5c}$
17	HUB (CFU/ml)	$4.3 \pm 0.1\times10^{4c}$	$6.3 \pm 0.1\times10^{4a}$	$5.2 \pm 0.01\times10^{5d}$	$6.4 \pm 0.1\times10^{4e}$	$9.9 \pm 0.01\times10^{4b}$

[a-e]Results are presented as mean ± standard error. Means with different superscript, the homogenous subset of means, (a, ab, b, bc, c, d and e) within the same rows indicate significant differences ($p < 0.05$), Legend: DO = Dissolved Oxygen; TOC=Total Organic Carbon; TPHs=Total Petroleum Hydrocarbons; PAHs=Polycyclic Aromatic Hydrocarbons; HUB=Hydrocarbon Utilizing Bacteria, and; THB=Total Heterotrophic Bacteria.

Table 3. DPR (Nigeria) and US EPA guidelines and standards for TPHs and PAHs

Parameters	Nigeria (DPR)	USEPA
TPHs (Inland-fresh waters) (mg/L)	10	-
TPHs (Nearshore-brackish/saline waters) (mg/L)	20	-
TPHs (mg/L)	-	5
PAHs (mg/L)	1	0.1

Sources: Department of Petroleum Resources (DPR2002)[43]; U.S. Environmental Protection Agency (2018)[44].

The biodegradation of hydrocarbon contaminants (TPHs and PAHs) for the study period of 12 weeks (using 20 g, 25 g, and 30 g urea fertilizer amendments) is also shown in Figs. 2 through 5. The results show a sharp decrease in TPHs and PAHs concentrations in the first four weeks. This indicates a period of active degradation by the microorganisms. After week 6, the degradation level decreased, and that may be attributed to the microorganisms transiting into the stationary phase after massive degradation had taken place between week 1 and 6. The results show an average percentage degradation of 99.9% in 12 weeks for TPHs for the 5 samples studied. Also, PAHs showed an average percentage degradation of 99.3% in 12 weeks for the five samples.

3.1.3 Control for Sample-A

The result of TPHs, PAHs, and the ratio of HUB and THB for Control Sample-A is shown in Fig. 6. The control sample did not show any appreciable decontamination.

3.1.4 Bioremediation Indicators for Sample-A

The result of bioremediation indicators for Sample-A using 30g of urea fertilizer is shown in Fig. 7. The corresponding result for the control sample is presented in Fig. 8. The bioremediation indicators for the amended sample, reflected the decontamination process, as against the control sample where the indicators were inactive.

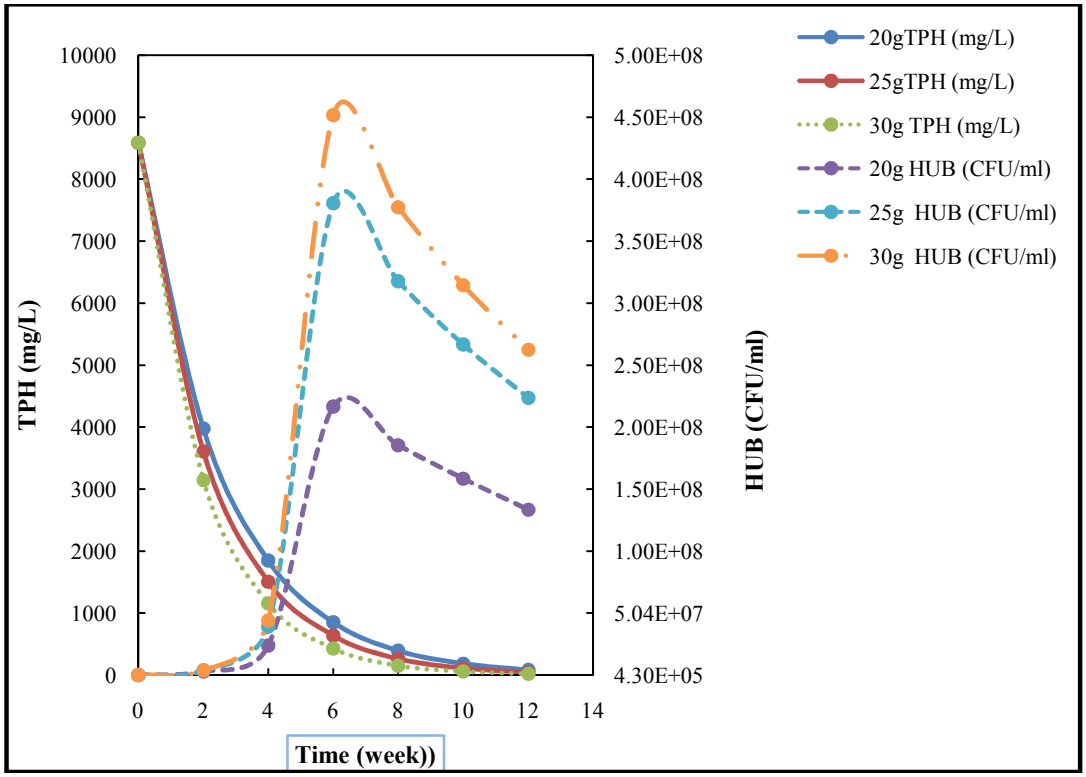

Fig. 2. Distribution of TPHs and HUB for Sample-A

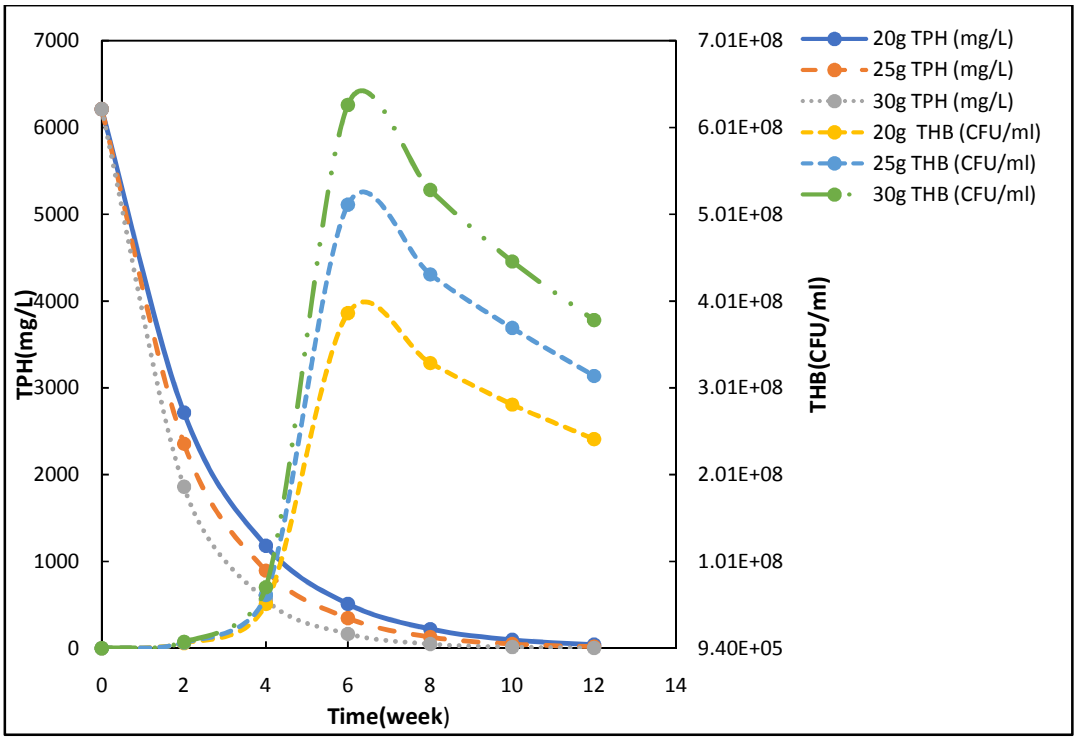

Fig. 3. Distribution of TPHs and THB for Sample-A

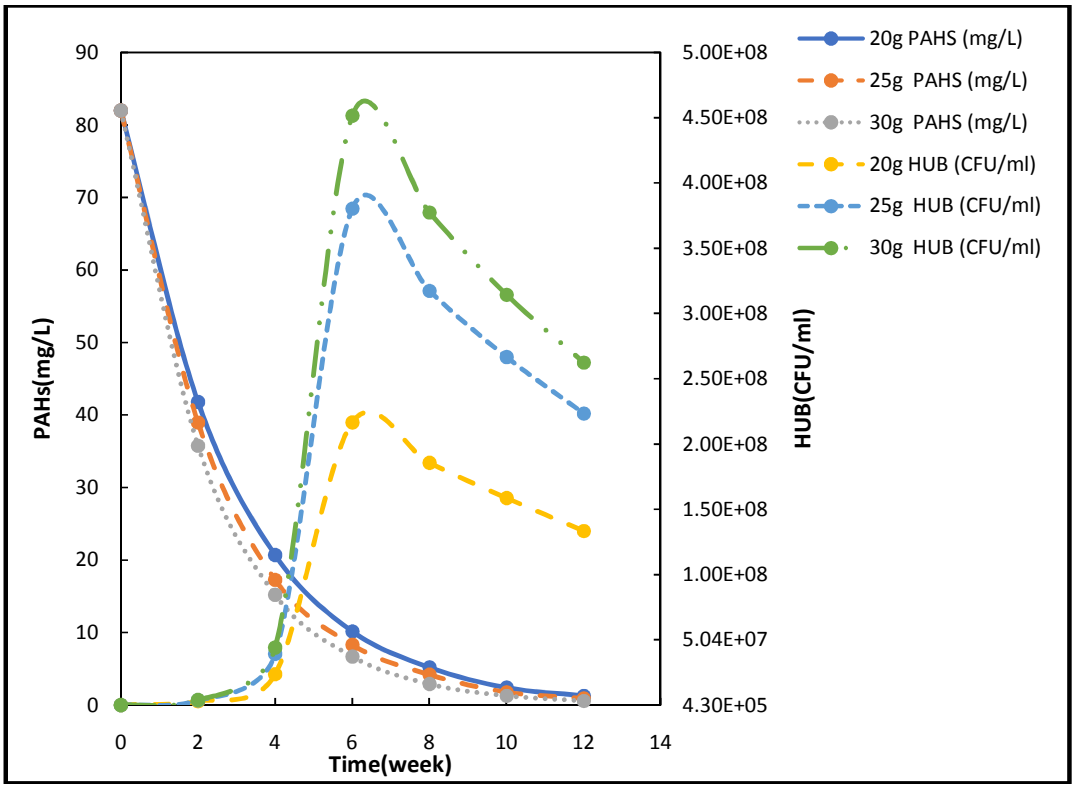

Fig. 4. Distribution of PAHs and HUB for Sample-A

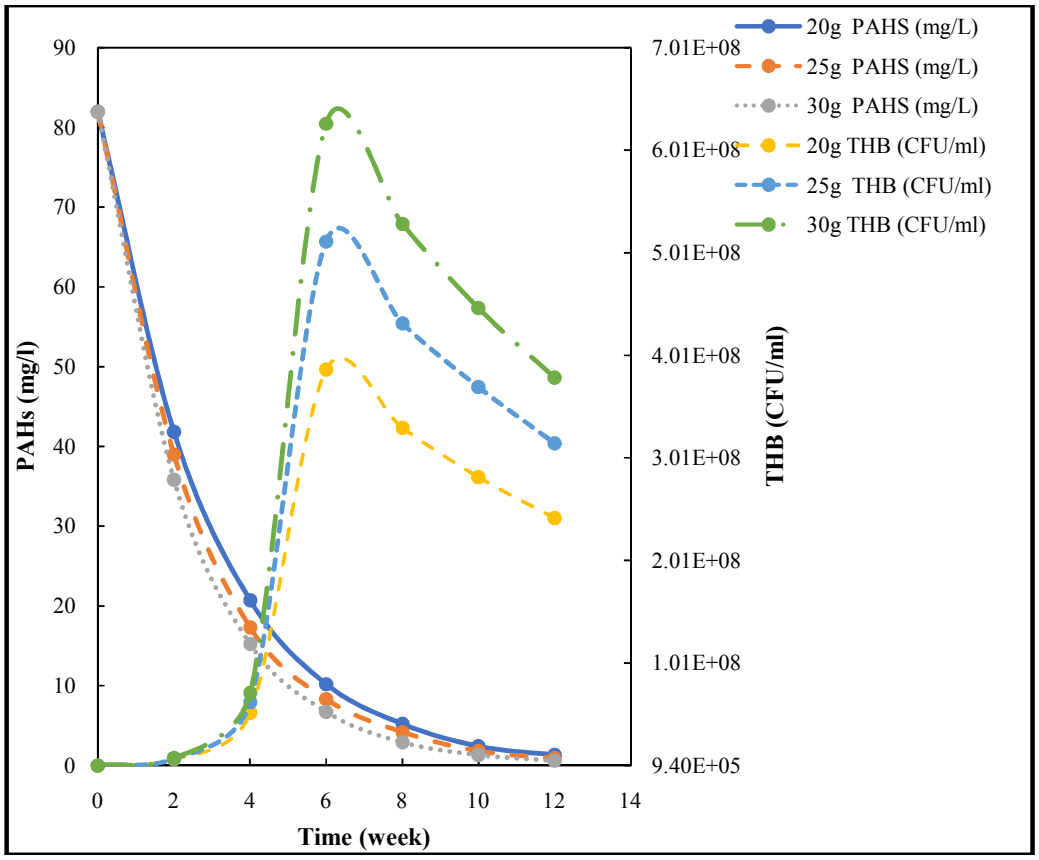

Fig. 5. Distribution of PAHs and THB for Sample-A

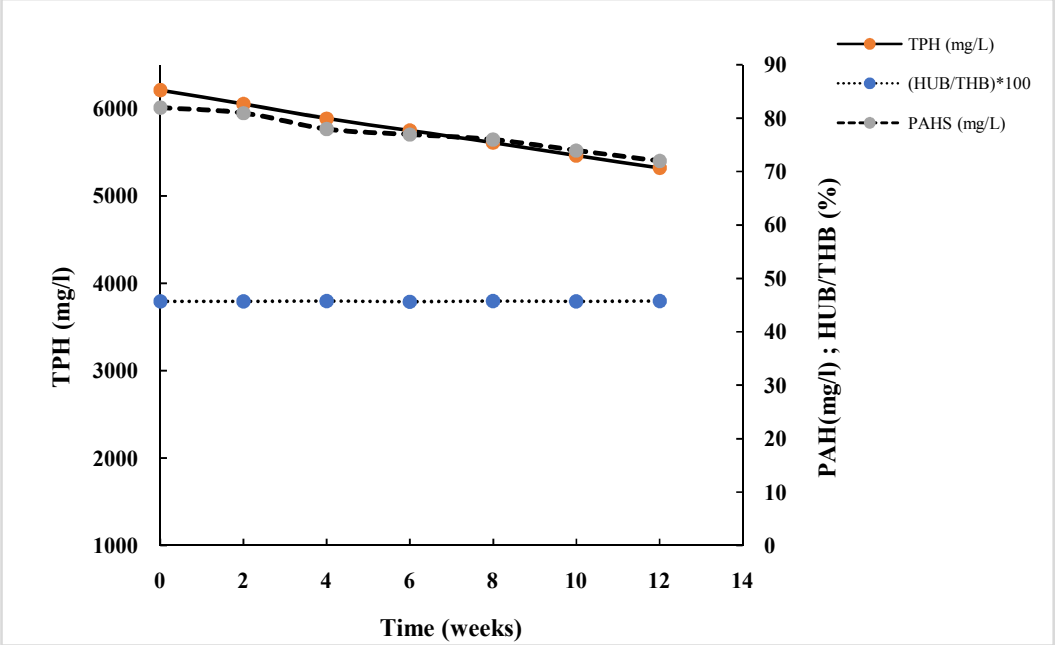

Fig. 6. Distribution of TPHs, PAHs and HUB/THB ratio for Control Sample-A

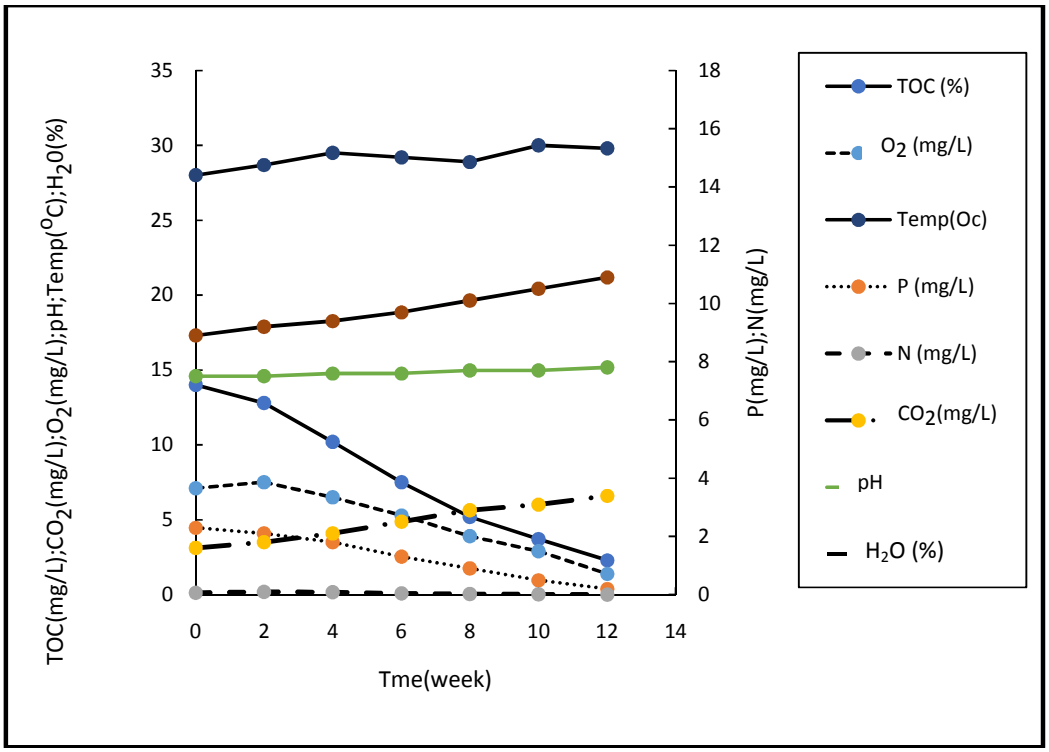

Fig. 7. Distribution of bioremediation indicators for treatment of Sample-A using 30g urea fertilizer

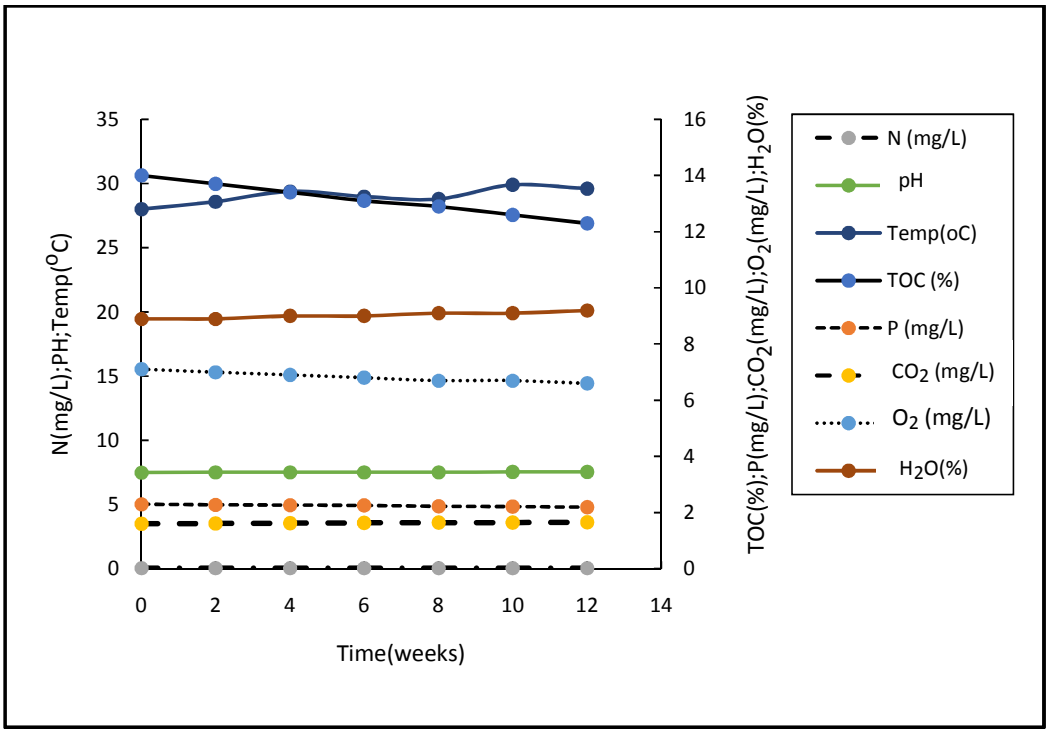

Fig. 8. Distribution of bioremediation indicators for control Sample-A

3.1.5 Percentage removal of TPHs and PAHs in Sample-A in week six and week twelve

The percentage removal of TPHs and PAHs in Sample-A using 30g urea fertilizer, in week six and twelve are shown in Fig. 9. Also shown in Fig. 9 is the corresponding TPHs and PAHs reduction in the control samples for week six and twelve.

3.1.6 Model for the prediction of residual concentration of TPHs and PAHs, and microbial growth using 20 g, 25 g, and 30 g urea fertilizer treatment of spent synthetic based mud

The average of the collected data (MUD A-E) with respect to the experimental set up with 20g urea fertilizer is presented in Table 4.

Table 5 shows a summary of regression power models of PAHs treatment using 20 g urea fertilizer. The exponential model is the best model with respect to R^2, Mean Square Error, MSE and Root Mean Square Error, RMSE values.

A repetition of regression power modeling was carried out for the other parameters, based on R^2, MSE, and RMSE values. The resultant model equations for biodegradation of TPHs and PAHs and microbial growth using 20 g, 25 g, and 30 g urea fertilizer are given in Table 6.

3.2 Discussion

3.2.1 Maximum allowable limits of hydrocarbon pollutants in waste media

The baseline results of the spent drilling mud (Table 2), show that the concentrations of TPHs and PAHs in the five samples exceeded the maximum allowable limits for Nigeria and US EPA (Table 3). The high levels of TPHs and PAHs recorded in the mud are capable of affecting the nutrient levels, aeration and soil microbial diversity, and can even enter the food chain if disposed untreated [23]. This means that the spent mud has to be treated before disposal. The Department of Petroleum Resources (DPR), the regulatory body in Nigeria, demands a reduction of TPHs to less than 10mg/L and 20mg/L for inland and nearshore waters disposal respectively, while the US EPA requires a concentration of less than 5mg/L. For PAHs, DPR requires a concentration of less than 1mg/L, while the US EPA demands less than 0.1 mg/L for effluent disposal. The remediation method employed in this study met the above limits for both TPHs and PAHs.

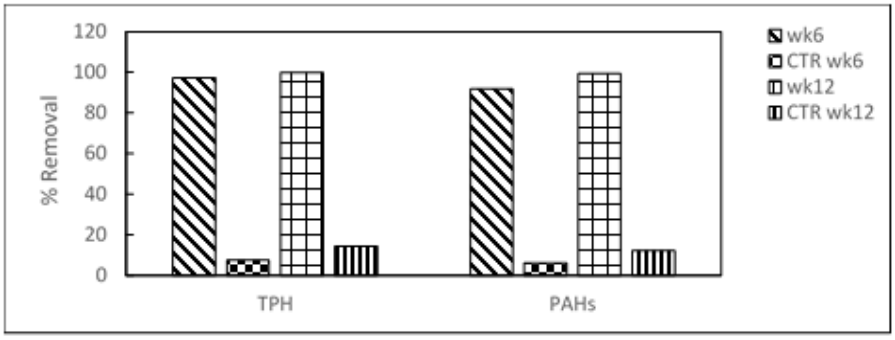

Fig. 9. Percentage removal of TPHs and PAHs in Sample-A for week 6 and 12

Table 4. Average results of petroleum contaminants (TPHs and PAHs) degradation and microbial counts using 20 g of urea fertilizer

Time (week)	THB (CFU/ml)	HUB (CFU/ml)	TPHs (mg/L)	PAHs (mg/L)
0	8.72×10^5	3.50×10^5	8373.6	88.06
2	6.24×10^6	2.94×10^6	3686.4	44.46
4	4.52×10^7	2.41×10^7	1620.4	21.88
6	3.33×10^8	2.12×10^8	714.6	11.48
8	2.86×10^8	1.80×10^8	314.0	5.72
10	2.45×10^8	1.52×10^8	139.0	2.86
12	2.10×10^8	1.29×10^8	62.0	1.48

Note: log_{10} equivalent of HUB and THB were used for the model

Table 5. Summary of regression power models of PAHs using 20, 25 and 30 g urea fertilizer treatment

Model type	Equation	R^2	MSE	RMSE
±Exponential	PAHs = $88.06e^{-0.341t}$	0.9999	0.054	0.233
Polynomial				
2nd order	PAHs = $0.9493t^2$ - 17.805t + 82.596	0.9755	36.50	6.041
3rd order	PAHs = $-0.1001t^3 + 2.7506t^2$ - 25.81t + 87.4	0.9987	2.521	1.588
4th order	PAHs = $0.008t^4$ - $0.2925t^3 + 4.1752t^2$ - 29.053t + 88.059	1	0.06	0.244
5th order	PAHs = $-0.0001t^5 + 0.0118t^4$ - $0.3324t^3 + 4.3436t^2$ - 29.288t + 88.071	1	0.108	0.328
6th order	PAHs = $-0.0002t^6 + 0.0077t^5$ -$0.0937t^4 + 0.3291t^3$ + 2.4632t2 -27.409t + 88.06	1		

± *The best model with respect to R^2, MSE and RMSE values*

Table 6. Model equations for TPHs and PAHs degradation and microbial growth using 20 g 25 g and 30 g urea fertilizer treatment

Parameter	Model type	Model equations	R2	MSE
20 g urea fertilizer application				
TPHs (mg/L)	Exponential	$8373.6e^{-0.409t}$	1.000	1.191
PAHs (mg/L)	Exponential	$88.06e^{-0.341t}$	0.9999	0.054
HUB (CFU/ml)	4th order Polynomial	$0.0009t^4 – 0.0228t^3 + 0.1343t^2$ + 0.2512t + 5.552	0.9944	0.021
THB (CFU/ml)	4th order Polynomial	$0.0009t^4$ - $0213t^3 + 0.1253t^2$ + 0.2333t + 5.9467	0.9943	0.017
25 g urea fertilizer application				
TPHs (mg/L)	Exponential	$8373.6e^{-0.472t}$	1	8.662
PAHs (mg/L)	4th order Polynomial	$0.0091t^4$ - $0.3283t^3 + 4.6054t^2$ - 30.892t + 88.049	1	0.055
HUB (CFU/ml)	4th order Polynomial	$0.0001t^4 – 0.0242t^3 + 0.1413t^2$ + 0.2734t + 5.5515	0.9944	0.022
THB (CFU/ml)	4th order Polynomial	$0.0009t^4 – 0.0224t^3 + 0.1315t^2$ + 0.2475t + 5.947	0.9943	0.019
30 g urea fertilizer application				
TPHs (mg/L)	Exponential	$8373.6e^{-0.571t}$	0.9997	126.751
PAHs (mg/L)	Exponential	$88.06e^{-0.404t}$	0.9998	0.025
HUB (CFU/ml)	4th order Polynomial	$0.001t^4 – 0.0251t^3 + 0.1459t^2 –$ 0.2902t + 5.5507	0.9947	0.022
THB (CFU/ml)	4th order Polynomial	$0.0001t^4 – 0.0234t^3 + 0.1373t^2$ + 0.2611t + 5.9473	0.9943	0.021

The measured pH values were within the neutral range (7.3 to 7.9). pH is an important factor that affects microbial growth [45]. The relationship between pH and microbial growth fits into a quadratic model: Higher growth in neutral media and lower in acidic and alkaline media. Temperature is in the mesophilic range. Both temperature and pH conditions support bioremediation [46]. Solubility of TPHs and PAHs increases with temperature, which improves their bioavailability [47]. Most hydrocarbon degrading microorganisms perform optimally in the mesothermic temperature range (20°C to 35°C) [45]. Though some microorganisms have been known to degrade TPHs and PAHs under acidic and alkaline conditions [48], most micro-organisms metabolize TPHs and PAHs in neutral pH ranges [49].

The measured dissolved oxygen had values that support bioremediation. Though bioremediation of organic contaminants such as TPHs and PAHs can take place under both aerobic and anaerobic conditions, it has been reported that the magnitude of anaerobic degradation is less than that of aerobic [50]. In aerobic degradation,

dissolved oxygen is needed for respiration of the microbes, and is required throughout the subsequent degradation process [51]. The aeration of the samples during biodegradation, provided more oxygen for the process.

The spent drilling mud contained low levels of micro nutrients such as nitrogen, phosphorous, potassium and calcium. The measured organic matter contents (total organic carbon: TOC) of the samples can be classified as average for spent drilling mud. TOC facilitates the moisture retaining capacity of the mud [52]. The measured average nitrogen level of 0.06% is low for effective microbial growth [50]. This is in line with several findings on hydrocarbon contaminated sites [53]. Also, the average phosphorous level of 5.4 mg/L was low and promoted microbial growth [54]. The high carbon-to-phosphorous (C/P) ratio resulting from crude oil addition, in crude oil-contaminated media, and the utilization of inorganic phosphorous by the microorganisms, which attack the hydrocarbons, are responsible for the low level of phosphorous recorded [55].

The ability of microorganisms to degrade hydrocarbons depends on the microbes' population [56]. The spent drilling mud microorganisms' number is usually in the range 10^4 to 10^7 Colony Forming Units (CFUs)/ml. This number should not be less than 10^3 per milligram of spent drilling mud for successful biodegradation [57]. The microbial load recorded in the five samples was good enough for bioremediation [58].

Bioremediation is a rate limiting process, best described by the Monod equation

$$\mu = (\mu_{max} * S) / (K_S + S)$$

where μ_{max} =maximum specific growth rate, K_S=Monod constant, S= substrate concentration.

The specific growth rate (μ) is controlled by the nature of the organism and the limiting nutrients in the medium, such as N and P. This leads to the uptake of the contaminants and subsequent removal i.e, the impacted medium is remediated. Moisture is essential in the biodegradation process for the transportation of foods, nutrients and waste products in and out of the microorganisms [58]. Moisture content of the mud samples ranged from 6.8 to 10.3%. The degradation of TPHs and PAHs support previous studies that by improving the limiting factors to bioremediation of hydrocarbon contaminated spent drill mud, the degradation rate would be improved [59]. The pH remained largely neutral throughout the treatment. The control samples showed low microbial growth. TPHs and PAHs degradation was also low.

Bioremediation indicators, TOC, nitrogen, dissolved oxygen, CO_2, and phosphorous recorded during the remediation period both for the stimulated samples and the control samples showed that the degradation of TPHs and PAHs were a result of bioremediation. For the stimulated samples, TOC, nitrogen, dissolved oxygen, and phosphorous, showed a decline because of their utilization by the microorganisms, while CO_2 and water, which are by-products of bioremediation, increased. However, in the control samples, these parameters showed slight changes, which could be attributed to other natural attenuation processes including volatilization, photo oxidation, etc. [56,60].

3.2.2 Nonlinear Regression Equations

Nonlinear regression equations developed for the petroleum contaminants (TPHs and PAHs) treatment with 20g, 25g, and 30g urea fertilizer show a high goodness of fit, R^2 of 0.999. With these models, it may no longer be necessary to repeat all the experiments in the treatment of spent drilling mud during bioremediation. Once the parameters in the model equations are established, the model can be used to predict the residual concentration of TPHs and PAHs at any time, to a very high accuracy. The microbial growth can also be predicted, accurately. This will give a good idea of when treatment would be completed and save a lot of time and resources in the treatment of spent drilling mud using this method.

4. CONCLUSION

Based on this study, the following conclusions can be drawn:

(1) Spent drilling mud from different fields have different concentrations of TPHs and PAHs.
(2) Urea fertilizer is effective in bioremediation of hydrocarbon impacted spent drilling mud. All of the five amended samples achieved more than 97% removal in 6 weeks. A removal of up to 99.5% was achieved in 12 weeks.

(3) The residual levels of TPHs and PAHs in the five spent drilling mud samples tested complied with Nigerian DPR and US EPA prescribed limits for disposal.

(4) Regression models of exponential and higher order polynomials were developed to predict with high accuracy, the residual concentration of TPHs and PAHs, at any given time, in a hydrocarbon - impacted spent drilling mud using urea fertilizer.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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