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Article

Utilising mycoremediation for treatment of petroleum-contaminated soils and sediments from Ogoniland, Niger Delta, Nigeria: A kinetic insight

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Abstract: The high prospect of mycoremediation and the lingering issues of Total Petroleum Hydrocarbons (TPHs), associated with crude oil pollution in Ogoniland, Niger Delta, Nigeria, necessitate investigations for sustainable remediation options. Therefore, mycoremediation of different contaminated soils (clayey, sandy, and loamy) and sediments collected within the study area was carried out using *Pleurotus* ostreatus and fermented palm wine, both optimized with Tween 80, for a period of 90 days. Results revealed variation in soils and sediments TPHs content, in the range of 120 to 525 g/kg dry soil (about 12% to 50% of TPHs contamination), which far exceeded the soil threshold value of 10 g/kg dry soil or 1%. Also, the TPHs concentrations in the soils and sediments, and the remediation efficiency were directly related to the textural properties, with the highest TPHs concentrations in clayey soils and the highest remediation efficiencies in loamy soils. Both mycoremediation agents, enhanced with Tween 80, achieved TPHs remediation above 98% in all the treatments (except in sandy soil). In all cases, the mycoremediation proceeded via pseudo second-order kinetics, and the removal rates peaked at 45–75 days. The kinetic insights also establish the initial TPHs concentration as one of the key factors influencing the remediation efficiency. This study further revealed that mycoremediation of TPHs works best in loamy soils; therefore, shifting soil properties towards those of loamy during mycoremediation is highly recommended. Consequently, with the abundant mycoremediation resources in the Niger Delta, mycoremediation can provide a sustainable option in the clean-up of the petroleum-contaminated soils and sediments.

Keywords: mycoremediation; palm wine; P. ostreatus; tween 80; Ogoniland; Niger Delta; soils; sediments; petroleum-contamination

1. Introduction

Ogoniland, Niger Delta, Nigeria, has a history of pollution and environmental degradation arising from crude oil spillage [1,2]. Since the early 70s when the first major oil spill was reported in the area, over 7000 spills have been reported, with many of the oil spill sites left untreated for decades [3–5] Although currently, oil production operations in the area have been suspended, there are still many oil facilities within the region. Some of these facilities have seriously deteriorated, while others are often vandalized, resulting in recurring spills [6,7]. There are three local government areas of Gokana, Tai and Eleme in Ogoniland, reportedly associated with these frequent spill sites; and about 1000 km squared area of Ogoniland is contaminated with crude oil, according to reports by UNEP [8], Nnoli et al. [9], and Anoliefo et al. [10]. Such contamination will take up to 25–30 years for clean-up and environmental restoration [11–13]. The crude oil spills in the area have spread into soil, water, rivers and sediments, with very high levels of Total Petroleum Hydrocarbons (TPHs) and associated compounds such as benzene and other toxic pollutants in environmental

matrices such as water reaching more than 1000 times the permissible level of drinking water standards [8,14]. In soils, levels of oil pollution have also been reported to have reached more than five and ten meters deep in many areas [8,10,15]. As of present, most soils, water and sediments of Ogoniland are still highly contaminated, even in places where remediation activities have reportedly been carried out. In addition to the unresolved pollution crises, there are also reports of oil firms allegedly dumping polluted soils in unlined pits [16,17]. These soils, water and sediments require suitable treatments, and locally available and sustainable resources could be the solution.

Many pollutants are associated with crude oil spills [18,19], but the main ones include Total Petroleum Hydrocarbons (TPHs), Polyaromatic Hydrocarbons (PAHs), and Trace metals [20–22]. TPHs consist of complex mixtures of hydrocarbon compounds of different fractions. These include linear straight and branched chain C6 through C35 hydrocarbons, as well as aromatics such as benzene, toluene, xylenes, naphthalene, and fluorene [23]. The pollutants associated with TPHs from crude oil spills have profound toxicity towards human health and other environmental variables [24]. These effects range from fatigue to headache, nausea, drowsiness, and long-term effects such as permanent damage to the central nervous system [25,26]. Compounds such as benzene, toluene, and xylene can affect the human central nervous system and can lead to death at high enough concentrations [25]. Other effects of TPHs include effects on the nervous system (headaches, dizziness, and peripheral neuropathy), blood (leukemia and other hematologic neoplasms), damage to the liver and kidney, irritation to the skin and eyes, gastritis, changes in semen, and elevated levels of serum creatinine [27]. Compounds such as benzene, benzo [a] pyrene, and gasoline have also been reported as carcinogenic or probably carcinogenic [28].

The above reflects the hazards and the associated health risk that the people of the Niger Delta, Nigeria, and Ogoniland in particular, have been exposed to in the many decades of the crude oil pollution, in addition to the aesthetic nuisance of the polluted environment.

The cost of remediation of Ogoniland is estimated at a billion dollars [8]. The huge amount involved and limited finances on the part of the government, along with other factors and logistics, have constantly delayed the commencement of the clean-up process. There are also issues of limited technology and resource availability for conventional clean-up approaches. However, the Niger Delta region of Nigeria, a typical tropical rainforest region, has vast nature-based resources that can help in the clean-up of the petroleum contamination. Such include bioremediation agents such as plants, fungi, compost, animal manures, and the rich microbiomes associated with tropical rain forests [29–31]. There is therefore a need to investigate and develop methods that are locally and readily available, and cost-effective, with fewer technological inputs for the clean-up of petroleum-contaminated soils and sediments in the area, to ensure environmental sustainability.

Many studies have reported the prospects of nature-based solutions in the treatment of petroleum-contaminted soils [32,33]. Studies also exist using artificially contaminated soils from the Niger Delta for remediation experiments [34–36]. However, studies using mycoremediation agents on typical crude oil-contaminated soils and sediments, taken from the sites of pollution in Ogoniland, Niger Delta, Nigeria, are very scarce. The lingering episodes of the oil spills in Ogoniland and the

associated hydrocarbon pollution and toxicity, call for the utilization of mycoremediation for the clean-up of crude oil pollution in the area, due to the abundant mycoremediation resources in the area.

The mycoremediation potential of *P*. ostreatus and palm wine, locally available in the Niger Delta, Nigeria, on petroleum-contaminated soils has previously been reported by (Dickson et al., [35]. These techniques have also been optimized for increased efficiency with the addition of Tween 80 [37]. The scale of environmental degradation by crude oil, the attendant cost of remediation, the associated human health risk, and the absence of readily available sustainable remediation techniques in the study area necessitate this investigation.

This study is aimed at assessing the prospect of mycoremediation in the treatment of the different soil types and sediments contaminated by crude oil in Ogoniland, Niger Delta, Nigeria. This study will also provide a kinetic insight to explore intrinsic information during the remediation process that can help for further optimization and utilization of mycoremediation in the clean-up of the polluted soils and sediments. The outcome will provide better insight, as well as readily available, cost-effective, and sustainable approach for the remediation of contaminated soils and sediments in Ogoniland, Niger Delta, Nigeria, and similarly affected areas.

2. Methodology

2.1. Sample collection

Soils of different textural types, namely, clayey, sandy, and loamy, contaminated by crude oil were sampled at a depth of 0–0.15 m at three different locations associated with crude oil pollution in Ogoniland, Nigeria, using the methods of BSI ISO/DIS 18400-203 [38]. The sampling locations were Ogale (0294996 N, 0532999 E), Gio (0304418 N, 0519421 E), and Bodo (0305325 N, 0510090 E). Petroleum-contaminated river sediments were also collected from Gio (0304429 N, 0519401 E) and Bodo (0307283 N, 0509572 E). The textural properties of the soils and sediments were initially assessed onsite by the method of hand feeling and ribbon [39,40]. A laser density particle size analyzer LS 13 was later used to evaluate the texture of the soil and sediments in the laboratory of Nottingham Trent University (NTU) School of Animal Rural and Environmental Science, Brackenhurst, UK, according to the methods reported by Yang et al. [41] and Yang et al. [42]. The soil and sediment samples that were collected from Ogoniland were packaged, transported to the glasshouse of NTU, Brackenhurst, and stored under airtight conditions by methods of BSI ISO/DIS, 18400-203, [43], prior to glasshouse activities.

2.2. Sample treatment and glasshouse set up

The study utilized 1.5-L plant pots, which were placed in a grow bag standard plant trays of size 100 × 40 × 5 cm. This was done to avoid seepages of the crude oil from the soil pots into the environment. The contaminated soils and sediments were amended with cow manure at a ratio of 1:6 [35]. The soils and sediments were respectively treated in a glasshouse with the *P*. ostreatus and fermented palm wine as reported by [35]. A previous study by Dickson et al. [37] had revealed that

mycoremediation treatments can be optimized by the addition of Tween 80; therefore, all the treatments in the present study were carried out with the addition of Tween 80.

Glasshouse pots for the treatments with the white-rot mushrooms, P. ostreatus, were prepared as follows: 10 g of the dried and grounded stumps of the palm tree were weighed out and added to amended soils. This was followed by the addition of 5 g of mushroom spawn, by uniformly spreading such into the soils. Next was to place a layer of 10 g of the substrates on top of the soil. Another 5 g of the mushroom spawns were correspondingly added to this layered palm substrate [35]. This approach allows for a dual application of the mushrooms to the contaminated soil by mixing the substrates with the soil and also by layering it on top of the soil, which was a modification of the usual practices of only applying mushroom spawns to layered substrate [44].

For the treatment sets with the fermented palm wine, palm wine was left overnight (12–18 h) in the open to ferment according to the methods of Santiago-Urbina and Ruíz-Terán [45]. Then 200 mL of the fermented palm wine was measured out by volume and added to each of the glasshouse pots containing the amended petroleum-contaminated soils and sediments. This was followed by spreading 25 mL of Tween 80 of a 5% Tween 80 solution as reported by Dickson et al. [37]. The application of the palm wine to the pots treated with the fermented palm wine was repeated each week during the treatment period.

2.3. Determination of TPHs concentrations in the samples, and remediation efficiency

The mycoremediation treatments were carried out under climatic conditions identical to those of Ogoniland, Nigeria, in the glasshouse facility of NTU Brackenhurst for a period of 90 days. During this time, sub-samples of the soils and sediments were respectively collected at the onset of the study (Time = 0 days) and at the intervals 30, 45, 60, 75, and 90 days. The soil and sediment samples taken were then prepared, and an analysis for TPHs concentrations and remediation efficiency was assessed according to the methods reported in Dickson et al. [35].

The soil and sediment samples collected at each interval were first air-dried, ground and homogenized, sieved through a 2 mm mesh, and extraneous materials removed prior to TPHs extraction and analysis using the methods of BS ISO 11464 [46]. The extraction of TPHs in samples was then carried out using a microwave-assisted extraction with a Milestone MA182-001 ETHOSUP Microwave system, with a 1:1 acetone-heptane according to the methods of USEPA 3546 [47] and Punt et al. [48]. The sample extracts and the TPHs standards were all analyzed in a GC-MS (model Agilent Technologies 7000 GC/MS Triple Quad with 7890 GC and 7693 Autosampler (USEPA 8270E). The methods of BS EN ISO 16703 [49] were used for the quantification of the TPHs in the soils and sediments, with the commercial TPHs gasoline-diesel range standard used as the analytical standard. Initial calibration of the instruments, followed by evaluation of the concentration of TPHs, alongside calibration verification, were all carried out.

The remediation efficiency of the treatments was evaluated as a ratio of the difference between the initial TPHs concentrations (e.g., at the interval $T = 0$) and that

of any particular interval (e.g., at T = 30) to the initial TPHs concentration (T = 0), expressed as a percentage.

$$\%\ \text{TPHs remediation at 30 days (T} = 30) = \frac{((\text{TPHs concentration at T} = 0 - \text{TPHs concentration at T} = 30))}{\text{TPHs concentration at T} = 0} \times 100\%$$

2.4. Kinetic modelling of the TPHs results data

For kinetic modeling of the TPHs results data, the concentrations of TPHs at the commencement of the experiment (T = 0 days) and at the different sampling times during remediation (Time (t) = 30, 45, 60, 75, and 90 days) were inserted into kinetic models of zero order, pseudo first order (PFO), and pseudo second order (PSO) [50,51].

2.4.1. Zero order (PFO) kinetic modelling

For zero-order kinetic modeling, Equation (1) was used, with a plot of $[A]_t$ against t. A regression analysis was also evaluated for all the treatments.

- A zero-order reaction is one whose rate is independent of concentration.
- Because the rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of −k.
- The value of k is negative because the concentration of the reactant decreases with time.
- The integrated rate law for a zero-order reaction also produces a straight line and has the general form:

$$[A]_t = [A]_0 - kt \quad (1)$$

- where $[A]_0$ is the initial concentration of reactant A.
- $[A]_t$ is the concentration of the reactant at any time (t).
- k is the removal rate constant.
- The equation is in the form of the algebraic equation for a straight line, $y = mx + b$,
- with $y = [A]_t$,
- $mx = -kt$,
- and $b = [A]_0$.
- A plot of A_t versus t for a zero-order reaction should give a straight line with a slope of $-k$.

The half-life of zero-order kinetics: If an increase in reactant concentrations increases the half-life ($t_{1/2}$) of the reactant, then the reaction has zero-order kinetics.

- For zero-order half-life,

$$t_{1/2} = [A]_0/2k \quad (2)$$

2.4.2. Pseudo first order (PFO) kinetic modelling

For pseudo first-order (PFO) kinetic modeling, Equation (3) was used, with a plot of $\ln[A]_0$ vs. t. A regression analysis was also evaluated for all the treatments.

- In a first-order reaction, the reaction rate is directly proportional to the concentration of one of the reactants.

- If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth.
- where $[A]_0$ is the initial concentration of reactant A at $t = 0$;
- k is the rate constant;
- $[A]_t$ = concentration of the reactant A at any time = t.
- The integrated rate law for PSO is:

$$ln[A]_t = l_n[A]_0 - Kt \quad (3)$$

- Because the equation has the form of the algebraic equation for a straight line, $y = mx + b$,
- with $y = \ln[A]_t$,
- and $b = \ln[A]_0$,
- a plot of $\ln[A]_t$ versus t for a first-order reaction should give a straight line with a slope of −k and an intercept of $\ln[A]_0$.

The half-life of first-order kinetics: If an increase in reactant has no effect on half-life ($t_{1/2}$), it progresses by first-order kinetics.

- For the first order,

$$t_{1/2} = 0.693/k \quad (4)$$

2.4.3. Second order (PFO) kinetic modelling

For pseudo second-order (PSO) kinetic modeling, Equation (5) was used, and a plot of $1/[A]_t$ against t. A regression analysis was also evaluated for all the treatments.

- The simplest kind of second-order reaction is one whose rate is proportional to the square of the concentration of one reactant.
- Consequently, doubling the concentration of A quadruples the reaction rate.
- For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

$$1/[A]_t = 1/[A]_0 + Kt \quad (5)$$

- Because the equation has the form of an algebraic equation for a straight line, $y = mx + b$,
- with $y = 1/[A]$,
- and $b = 1/[A]_0$,
- a plot of $1/[A]_t$ vs. t gives the slope k.

The half-life of second-order kinetics: If an increase in reactant decreases the half-life ($t_{1/2}$), the reaction has second-order kinetics.

- For second order,

$$t_{1/2} = 1/k[A]_0 \quad (6)$$

2.4.4. Criteria for model fit for the TPHs removal kinetics

The criteria for model fit were determined using statistical analysis of the *R*-square values (from the kinetic modeling and regression analysis), Pearson correlation coefficient, standard error and the relative mean squared error (RMSE), in addition to a paired two-sample *t*-test for means [52,53]. These statistical tests were carried out

on the pair of fitting data for each model, e.g., [A_t] vs. T for Zero order, ln[A]$_0$ vs. T for PFO, and 1/[A]$_t$ vs. T for PSO, according to Dickson et al. [37]. The uniqueness of each data point to fit the models, as indicated by the shape of the linear plot, and inferences from the statistical analysis were used to determine the associated TPHs removal kinetics of the different treatments.

2.5. Data quality, and scope of the study

For each of the treatments, the laboratory and instrumental analysis were carried out in triplicates. For the collection of soil and sediment samples during the treatments, composite soil and sediment samples that were properly homogenized were used for the analysis. Samples were taken on the exact day of remediation evaluation and prepared and analyzed within 24 h to prevent loss of TPHs due to continuous biodegradation.

Generally, for kinetic modeling, several studies have recommended a minimum of at least 3 measured experimental data points [54–56]. All the modeling in this study made use of 6 measured experimental data, which were taken at T = 0, 30, 45, 60, 75, and 90 days. Statistical analyses carried out on the data include ANOVA, paired t-tests, regression, correlation and error analysis. The statistical analyses were carried out using MS Excel 2026.

Further statistical analyses (ANOVA) were also carried out to evaluate possible differences in TPHs concentrations, remediation efficiency, and TPHs removal rates in the treatments, among the various soil textural classes (clayey, sandy, and loamy soils), and the sediments. Also, a paired T-test was used to assess possible differences between the two mycoremediation agents (P. ostreatus and fermented palm wine) in each of the soils. Thus, paired T-TESTs were carried out for T1 against T2, T3 against T4, T5 against T6, T7 against T8, and T9 against T10, with respect to TPHs concentrations, remediation efficiency, and TPHs removal rates.

3. Results

3.1. Soil texture and TPHs concentrations in the samples

Textural classification of the soil samples identifies each of the soils as clayey, sandy, and loamy, and the sediments as clayey sediments (**Table 1**).

Table 1. Textural classification of the soil and sediments samples.

SN	Coordinates		Sample locations	Soil particle size composition (%)			Textural class
	N	E		Clay	Sand	Silt	
1	0294996	0532999	Ogale, Ogoniland, Niger Delta, Nigeria	20.0	40.0	40.0	Loamy soil
2	0304418	0519421	Gio, Ogoniland, Niger Delta, Nigeria	3.0	90.0	7.0	Sandy soil
3	0305325	0510090	Bodo, Ogoniland, Niger Delta, Nigeria	70.0	10.0	20.0	Clayey soil
4	0307283	0509572	Bodo, Ogoniland, Niger Delta, Nigeria	65.0	10.0	15.0	Clayey sediment
5	0304429	0519401	Gio, Ogoniland, Niger Delta, Nigeria	65.0	10.0	15.0	Clayey sediment

High levels of TPHs concentrations were observed in the soil and sediment samples from Ogoniland, Nigeria (**Tables 2** and **3**). The highest TPHs contamination of 540 g/kg dry weight of soil was found in clay soil (**Tables 2** and **3**). This was followed by loamy soil (210 g/kg dry weight), then sandy soils (120 g/kg dry weight of soil). These amount to about 12% to 50% TPHs concentration in the soils and sediments of the study area. The sediments had TPHs concentrations range of 240–370 g/kg dry weight of sediments, which was about 24%–37% TPHs contamination. The TPHs concentrations varied from site to site and generally reduced during the treatment regime, both in the control and treated soils and sediments (**Tables 2** and **3**).

With respect to the soil types, the concentrations of TPHs were generally higher in the clay soil than in the loamy and sandy soils, with sandy soil having the lowest concentrations of the TPHs (**Tables 1–3**). The sediments both had TPH concentration ranges that were below those of the clayey soil but higher than those of the loamy and sandy soils. Sediments from Bodo had higher levels of TPHs compared to those of Gio. Both *P. ostreatus* and fermented palm wine exhibited remarkable reductions in the TPH concentrations during the treatments, compared to the controls (**Tables 2** and **3**).

The statistical analysis revealed a significant difference in the TPHs concentrations among the soil samples (clayey, sandy, loamy and the sediments) during the mycoremediation treatments (p-values for ANOVA > 0.05). There was also a significant difference in the % remediation efficiency of the mycoremediation treatments among the different soils and sediments (p-values for ANOVA > 0.05, in the respective comparison, **Table S1** in supplementary material). Similar observations were obtained for the TPHs removal rates during the mycoremediation treatments (**Table S1** in supplementary material). However, a comparison of the remediation efficiency of the two mycoremediation agents (P. ostreatus and fermented palm wine) revealed no significant differences in their % remediation efficiency and TPHs removal rates (**Table S1** in supplementary material). This is observable in the paired T-TEST for the treatment pairs, T1 against T2, T3 against T4, T5 against T6, T7 against T8, and T9 against T10, with respect to TPHs concentrations, remediation efficiency, and TPHs removal rates (ANOVA p > 0.05, **Table S1** in supplementary material).

Table 2. TPHs concentrations in the treated soils and sediments of the study area.

TPHs concentrations in the soil samples during the mycoremediation treatments (g of TPHs per kg of soil)										
	P. ostreatus on clayey soil from Bodo	**Fermented Palm Wine on clayey soil from Bodo**	**Fermented Palm Wine on clayey soil from Bodo**	**Fermented Palm Wine on sandy soil from Gio**	**P. ostreatus on loamy soil from Ogale**	**Fermented Palm Wine on loamy soil from Ogale**	**P. ostreatus on Sediments from Bodo**	**Fermented Palm Wine on Sediments from Bodo**	**P. ostreatus on Sediments from Gio**	**Fermented Palm Wine on Sediments from Bodo**
Time (days)	**T1**	**T2**	**T3**	**T4**	**T5**	**T6**	**T7**	**T8**	**T9**	**T10**
0	525.01	531.24	120.61	124.26	212.85	215.52	239.61	241.56	362.71	369.12
30	495.01	515.12	116.95	119.95	168.47	191.47	222.34	223.81	352.11	357.34
45	485.25	495.36	112.46	116.46	58.47	87.87	193.43	211.11	295.63	298.63
60	4.12	3.13	57.00	17.00	0.15	0.17	5.89	1.11	6.51	1.23
75	2.91	1.93	29.13	9.13	0.06	0.05	4.11	0.11	2.99	0.12
90	2.44	1.011	23.2	5.05	Below quantification limit (BQL)	Below quantification limit (BQL)	3.03	Below quantification limit (BQL)	2.45	Below quantification limit (BQL)

Table 3. Data for control soils and sediments during the treatments (TPHs concentrations (g of TPHs per kg dry soil/sediment), removal efficiency, and removal rates).

	Clayey soil from Bodo	**Sandy soil from Gio**	**loamy soil from Ogale**	**Sediments from Bodo**	**Sediments from Gio**
Time (days)	**T1'**	**T2'**	**T3'**	**T4'**	**T5'**
0	535.19	122.21	229.01	239.01	360.58
30	503.09	112.20	205.20	215.20	328.19
45	474.89	111.93	201.93	211.93	322.35
60	470.89	111.47	198.47	209.47	319.54
75	469.52	110.33	195.33	193.33	287.80
90	459.19	98.73	178.73	191.73	286.94
% Remediation efficiency of the control soils and sediments					
Time (days)	**T1'**	**T2'**	**T3'**	**T4'**	**T5'**
0–30	6.00	8.19	10.40	9.96	8.98
30–45	5.61	0.24	1.60	1.52	1.78
0–45	11.27	8.42	11.83	11.33	10.60
45–60	0.84	0.41	1.71	1.16	0.87
0–60	12.01	8.79	13.34	12.36	11.38
60–75	0.29	1.02	1.58	7.70	9.93
0–75	12.27	9.72	14.71	19.11	20.18
75–90	2.20	10.51	8.50	0.83	0.30
0–90	14.20	19.21	21.96	19.78	20.42
TPHs removal rates in the control soils and sediments (g of TPHs/kg of soil per day)					
Time (days)	**T1'**	**T2'**	**T3'**	**T4'**	**T5'**
0–30	1.07	0.33	0.79	0.79	1.08
30–45	1.88	0.02	0.22	0.22	0.39
0–45	1.34	0.23	0.60	0.60	0.85
45–60	0.27	0.03	0.23	0.16	0.19
0–60	1.07	0.18	0.51	0.49	0.68
60–75	0.09	0.08	0.21	1.08	2.12
0–75	0.88	0.16	0.45	0.61	0.97
75–90	0.69	0.77	1.11	0.11	0.06
0–90	0.84	0.26	0.56	0.53	0.82

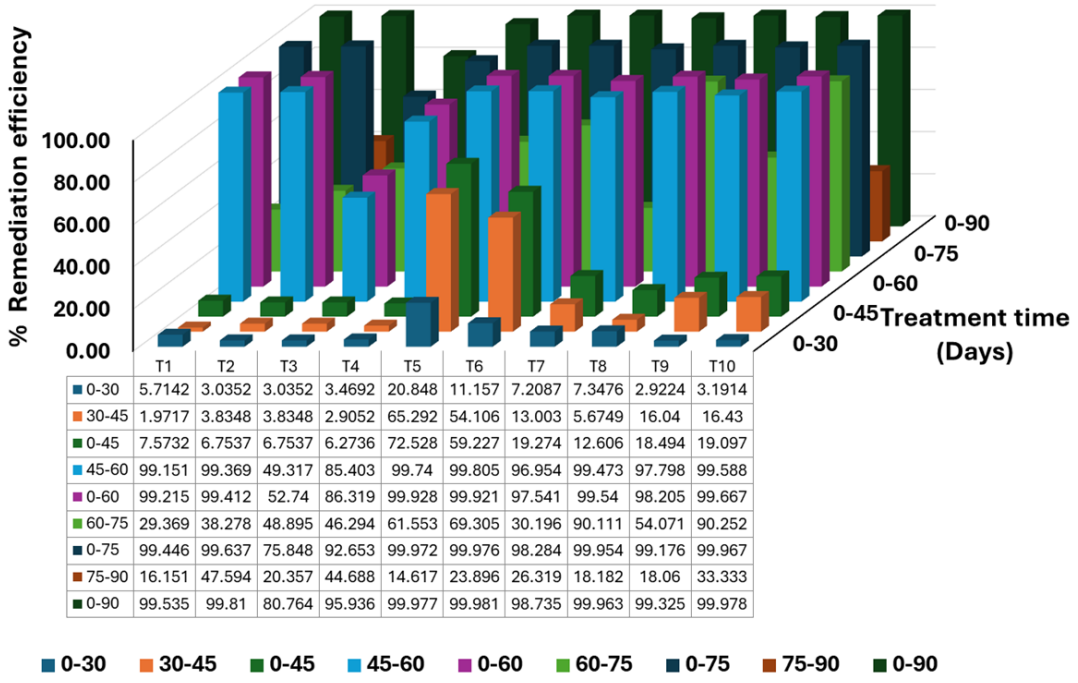
3.2. TPHs remediation efficiency, and removal rate during the mycoremediation treatments

The TPHs remediation efficiency of both agents tends to be low at the onset of the remediation treatments at 0–30 days (**Figure 1**), generally below 10% (except for the treatment with P. ostreatus on loamy soil, which had 21%). A similar scenario is observed again during the interval 30–45 and 0–45 days, with remediation efficiency still less than 10% in most cases, and at most 16%. The exceptions during these intervals were for the treatments on the loamy soil, which had 65% and 73% for P. ostreatus at the intervals 30–45 days and 0–45 days, respectively, and that of

Fermented Palmwine on the loamy, which had 54% and 59% TPHs reduction at 30–45 days and 0–45 days, respectively.

All the treatments (except the sandy soils) had TPHs remediation efficiency greater than 98% from the interval of 45–60 days and 0–60 days (**Figure 1**, **Table S1** in supplementary material). During these intervals, the TPHs remediation efficiency of the agents on the sandy soils was 49% and 53%; and 85% and 86%, respectively, for P. ostreatus and fermented palm wine. While most of the treatments (except the sandy soils) still maintained an overall remediation efficiency of greater than 98% after 60 days of the treatment, the sub-intervals 60–75 and 75–90 days had lower TPH removal efficiencies (**Figure 1**, **Table S1** in supplementary material). The treatments involving the sandy soils increased periodically with the treatment time, to the maximums of 81% for P. ostreatus and 96% for the fermented palm wine, at 90 days.

The TPHs removal rates varied among the treatments during the mycoremediation period, with all the treatments having the highest TPHs removal rate within the interval of 45 to 60 days (**Figure 2**). The lowest TPHs removal rates were observed for the periods 0–30 days, 60–75 days, and 75–90 days. The highest TPHs removal rate of about 32–33 g of TPHs per kg dry soil per day was observed for the treatment involving the clayey soil during the interval of 45 to 60 days (**Figure 2**, **Table S1** in supplementary material). Also, the treatments involving the sediments also had relatively high TPHs removal rates (13–20 g of TPHs per kg dry sediments per day) during the same interval. The TPHs removal rates at the intervals 45–60 and 0–60 days were higher than the other intervals for each treatment and correlated directly with the TPHs removal efficiency.



	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
0-30	5.7142	3.0352	3.0352	3.4692	20.848	11.157	7.2087	7.3476	2.9224	3.1914
30-45	1.9717	3.8348	3.8348	2.9052	65.292	54.106	13.003	5.6749	16.04	16.43
0-45	7.5732	6.7537	6.7537	6.2736	72.528	59.227	19.274	12.606	18.494	19.097
45-60	99.151	99.369	49.317	85.403	99.74	99.805	96.954	99.473	97.798	99.588
0-60	99.215	99.412	52.74	86.319	99.928	99.921	97.541	99.54	98.205	99.667
60-75	29.369	38.278	48.895	46.294	61.553	69.305	30.196	90.111	54.071	90.252
0-75	99.446	99.637	75.848	92.653	99.972	99.976	98.284	99.954	99.176	99.967
75-90	16.151	47.594	20.357	44.688	14.617	23.896	26.319	18.182	18.06	33.333
0-90	99.535	99.81	80.764	95.936	99.977	99.981	98.735	99.963	99.325	99.978

Figure 1. Remediation efficiency of the mycoremediation treatments.

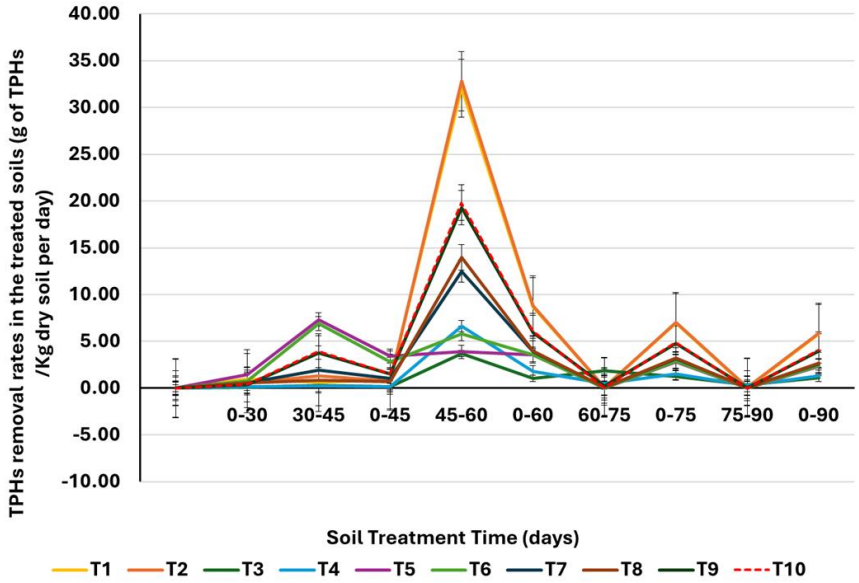


Figure 2. TPH's removal rates during the mycoremediation (values are in g of TPHs per kg dry soil/sediments per day).

3.3. TPHs removal kinetics of the mycoremdiation process

The TPHs removal kinetics of the mycoremediation treatments all progressed by pseudo second-order kinetics (**Table 4**, **Figure S1** in supplementary material). For T1 (P. ostreatus on clayey soil from Bodo), the *R*-square values for pseudo second-order (PSO) were the highest, while the *R*-square values for both zero order and PSO were below the 0.8 threshold. Although the standard error for Zero was the lowest, the *R*-square values take preeminence here. Again, the Pearson correlation (PC) and the Root Mean Square Error (RMSE values favor PSO. Thus, the removal kinetics will predominantly follow PSO (**Table 4**, **Figure S1**, supplementary material). The same trend is observed for T2 (fermented palm wine on clayey soil from Bodo) and T7 (P. ostreatus on sediments from Bodo).

For T3 (P. ostreatus on clayey soil from Bodo), the *R*-square values for PSO are the highest; however, here, the *R*-square values for both zero order and pseudo first order (PFO) are above the 0.8 threshold (**Table 4**, **Figure S1** in supplementary material). Therefore, we see some aspects of zero-order and pseudo-first-order kinetics here too. Consequently, the kinetics here are likely a mix of kinetics but will predominantly follow PSO. A similar trend is observed for T5 (P. ostreatus on loamy soil from Ogale) and T6 (fermented palm wine on loamy soil from Ogale).

In the case of T4 (fermented palm wine on sandy soil from Gio), the *R*-square values for PSO are the highest; however, the *R*-square values for Pseudo first order (PFO) are also above the 0.8 threshold (**Table 4**, **Figure S1** in supplementary material). Therefore, we see some aspects of pseudo-first-order kinetics here too. Hence, the kinetics here is likely a mix of PFO and PSO kinetics but will predominantly follow PSO. A similar trend is observed for T8 (fermented palm wine on sediments from Bodo), T9 (P. ostreatus on sediments from Gio), and T10 (fermented palm wine on sediments from Bodo).

Table 4. Summary of the kinetic modelling of the mycoremediation treatments.

Soil Treatment	Kinetic models	*R*-Square Values from plotted graphs	*R*-Square Values from Regression analysis			Standard Error (SE)	Relative mean squared error (RMSE)**	Pearson Correlation (PC)	Comments * *R*-square values greater than 0.8 are considered a good fit [57,58] ** The SE values indicate a measure of precision, while the RMSE values are a measure of the accuracy of each model [59]
		R-Square Values form plotted graphs	Multiple R	R Square	Adjusted R Square				
T1 (P. ostreatus on clayey soil from Bodo)	Zero Order	0.7501	0.8661	0.7501	0.6876	0.4942	152.8075	−0.8661	The *R*-square values for Pseudo second order (**PSO)** are the highest, and the *R*-square values for both Zero order and PSO are below the 0.8 threshold*. Again, the PC and RMSE values favor PSO. Thus, the removal kinetics will predominantly follow **PSO**.
	PFO	0.7740	0.8798	0.7740	0.6986	13.0196	0.9268	−0.8798	
	PSO	**0.9244**	**0.9615**	**0.9244**	**0.8992**	**7.5296**	**0.2340**	**0.9615**	
T2 (Fermented palm wine on clayey soil from Bodo)	Zero Order	0.7443	0.8627	0.7443	0.6803	158.6473	0.4768	−0.8627	The *R*-square values for **PSO** is the highest, and the *R*-square values for both Zero order and PSO are below the 0.8 threshold*. Again, the PC and RMSE values favour PSO. Thus, the removal kinetic will predominantly follow **PSO**.
	PFO	0.7868	0.8870	0.7868	0.7157	12.6451	0.2843	−0.8870	
	PSO	**0.9141**	**0.9561**	**0.9141**	**0.8855**	**8.0252**	**0.2947**	**0.9561**	
T3 (P. ostreatus on clayey soil from Bodo)	Zero Order	0.8283	0.9101	0.8283	0.7853	15.0128	0.1984	−0.9101	The *R*-square values for **PSO** is the highest, however, here, the *R*-square values for both Zero order and Pseudo first order (PFO) are above the 0.8 threshold*. Therefore, we see some aspects of Zero order and Pseudo first order kinetics here too. Therefore, the kinetics here is likely a mix kinetics, but will predominantly follow **PSO**.
	PFO	0.8153	0.9029	0.8153	0.7537	11.7699	0.0552	−0.9029	
	PSO	0.9227	0.9606	0.9227	0.8969	7.6161	0.1917	0.9606	
T4 (Fermented plam wine on sandy soil from Gio)	Zero Order	0.7730	0.8792	0.7730	0.7163	17.2596	0.5022	−0.8792	The *R*-square values for **PSO** is the highest, however, the *R*-square values for Pseudo first order (PFO) is also above the 0.8 threshold*. Therefore, we see some aspects of Pseudo first order kinetics here too. Therefore, the kinetics here is likely a mix of PFO and PSO kinetics, but will predominantly follow **PSO**.
	PFO	0.8095	0.8997	0.8095	0.7460	11.9531	0.1268	−0.8997	
	PSO	**0.9072**	**0.9525**	**0.9072**	**0.8763**	**8.3415**	**0.2834**	**0.9525**	

Table 4. (*Continued*).

Soil Treatment	Kinetic models	*R*-Square Values from plotted graphs	*R*-Square Values from Regression analysis			Standard Error (SE)	Relative mean squared error (RMSE)**	Pearson Correlation (PC)	Comments * *R*-square values greater than 0.8 are considered a good fit [57,58] ** The SE values indicate a measure of precision, while the RMSE values are a measure of the accuracy of each model [59]
		R-Square Values form plotted graphs	Multiple R	R Square	Adjusted R Square				
T5 (P. ostreatus on loamy soil from Ogale)	Zero Order	0.8687	0.9321	0.8687	0.8359	13.1264	0.4924	−0.9321	The *R*-square values for **PSO** is the highest, however, here, the *R*-square values for both Zero order and Pseudo first order (PFO) are above the 0.8 threshold*. Therefore, we see some aspects of Zero order and Pseudo first order kinetics here too. Therefore, the kinetics here is likely a mix kinetics, but will predominantly follow **PSO**.
	PFO	0.8584	0.9265	0.8584	0.8112	10.3050	0.6833	−0.9265	
	PSO	**0.9209**	**0.9596**	**0.9209**	**0.8946**	**7.7012**	**3.2371**	**0.9596**	
T6 (Fermented plam wine on loamy soil from Ogale)	Zero Order	0.8622	0.9285	0.8622	0.8277	13.4487	0.4384	−0.9285	The *R*-square values for **PSO** is the highest, however, here, the *R*-square values for both Zero order and Pseudo first order (PFO) are above the 0.8 threshold*. Therefore, we see some aspects of Zero order and Pseudo first order kinetics here too. Therefore, the kinetics here is likely a mix kinetics, but will predominantly follow **PSO**.
	PFO	0.8390	0.9160	0.8390	0.7854	10.9879	0.7050	−0.9160	
	PSO	**0.9097**	**0.9538**	**0.9097**	**0.8796**	**8.2308**	**0.3082**	**−0.9160**	
T7 (P. ostreatus on Sediments from Bodo)	Zero Order	0.7983	0.8935	0.7983	0.7479	16.2692	0.4191	−0.8935	The *R*-square values for Pseudo second order (**PSO)** is the highest, and the *R*-square values for both Zero order and PSO are below the 0.8 threshold*. Again, the PC and RMSE values favour PSO. Thus, the removal kinetic will predominantly follow **PSO**.
	PFO	0.7988	0.8937	0.7988	0.7317	12.2847	0.2159	−0.8937	
	PSO	**0.9452**	**0.9722**	**0.9452**	**0.9269**	**6.4111**	**0.2015**	**0.9722**	
T8 (Fermented Palm Wine on Sediments from Bodo)	Zero Order	0.7712	0.8782	0.7712	0.7139	17.3308	0.4586	−0.8782	The *R*-square values for **PSO** are the highest; however, the *R*-square values for Pseudo first order (PFO) are also above the 0.8 threshold*. Therefore, we see some aspects of pseudo-first-order kinetics here too. Therefore, the kinetics here is likely a mix of PFO and PSO kinetics but will predominantly follow **PSO**.
	PFO	0.8098	0.8999	0.8098	0.7465	11.9422	0.5011	−0.8999	
	PSO	**0.8318**	**0.9120**	**0.8318**	**0.7757**	**11.2330**	**0.4715**	**0.9120**	

Table 4. (*Continued*).

Soil Treatment	Kinetic models	*R*-Square Values from plotted graphs	*R*-Square Values from Regression analysis			Standard Error (SE)	Relative mean squared error (RMSE)**	Pearson Correlation (PC)	Comments * *R*-square values greater than 0.8 are considered a good fit [57,58] ** The SE values indicate a measure of precision, while the RMSE values are a measure of the accuracy of each model [59]
		R-Square Values form plotted graphs	Multiple R	R Square	Adjusted R Square				
T9 (P. ostreatus on Sediments from Gio)	Zero Order	0.7876	0.8875	0.7876	0.7345	16.6951	0.4325	−0.8875	The *R*-square values for **PSO** are the highest; however, the *R*-square values for Pseudo first order (PFO) are also above the 0.8 threshold*. Therefore, we see some aspects of pseudo-first-order kinetics here too. Therefore, the kinetics here is likely a mix of PFO and PSO kinetics but will predominantly follow **PSO**.
	PFO	0.8083	0.8991	0.8083	0.7444	11.9895	0.2292	−0.8991	
	PSO	**0.9365**	**0.9677**	**0.9365**	**0.9153**	**6.9004**	**0.2330**	**0.9677**	
T10 (Fermented Palm Wine on Sediments from Bodo)	Zero Order	0.7868	0.8870	0.7868	0.7335	16.7282	0.4437	−0.8870	The *R*-square values for **PSO** are the highest; however, the *R*-square values for Pseudo first order (PFO) are also above the 0.8 threshold*. Therefore, we see some aspects of pseudo-first-order kinetics here too. Therefore, the kinetics here is likely a mix of PFO and PSO kinetics but will predominantly follow **PSO**.
	PFO	0.8145	0.9025	0.8145	0.7526	11.7957	0.4709	−0.9025	
	PSO	**0.8375**	**0.9152**	**0.8375**	**0.7834**	**11.0387**	**2.1746**	**0.9152**	

4. Discussion

4.1. TPHs concentration in the soils and sediments

TPHs values in the soil types and sediments in the present study varied from 120 to 540 g/kg dry soil/sediment and were significantly different among the soil types and sediments (**Tables 2** and **3**, **Table S1** in supplementary material). These values are quite higher than the soil threshold limit of 10 g/kg dry soil or 1% [60–62]. Therefore, people in contact with these soils and sediments will likely experience the health hazards associated with TPHs toxicity.

The range of TPHs values obtained in the present study (120–540 g/kg dry soil) is comparable to 150–450 g/kg of (Dickson et al., [37] and the 420 g/kg reported by Kim et al. [60]. However, the soils reported by Dickson et al. [27] and Kim et al. [63] were both silty loam soils, while those of the present study ranged from clayey, sandy, loamy, and sediments. Brazauskiene et al. [64] demonstrated that soil texture can influence the concentrations and speciation of soil pollutants. In the present study, it is observed that the highest concentration of TPHs was in the clay soil, followed by the sediments, loamy soil, and lastly sandy soil. The implication here is that soil textural properties can influence the TPH's holding capacity. However, these samples were collected at different locations, associated with varying distances from the contaminating source, and also the age and duration of the oil spills. Therefore, in corroboration with Khan et al. [65], there may be other factors that may also influence the variation of the TPHs concentrations in the various soil types and sediments from Ogoniland, Nigeria, in addition to the soil textural classes.

The oil spills in Ogoniland have been reported as far back as the 70s, with many of the spill sites left untreated for decades, with recurring spills [3]. Dickson et al. [37] reported that the age and duration of oil spills can lead to high concentrations of TPHs in soils. Also, Palinkas et al. [66] and Babatunde [67] both stated that oil pollution is worse in the proximity of the source. Therefore, in addition to textural properties, the variations in TPHs concentrations at the different sampling points associated with the soil types and the sediments from Ogoniland may also be due to the age and duration of the oil spills, in addition to their respective distances from the contamination source. Some of the samples were collected from points of direct impact, while others were obtained some distances away from contaminant sources due to site barriers. Again, some of the samples were also collected from areas with recurring pollution. These observations explain the variation in TPHs concentrations in the soils and sediments of the area in the present study. Therefore, the range of TPHs concentrations in soils and sediments will be a function of textural class, the age and duration of the oil spills, as well as their respective distances from the contamination source. Timely treatment of the contaminated sites would help reduce the cumulative effects of these contaminants, prevent leaching, and contaminants transport to other locations and biological systems.

The highest concentration of TPHs was observed on the clayey soils, followed by the sediments, loamy, and then sandy soils. Clay soils have smaller particles [68], characterized by a very fine texture, with a sticky and plastic feeling when wet as a consequence of their small, tightly packed particles [69]. The cohesive and adhesion

properties of clay soils are also higher compared to other soils [70]. Thus, crude oil contaminants are more tightly bound to the clay particles than in other soil types [71], thereby providing the capacity to hold on to higher concentrations of TPHs, as observed in this study. The textural properties of river sediments vary depending on the river's flow and source but most often consist of a mix of sand, silt, and clay particles [72,73]. The proportion of each particle in the sediments depends on the depositional environment. It has been reported that river sediments with a higher clay content will exhibit similar sticky, plastic properties to clay soil when wet, similar to those of the clay soil [74,75]. The textural properties of the sediments in this study were closely related to those of clay (**Table 1**); therefore, the observed trend in the TPHs concentrations in the soils and sediments should be expected.

4.2. TPHs remediation efficiency during the mycoremediation treatments

Al-Dhabaan [76] used some specific fungi isolated from Dhahran in Saudi Arabia to carry out mycoremediation of crude oil contaminated soil. The study revealed remediation of levels of 58% for Aspergillus niger, 51% for *Aspergillus spelaeus*, and 47% for *Aspergillus polyporicola*. The result obtained in the present study revealed far higher levels of remediation efficiency. These may be due to several reasons. First, the present study was carried out with the addition of Tween 80, which has the known effect of enhancing the remediation efficiency of TPHs remediation agents in soils [77,78]. Again, the palm wine used in the present study is a consortium of microorganisms, principally yeast, which also revealed the synergistic effect of such an association in mycoremediation [79]. Also, Dickson et al. [35] had reported that the addition of cow manure during phytoremediation of petroleum-contaminated soils aids in supplying functional soil microbes, which can synergistically enhance the remediation efficiency of the agents as well. Finally, the white rot fungus, P. ostreatus, has extensive mycelia [80,81], which can aid better penetration into the soils and sediments for remediation action. The remediation output in the present study, particularly with mycoremediation agents that are readily available in the Niger Delta region of Nigeria, indicates a promising potential of utilizing the technique for clean-up of petroleum-contaminated soils and sediments in Ogoniland and other parts of the Niger Delta, Nigeria.

The low TPHs remediation efficiency of both mycoremediation agents (P. ostreatus and fermented palm wine), observed at the onset of the remediation treatments, may be due to a number of factors. These include the relatively low bioavailability of the TPHs in the soils and sediments; low activity of soil microbes usually associated with soils highly contaminated with crude oil; and the time for the mycoremediation agents to adapt to the contaminated environment before exerting their actions on the TPHs. The treatment of the contaminated soils and sediments in the present study was all optimized with Tween 80 because previous studies by Dickson et al., [37] had demonstrated that Tween 80 generally enhanced the remediation efficiency of the mycoremediation agents, P. ostreatus and fermented palm wine. Khan et al. [65] stated that sites associated with long-term contamination are dominated by the strongly bound or recalcitrant fraction of hydrocarbons, which are not readily bioavailable. Therefore, solubilizing agents are required during the

treatments of such soils, which was offered by the addition of Tween 80 in the treatments carried out in the present study. The addition of Tween 80, with time allowed for the availability of TPHs, and consequently the actions of the agents. However, as observed in the present study, the addition of Tween 80 may require some time and other factors for effective remediation to set in.

With respect to soil microbial activities, studies such as Timmerman et al. [82] and Franco et al. [83] have reported decrease in soil microbial communities in soils contaminated with crude oil. Also, a subsequent increase in soil microbial activities, as the TPHs remediation in soils progressed has also been documented [83–85]. Therefore, the low TPHs removal on the onset of the remediation would also be associated with low soil microbes, and vice versa. This argument corroborates that of Margesin et al. [86], who demonstrated an increase in soil microbial population during biostimulation treatment of petroleum-contaminated soils. This observation implied that a time frame is also required for remobilization of the soil microbes that will aid the mycoremediation as well. Accordingly, identifying factors that will aid the timely remobilization and increase in soil microbial populations will also help in the further timely enhancement of the mycoremediation process.

Another factor that may play out here would be the time for the mycoremediation agents (P. ostreatus and fermented palm wine) to adapt to the highly contaminated soils before exerting their actions on the TPHs. Adenipekun and Lawal [87] stated that mycoremediation agents do not require preconditioning before application. While this might be true in the context of the overall remediation efficiency of the agents, the result of this study suggest that preconditioning of mycoremdiation agents to the contaminated soil may help in early adaptation, which can help to reduce the overall duration of the mycoremediation treatment. Therefore, further investigations into factors that can enhance timely adaptation of mycoremediation agents during remediation of highly contaminated soil are required.

A quick glance at the intervals 30–45 days and 0–45 days, respectively, for P. ostreatus on the loamy soil revealed 65% and 73% TPHs removal, which were significantly higher than those of the other soil treatments (**Figure 1**, **Figure S2**, **Table S1** in supplementary material). This same trend was observed for the treatments with fermented palm wine on the loamy soil (the TPHs removal efficiencies were 54% and 59% during the same interval (30–45 days and 0–45 days), remarkably higher than those of the other soil types and sediments). The observed better TPHs removal efficiency of both agents on the loamy soil would be a function of its textural properties. Loamy soil is a mixture of sand, clay and silt particles in equal or nearly equal proportion [88]. This allows for easy distribution and interaction among other soil factors, contaminant molecules, and the mycoremediation agents. The ease of such interactions aids the increased efficiency of the remediation in the loamy soil, compared to the other soils and sediments. Clay soils are very sticky and dense [89].The addition of organic manure loosens the clay particles and allows for the penetration of mushroom mycelia for remediation [90], yet the interaction therein will not be compared to those of the loamy soils. Soil particles are loosely held in sandy soils. Sandy soils also have larger pore spaces. The addition of organic manure binds the sandy particles [91]. However, the sandy soils may also be associated with too many pollutant particles in soil pores, which can cause pollutant stress on the agents

and less remediation efficiency. A further mixing of the substrates and mushroom with the sandy soil can result in sandy particles and the contaminant molecules being further apart from contact with the mushroom mycelia. Thus, the observed trend in the remediation of the efficiency of *P. ostreatus* on the different soil types.

The above findings established that mycoremediation of TPHs works best in loamy soils, therefore, shifting soil properties towards those of loamy during mycoremdiation is highly recommended. Clay soils can be improved to loamy soils by the addition of appropriate particles of sand and silt, in addition to other amendments such as compost, organic and animal manure, as well as sand particles [90,92]. Similarly, sandy soils can also be adapted to being more loamy. This outcome is further highlighted in the overall remediation efficiency after 90 days (**Table 2**, **Figure 1, Figure S2** in supplementary material). It is observed here that the overall remediation of the sandy soil treatments was still below 90% for the treatment with P. ostreatus, which implies that the remediation on the sandy soil can be improved by improving the soil textural properties towards those of the loamy soil.

A comparison of the remediation efficiency of the mycoremediation agents (*P. ostreatus* and Fermented Palm wine) obtained in the present study on petroleum-contaminated soils to those of Tibshelf, Derbyshire, UK [37], demonstrates that methods developed with the soils from Tibshelf, UK, can be reliably applied to soils in the Niger Delta, Nigeria. This finding is beneficial for both research and real-life applications. In Dickson et al. [37], conditions were replicated to represent those typical of the Niger Delta, Nigeria, with temperatures at 15 ℃–25 ℃ and watering conditions in the glasshouse. The study also utilized typical real-life petroleum-contaminated soils (taken from contaminated sites), the soils were amended with cow manure, and it was carried out under unsterilized conditions. These would allow for easy applications of the methods either in situ or in bioremediation plants.

Generally, the TPHs concentrations in the soils and sediments of the study area were higher than the soil threshold values of 10,000 mg of TPHs per kg dry soil [93]. As observed in this study, the mycoremediation of the contaminated soils and sediments with *P. ostreatus* and fermented palm wine was able to reduce the TPHs concentrations in the soils to values within the soil threshold levels. Similar outcomes were not obtainable in the control soils and sediments (**Table 3**). These outcomes accordingly demonstrate that mycoremediation can be utilized in both temperate and tropical soils and is a feasible option for the treatment of the highly contaminated soils and sediments in Ogoniland, Niger Delta, Nigeria.

4.3. TPHs removal kinetics of the mycoremdiation process

The TPHs removal rates revealed the peak period of the mycoremediation activities was within the interval 45–60 days (**Figures 1** and **2**). As it is, both the TPHs remediation efficiency and removal rate were quite low before 45 days. These insights require some careful considerations for intrinsic inferences therein. First, what factors would have limited the removal rate and efficiency before the 45 days, and then, what factors would have enhanced such after 45 days? Also, are the removal efficiency and rates after the 45–60 days interval enough to continue the remediation treatment for the remaining 90 days, or would it be logical to end the remediation treatment in a

time frame less than 90 days? The kinetic insight from the TPHs removal kinetics, in terms of the TPHs removal rates, and the kinetic modeling will help in making plausible scientific deductions and conclusions on these.

The TPH's removal kinetic modeling revealed that all the mycoremediation treatments progressed by pseudo second-order kinetics (PSO). In some cases, the possibility of mixed kinetics, but predominantly progressing via the PSO, was also observed (**Table 4**). According to Ho [94], the reaction rate of second-order kinetics is a function of the initial concentration. Therefore, it suffices to say that the TPHs removal rates and removal efficiency would have slowed down until an appropriate concentration, which was ideal for the PSO to set in, was achieved. Also, in PSO, the reaction rates are exponentially related to a change in concentrations [54], which explains why a high remediation efficiency and TPHs removal rates was achieved within a short interval of 45–60 days, compared to the entire duration of the mycoremediation treatments.

Furthermore, the low TPHs removal efficiency and removal rates observed at other intervals indicate that other kinetics (of zero order and pseudo first order-PFO) would have operated at those intervals. Thus, the mix kinetics projected for some of the treatments (**Table 4**) seem plausible, with the PSO being the determinant kinetics as indicated.

A further look at the TPHs removal rates at the interval of 0–45 days (**Figure 2**) highlights that certain factors would have limited the TPHs removal efficiency at this interval. Some of the factors already discussed include TPHs solubility and availability, the activity of soil microbes, and the time taken for mycoremediation agents to adapt to the contaminated soils and sediments. Therefore, factors that would aid increased TPHs solubility and availability, enhance soil microbial activities, and allow earlier adaptation of the agents at the earlier stages of the remediation treatments (0–45 days) will increase the TPHs removal efficiency of the agents. One of such factors, as already specified, is the initial TPHs concentrations in the soils and sediments.

The initial TPHs concentrations in the treatments ranged from 120 to 525 g/kg dry soil/sediment. These concentrations are also associated with the interval 0–45 days, where there was little decrease in the TPHs concentration (less than 20% for most treatments, except the loamy soil). At the interval of 45–60 days (which is associated with the peak of the TPHs removal rate and removal efficiency), the TPHs concentration was 58 to 460 g/kg dry. Specifically, the TPHs concentrations for the treatments at these intervals were 490, 460, 110, 120, 59, 88, 190, 210, 300, and 300, for the respective treatments, against the values at the onset of the experiment (**Table S1**, supplementary material). Since these TPHs concentrations were associated with the maximum TPHs removal rates and remediation efficiencies, it can be deduced that using these concentrations as the initial concentrations of TPHs in the soils and sediments would have increased the remediation process, particularly with respect to reducing the time required for the treatments of the soils and sediments. Therefore, readjustment of the initial TPHs concentration in highly contaminated soils and sediments is required for an overall enhanced remediation efficiency. Such can be achieved by diluting the highly contaminated soils and sediment with substances such as pristine soils and other amendments, e.g., compost, organic manures, and biochars.

These factors can help enhance the TPHs removal rates and remediation efficiency at the early stages of the process.

It was also observed that after 60, and at most 75 days, the removal efficiency for most of the treatments (except the sandy soils) had attained greater than 98% (**Figure 1**, **Table S1** in supplementary material). Therefore, the mycoremediation treatment for the soils and sediments should have ended at about 75 days for the other treatments, except the sandy soils.

Consequently, the factors that would have limited the TPHs removal rates and remediation efficiency in the early stages of the treatment would include high initial concentrations of the TPHs in the soils and sediments, low TPHs solubility and availability, low activity of soil microbes, and the time taken for mycoremediation agents to adapt to the contaminated soils and sediments. On the other hand, factors that would have helped to enhance the TPHs removal rates and remediation efficiency in the intervals after 45 days, specifically 45–60 days, will include optimal concentrations of the TPHs, increased TPHs solubility and availability, increased soil microbial activities, and the adaptation of mycoremediation agents to the contaminated soils and sediments.

4.4. Feasibility of large scale application of the mycoremediation process

The study was actually carried out replicating environmental variables that are identical to those of Ogoniland, Niger Delta, Nigeria. Such include using typical crude oil contaminated soils and sediments taken from sites of contamination in Ogoniland, Nigeria, and replicating similar climatic conditions of the Niger Delta, Nigeria. Therefore, replicating this in real-life commercial applications is highly feasible. Also, the abundance of the mycoremediation agents used in the present study (palm wine and P. ostreatus) in the Niger Delta region of Nigeria makes the technique very promising. Further details on the commercial feasibility of nature-based solutions in the remediation of petroleum-contaminated soils have been discussed in Dickson et al [37].

5. Conclusion

The present study revealed that both soils and sediments of Ogoniland, Niger Delta, Nigeria, have been impacted with high levels of TPHs from crude oil pollution. This study has also revealed that *P. ostreatus* and fermented palm wine can be used for the remediation of petroleum-contaminated soils in both temperate and tropical climates.

Other deductions from the present study include:

- Soil textural properties can influence TPHs holding and remediation capacity. In the present study, the highest TPHs concentration was found in the clayey soils, followed by river sediments, then loamy and sandy soils.
- Other factors that can also influence the TPHs concentrations in soils and sediments include the age and duration of the oil spills, as well as their respective distances from the contamination source.

- The efficiency of mycoremediation treatment is better in loamy soils; therefore, shifting soil textural properties towards those of a loamy soil can also help to increase the efficiency of mycoremediation.
- Kinetic modeling of the mycoremediation treatments has revealed that the mycoremediation of the soils and sediments progressed by pseudo second-order kinetics. It has also revealed the need for further dilution of highly contaminated soils and sediments to achieve optimal initial concentrations for the best mycoremediation outcomes.
- Remediation of most of the highly contaminated soils and sediments was completed before the 90 days.
- Mycoremediation can work for both temperate and tropical soils. Therefore, the technique is a feasible option for the treatment of the highly contaminated soils and sediments in Ogoniland, Niger Delta, Nigeria.

Supplementary materials: The supplementary material contains information on the following: Raw data for TPHs concentrations, Removal efficiency, and removal Rates, in the soil samples during the treatments; with the results from statistical analysis; Kinetic modelling of the mycoremediation treatments, including the kinetic graphs for each treatment and each of Zero order, PFO and PSO; Graphical presentation of Remediation efficiency of the mycoremediation Treatments with error bars.

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