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Bioremediation of TPH in Petroleum Hydrocarbon Contaminated Clay Soil with an Emerging Nutrient (Solpawa SBR-X^{TM})

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Abstract

This research focuses on the bioremediation of total petroleum hydrocarbons (TPH) in petroleum hydrocarbon contaminated clay soil with an emerging nutrient (Solpawa SBR-X^{TM}). A laboratory experiment was set up and successfully carried out in order to monitor TPH concentration among the various reactors (T_1, T_2, T_3, and T_4). This process was monitored for 7 days, 12 days, 22 days, 32 days, 42 days, and 52 days, respectively, for reactors 1, 2, 3, and 4. The results showed similar remediation trend at day 52 with little variance in reactor T2 compared to others treated apart from the control reactor, which is labelled T1. Also, close examination was carried out to ascertain the TPH reduction percentage among the various reactors. The result revealed that after 52 days of treatment, the TPH concentration reduced by 93.63%, 91.72%, and 86.05% for T2, T3, and T4 respectively, for all the treatments excluding the control (T1). This was because of the Solpawa soil conditioner (SSC) and the booster. A better reduction in TPH was observed in reactor T2 with 1265.3 mg/kg (reduction of 93.63%), which dropped below the aforesaid regulatory intervention value but was still above the target value of 50 mg/kg spelt out by the Nigeria regulatory framework. The TPH of the contaminated soil dropped from an initial average of 19086.7 mg/kg for all treatment to 1265.3 mg/kg (representing 93.63% TPH reduction) at the depth of 0.3 m after 40 days of treatment with the SSC working solution of 1:4. Overall, TPH reduction across the reactors reduced with decrease in the level of SSC in the working solution. However, there were significant differences ($P > 0.005$).

Keywords: Solpawa nutrient, bioremediation, crude oil, clay soil

INTRODUCTION

Petroleum hydrocarbons are made up of short-chain hydrocarbons such as aromatic compounds, alicyclic, paraffin, and nonhydrocarbon compound such asphaltene, heterocyclic nitrogen, metalloporphyrin, naphthenic acid, phenol, thiol, and sulfur compounds [1]. Petroleum hydrocarbons are the major source of energy for extensive use in the world for human sustenance and industry [1]. Petroleum hydrocarbons contamination occurs often during production, exploration, transportation, maintenance, and storage [2]. Crude oil–contaminated soil has catastrophic and disastrous consequences on human and other biotic components of the ecosystem. The release of these compounds into the environment either by anthropogenic activities or accidentally results to soil and water pollution and directly or indirectly affects all aspects of life [2–4]. Although several remediation approaches of petroleum hydrocarbon

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contaminated soil have been canvassed and recommended, there is need for more cost effective, environmentally friendly technique using materials locally formulated for hydrocarbon degradation. Biological treatment (bioremediation) technique has been proven to be eco-friendly and relatively cheap [5] compared to physical and chemical treatments (solidification/stabilization, thermal desorption, incineration, etc.). Biostimulation, which is an aspect of bioremediation, is among the actively used techniques [6–8]. These spills introduce toxins that largely affect the nutrient distribution of the receiving bodies causing nutrient imbalance and microbial death created by the contaminating oil. To rejuvenate the microbial population and balance the nutrient distribution in soil, nutrients must be applied within recommended environmental constraints.

At the moment, there is a dearth of information in the open literature on how to tackle this problem in the Niger Delta without huge financial implications in foreign exchange due to dependence on imported nutrients. Besides, soil is highly variable in terms of nutrient distribution partly caused by the nutrient imbalance and microbial death created by the contaminating oil. Therefore, a need exists to evolve a bioremediation nutrient with locally available materials to overcome this challenge. This informed the decision of an indigenous scientist to develop Solpawa SBR-X™ in line with the local content initiative of the Nigerian Government is shown in Figure 1.

Figure 1. Solpawa soil booster and Solpawa soil conditioner.

Solpawa SBR-X™ is a scientifically formulated soil bioremediation system proposed to have the ability to release nutrients into the soil to stimulate microbial activities. Therefore, this study investigates remediation potential of weathered hydrocarbon-contaminated clay soil with an emerging nutrient formulated with local materials.

MATERIALS AND METHODS

The Study Area

The research work was carried out in the southern region of Nigeria also known as the Niger Delta region as shown in Figure 2. But the core Niger Delta is Delta State. Several researchers [1, 9] have reported the studies conducted by Niger Delta Development Commission (NDDC) that the region occupies a surface area of about 112,110 km^2. It represents about 12% of Nigeria's total surface area and has about 450 km^2 coastlines and is the world's second largest delta and terminates at Imo Rivers. The region as 20,000 km^2 is the largest of all wetlands in Africa as well as the third largest [9].

Sampling and Synthesis of Solpawa SBR-X™ Nutrient

Shovels were used to gather aliquots from the Obio/Akpor local government region in Rivers state, Nigeria, at a depth of 0 to 0.3 meters. Shovels were used to gather aliquots from the Obio/Akpor local government region in Rivers state, Nigeria, at a depth of 0 to 0.3 meters. The crude oil used for this research was collected from one of the oil exploration companies situated in this region. Solpawa SBR-X™ is a locally made nutrient in line with the local content act of Nigeria. The nutrient was collected from Solpawa Bioremediation Products Company, Lagos, Nigeria in accordance with relevant regulatory framework [10].

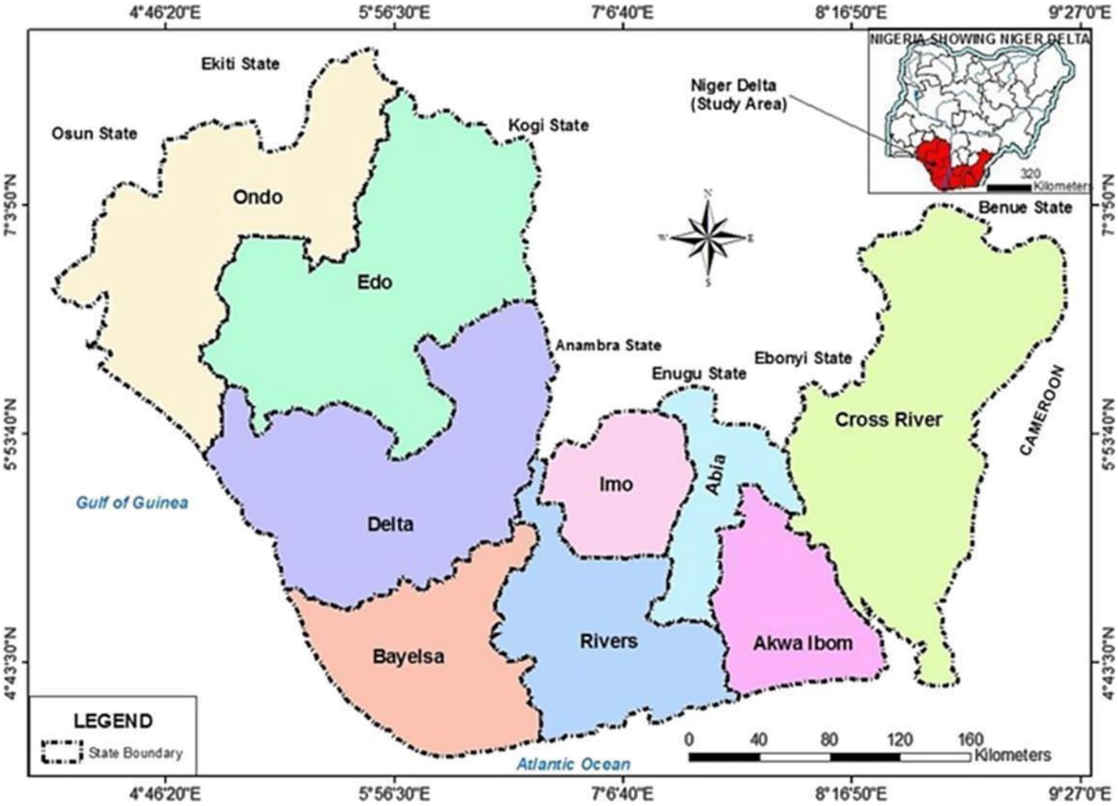

Figure 2. Map of Niger Delta region of Nigeria showing states.

Solpawa SBR-X™ as a Bioremediation Nutrient

Solpawa SBR-X™ products are manufactured, sold, and applied as part of a system – Solpawa SBR-X™ Soil Remediation System (SSRS) – which combines the Solpawa Soil Conditioner (SSC)(liquid) and the Solpawa Soil Booster (SSB) (granular). The Solpawa SBR-XTM Soil Remediation System (SSBRS) is principally developed for environmentalists, cleaning, and bioremediation contractors, crude oil producers, and refineries who are particular about reducing in situ total petroleum hydrocarbons (TPH) in crude oil polluted soil and hard surfaces within a short time in line with local regulatory framework [11].

Solpawa SBR-X™ Soil Conditioner

An example of a brown liquid bio-emulsifier is Solpawa SBR-XTM Conditioner (SSC). It is strongly lipophilic or oil loving. SSC works by drawing the hydrocarbons from the soil's or a hard surface's surface. Following their mobilization, the hydrocarbons are emulsified in the SSC solution, which renders them water miscible, non-volatile, and non-combustible.

First applied, SSC facilitates bioremediation. It is water-based, making it simple to combine, safe, and easy to use. It is a concentrate that is diluted with water to generate a functional solution..

Solpawa SBR-X™ Soil Booster

Brown particle organic plant extract Solpawa SBR-X TM Soil Booster (SB) provides the first matrix for lipophilic organisms. SSB stimulates and sustains active bioremediation of crude oil, petrochemicals polluted soil. The organisms metabolize the crude oil, petrochemical to carbon dioxide and water. SSB is applied to soil already treated with SSC.

Applying SSB is as simple as spreading it over the damaged soil and misting it with water. It is both safe and simple to apply. It was applied on weathered petroleum contaminated clay soil type with the hope to ascertain the claim of its producers of it not just remediating the contaminants but restoring the soil properties and living it richer than it was originally.

Experimental Set-up

The set-up consisted of four reactors including a control with three replicates. The reactor used was a 100 cm^3 volume of container with top diameter of 100 cm, base diameter of 100 cm and depth of 100 cm. The simulation of contaminated soil sample was achieved using Bonny light crude oil. After contaminating the soil with crude oil, the experimental set-up was left for 7 days to incubate, prior commencement of treatment with the Solpawa (Figure 1). On the seventh day, a cocktail of SSC mixed with water at ratios of 1:4, 1:6 and 1:8 was administered into the contaminated soil in the different reactors with exception of the control (Table 1). These were allowed to stay for 5 days undisturbed to allow the cocktail mixtures to infiltrate into the contaminated soil and samples were collected at the depth of 0.3 m from the reactors before taken to the laboratory for analysis. On the 12th day another treatment was introduced to the soil samples in the reactors. This treatment was the addition of SSB to the reactors at the ratio of 1:12 (2.5 kg of Solpawa booster and 30 kg of soil). Tilling of the treated media was carried out twice weekly for the period of remediation to ensure proper aeration [12].

Table 1. Experimental mix proportions.

Reactor	Mix Proportion
T_1	30 kg of soil + 1 kg of crude oil + no treatment (control)
T_2	30 kg of soil + 2.5 kg SSB +1 kg of crude oil + SCC/water (1:4)
T_3	30 kg of soil + 2.5 kg SSB +1 kg of crude oil + SCC/water (1:6)
T_4	30 kg of soil +2.5 kg SSB + 1 kg of crude oil + SCC/water (1:8).

SSB, Solpawa soil booster; SSC, Solpawa soil conditioner.

Sample Analysis

Ascorbic acid method was used to determine available phosphorus. The modified Kjeldahl method was employed to determine total nitrogen [12]. The hydrometer method was used to determine the particle size distribution (PSD), soil texture was determined by the United States Department of Agriculture (USDA) soil textural classification triangle using TAL for windows computer software. The sample was chemically dried using anhydrous sodium sulphate. The extraction was conducted separately by using 10 mL dichloromethane and *o*-terphenyl was used as surrogate. After which, the combined extraction solvent and sample was agitated by shaking for 45 minutes with vortex mixer and glass wool/glass funnel was used as decant extract. The extract was allowed to concentrate for 1 minute before injecting into the gas chromatograph for TPH analysis [3].

The reduction percentage of hydrocarbons was determined using Equation 1.

$$\text{Percentage of reduction} = \frac{X_1 - X_2}{X_1} \times 100 \quad (1)$$

where X_1 is the initial TPH concentration, X_2 is the final TPH concentration in the treated contaminated clayey soil.

Statistical Analysis

Two-way analysis of variance (ANOVA) was used to determine the significant difference in the mean values of TPH polluted soil remediated with Solpawa. This was done based on the *F*-test at 95% confidence level, which was implemented using Microsoft Excel 2019 toolbox.

RESULTS AND DISCUSSION

Physicochemical Characteristics of Uncontaminated Soil

Table 2 shows the physical and chemical characteristics of the unpolluted soil. The soil consists of 5.6% sand, 31.09% silt, and 63.31% clay soil as shown in Figure 3 and Table 2.

Table 2. Physicochemical characteristics of uncontaminated soil.

Soil Properties	Value
TPH (mg/kg)	14.09
Particle size distribution	
Sand (%)	5.60
Silt (%)	31.09
Clay (%)	63.31
Textural class	Clay soil

TPH, total petroleum hydrocarbons.

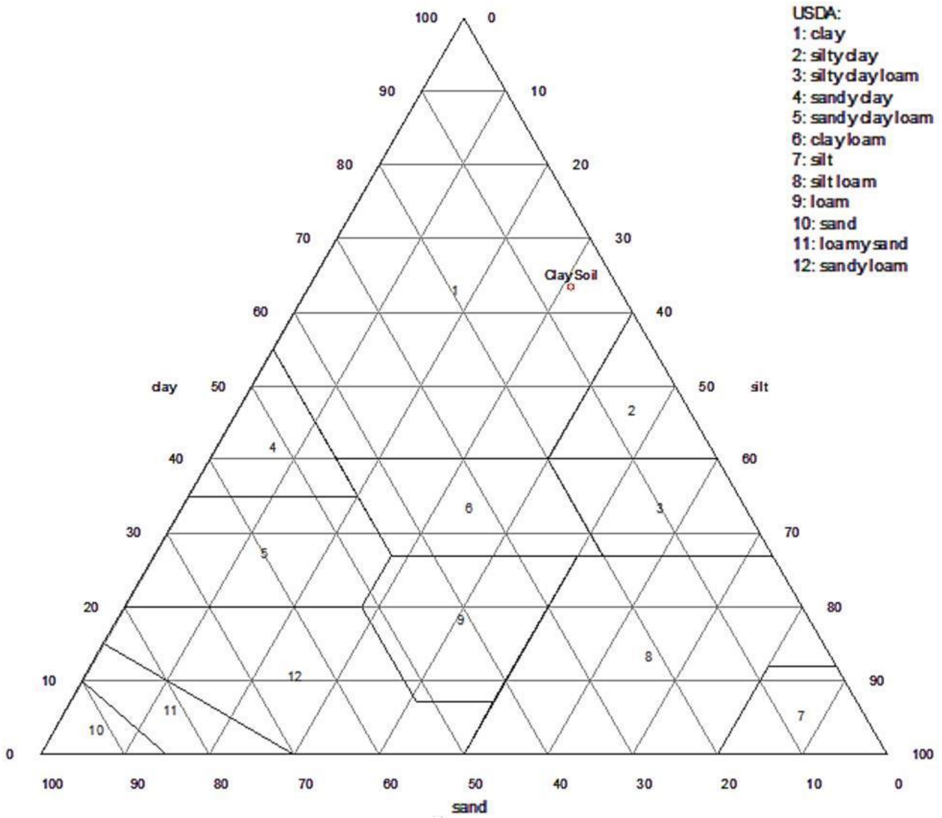

Figure 3. The USDA Soil Textural Classification Scheme, as determined by TAL® for Windows v. 4.2 (Christopher Tech Boon Sung, China), is the basis for the soil textural triangle utilized in this study, which shows Clay (No. 1) as the texture of the soil.

Fertilizing Value of Solpawa Conditioner and Booster

The initial NPK (nitrogen, phosphorus, potassium) characteristics determined were used as indices for evaluation of the fertilizing value (i.e., remediation potential) of the Solpawa products. Table 3 shows the NPK values of the Solpawa conditioner and booster. As can be observed, the Solpawa booster (granular form) had a higher fertilizing value than the conditioner (liquid form). Compared with the recommended fertilizer value of 3:2.5:0.5 (N:P:K) for materials, both the booster and conditioner far exceeded these typical values. This suggests that both Solpawa booster and conditioner are excellent candidates for remediation purposes, which justifies the use of the products for remediation works [4].

Residual Soil TPH in Crude Oil–Polluted Clay Soil

The mean TPH concentration in the contaminated media on the seventh day at 0.3 m depth after mixing the soil and crude oil was 19087 mg/kg for all treatment. This corresponds to the seventh day after contamination in the bar chart (see Figure 4). The TPH concentration in the soil–crude oil mixtures over a period of 52 days is shown in Figure 4.

Table 3. NPK (nitrogen, phosphorus, potassium) values of Solpawa soil conditioner and Solpawa soil booster.

Properties (mg/kg)	Solpawa Conditioner	Solpawa Booster
N	103.560	261.450
P	1.241	7.592
K	180.903	569.191

There is a need for the soil to be reclaimed before use for agricultural purposes. After 12 days, there were drop in TPH, which varied among treatment [9, 13]. The TPH decreased in T2, T3, T4 including the T1, which is the control reactor. It was observed that the difference among the treatments were significant ($P < 0.05$). However, T2 had the highest TPH reduction of 9% (18,075 mg/kg) is shown in Figure 5 Although this value was still above the local regulatory framework as recommended by Nigerian Upstream Petroleum Regulatory Commission [12].

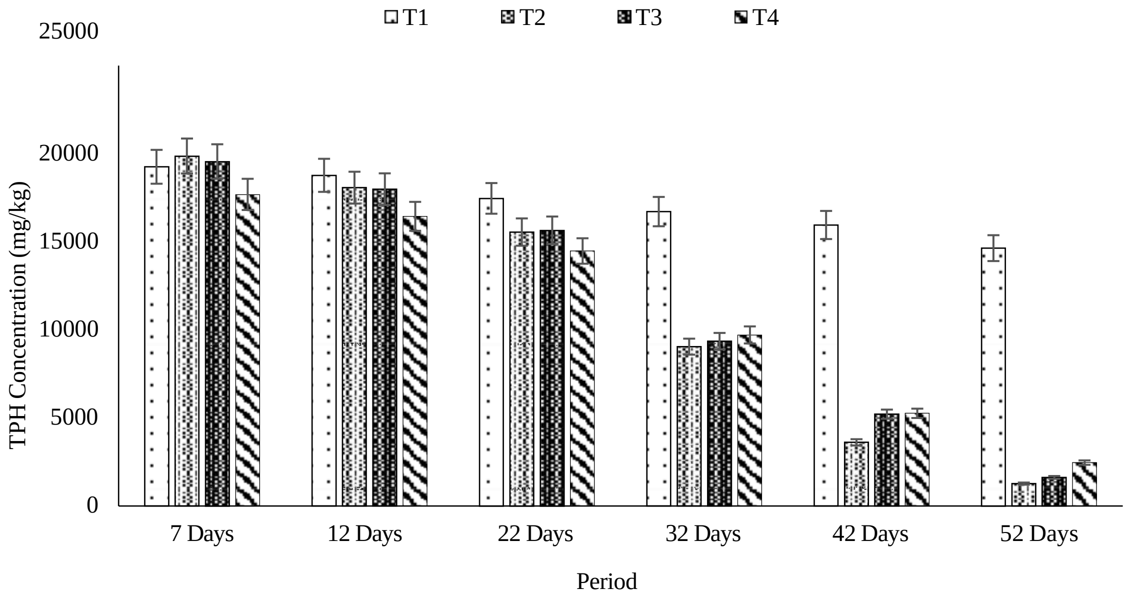

Figure 4. Total petroleum hydrocarbon (TPH) concentration among the various reactors (T_1. T_2. T_3, and T_4). Error bar on chart represents percentage.

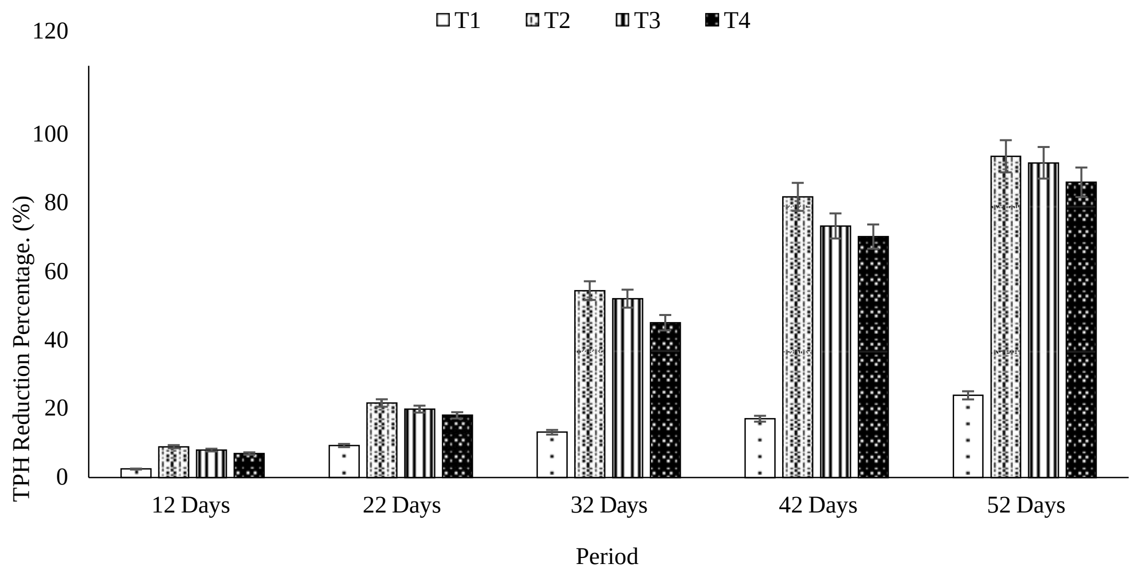

Figure 5. Total petroleum hydrocarbon (TPH) reduction percentage among the various reactors (T_1. T_2. T_3, and T_4). Error bar chart represents percentage.

At 32 days after applying the treatment, the contaminant decreased to 9037 mg/kg for which 54.5% TPH reduction was achieved for treatment T2, followed by T3 (9352.7 mg/kg), T4 (9037.6 mg/kg) including T1 (16705.6 mg/kg), in that order. This is similar with the findings of Okparanma et al. [4] stating that the remediation of TPH increased with time, the remediation in the first 30 days is often high and becomes slow thereafter.

At 52 days, the same remediation trend was maintained, further decrease occurred in T2 compared to other treatments with exception of the control reactor (T1). The TPH reduction level was generally slower at 52 days compared to the level at 32 days (see Figure 4), which conforms to the common trend as stated by [2, 3, 9], where fast degradation phase precedes a slow phase. The fast phase is limited by microbial degradation rate of free TPH, while the slow phase is limited by much slower desorption rate of soil sequestration TPH and high concentration of recalcitrant compounds [14–16].

The performance of SSC/water mixed ratios in the crude oil contaminated soil compared to their uncontaminated counterparts varied between the treatments (Table 1). After 52 days of treatment, the TPH concentration reduced by 93.63%, 91.72%, and 86.05% for T_2, T_3, and T_4, respectively. This can be attributed to the Solpawa conditioner and the booster. However, the TPH reduction level in the control reactor was very low (23.95%). A better reduction in TPH was observed in T2 with 1265.3 mg/kg (reduction of 93.63%), which dropped below the aforesaid regulatory intervention value but still above the target value of 50 mg/kg spelt out by the Nigeria regulatory framework. As shown in Figure 4, TPH concentrations decreased with reduction in Solpawa conditioner-to-water ratio administered to the contaminated clay soil over time [17, 18].

CONCLUSION

The bioremediation potential of Solpawa over a period of 52-day period, with a view to assess.

Their suitability for remediating petroleum hydrocarbon–polluted clay soil at 0.3 m depth. The Solpawa was mixed with water at different quantities (1:4, 1:6, 1:8) and control with no treatment. The crude oil contaminated soil had an initial TPH content for all treatment ranged from 17682 to 19863 mg/kg (mean value of 19086.7 mg/kg). The TPH content reduced to 9037.6 mg/kg in reactor accommodating SSC/water ratio of 1:4. At 52 days, T_2 received the highest degradation rate of 1265.3 mg/kg (reduction of 93.63%). The TPH reduction sequence was $T_3 > T_4 > T_1$. However, it is still above the target value of 50 mg/kg as stipulated in the local regulatory framework. Thus, Solpawa nutrient has the potential to reclaim crude oil–contaminated soils.

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