ISSN: 2795-2215

Journal of Newviews in Engineering & Technology
Faculty of Engineering
Rivers State University, Port Harcourt, Nigeria.

Email: rsujnet@gmail.com | Homepage: https://rsujournal.com

Kinetic and Comparative Studies of Synthetic and Organic Fertilizers in the Remediation of Hydrocarbon-Polluted Soil

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ARTICLE INFO

Article History
Received: 14 July 2024
Received in revised form: 2 November 2024
Accepted: 12 November 2024
Available online: 31 October 2026

Keywords
Biostimulation; Biofertilizer; First-order Kinetics; Land Contamination; Pseudo-first-order Kinetics

ABSTRACT

Adoption of organic fertilizer (biofertilizer) for the bioremediation of hydrocarbon-contaminated soil could help reduce dependence on chemically formulated fertilizers. In a 42-day bioremediation of hydrocarbon-polluted soil, kinetic and comparative studies were carried out by the application of NPK-fertilizer and biofertilizers obtained from the biodigestion of aged and fresh cow dung. Three portions of the contaminated soil were treated with aged biofertilizer (A), fresh biofertilizer (B), and NPK-fertilizer (C), while the fourth portion served as the control without treatment. Pseudo-first-order kinetic model was used for the prediction of the biodegradation rate constants by regression analysis. In addition to microbial loads (among other properties), gravimetric technique was used for determining total hydrocarbon content in the soil before, during, and after remediation. Results showed that the bioremediation efficiency, 42 days after remediation, were 34.04, 61.94, 66.82, and 50.90% for the control, cell A, cell B, and cell C, respectively. The pseudo-first-order reaction rate constants for cells A, B, C, and control were 0.0196, 0.0197, 0.0151, and 0.0057 day^{-1}, respectively. The study concludes that hydrocarbon-polluted soils could be decontaminated with these biofertilizers with varied hydrocarbon-degrading abilities proportional to their microbial loads. © 2026 Authors. All rights reserved.

1. Introduction

Crude oil, a complex mixture of thousands of hydrocarbons, is categorized into four namely: the Saturates, Aromatics, Resins, and Asphaltenes (SARA) (Adams et al., 2017). It is harmful (physically, chemically, and biologically) to soil because it contains several toxic compounds in relatively high concentrations (UNEP, 2011) and is thus classified as an environmental pollutant (UNEP, 2018). Nigeria is very much dependent on crude oil as a fuel and energy source as well as the primary feedstock for many chemical and petrochemical industries. The increase in demand for crude oil has increased its production, transportation, and refining, which in turn has resulted in gross pollution of the environment, especially soil pollution in the Niger Delta region (Medjor et al., 2012; Deinkuro et al., 2021).

Nigeria, especially the Niger Delta region, suffers extensive environmental degradation occasioned by several factors including gas flaring (Brandt,

2020) and oil spills (UNEP, 2011; Zabbey et al., 2017). The pollution of soil by crude oil and other petroleum products due to spills resulting from equipment failure, and pipeline vandalization has become a serious environmental problem because of the potential consequences on the ecosystem and human health (Nuhu et al., 2021; Izionworu et al., 2021). The Niger Delta region of Nigeria, the seat of oil and gas production activities in Nigeria and home to a vast mangrove forest (Okonkwo et al., 2015) is faced with an increasing soil pollution challenge because of widely identified reasons in the literature (e.g., Nuhu et al., 2021); and in recent years the risk has doubled with increase in artisanal refining of crude oil in the region. Artisanal refining, locally referred to as *Kpo Fire*, is a home-grown unregulated distillation of crude oil to produce petrol, diesel, and kerosene in the creeks of Bayelsa State, Rivers State and other crude oil-rich States in Nigeria that has been established as destroying the Niger Delta region of the country. This activity discharges crude oil on the soil causing serious soil degradation in the region (Izionworu et al., 2021).

The most environmentally friendly way to decontaminate the soil is by applying methods based mainly on the metabolic activities of micro-organisms (Ibiene et al., 2011; Tangahu et al., 2017). Remediation of hydrocarbon-contaminated soils is a real-world challenge (Ugwoha et al., 2020); and over the years several methods have been developed and investigated for the remediation of hydrocarbon-contaminated soils. Some of the major methods are physicochemical, thermal and biological techniques (Nuhu et al., 2021; Deinkuro at al. 2021). The choice of method to use depends on the physical, chemical, and biological properties of both the contaminants and soil (Ibiene et al., 2011).

Bioremediation has appeared to be the most desirable method due to its simplicity, cost-effectiveness and eco-friendliness. Bioremediation is a treatment process that uses naturally occurring micro-organisms to degrade organic substances into carbon dioxide (CO_2) and water (Johnsen et al. 2005). However, researchers continue to gather information on ways of mitigating contaminated soils. Adams et al. (2017) studied the bioremediation of crude oil contaminated soil using agricultural wastes (rice husks and chicken dung) with results indicating that rice husks removed more hydrocarbons compared to chicken dung under same conditions.

Ibiene et al. (2011) also studied bioremediation of hydrocarbon-contaminated soil in the Niger Delta using spent mushroom compost and other organic wastes (cow and chicken droppings). The spent mushroom recorded the highest degradation rate at 99.9% compared to cow dung and poultry droppings with 97.83 and 98.21% degradation rates respectively. Ugwoha et al. (2020) investigated the removal efficiency of pig droppings. It was concluded that using agro-organic waste materials such as pig dropping and pig bone char offer an effective solution to the problem of contamination of soil with crude oil. Again, Akuma and Durojaye (2020) compared the performance of chemical fertilizer and biofertilizer from cow dung in remediating crude oil contaminated soil. It was observed that the biofertilizer was more effective in remediating crude oil-contaminated soil.

Apparently, Nigeria is blessed with agricultural wastes and by-products (e.g. cow dungs) which are considered useless to the ordinary man but is useful materials to modify the soil physical and chemical properties as well as release nutrients for microbial activities (Nuhu et. al. 2021; Adam et. al., 2017). The accumulation of agricultural waste and by-products without proper programmes for collection, transportation and disposal constitute a major environmental problem. More so, the use of cow dung to increase biodegradation of contaminated soil adds value to the management of slaughter waste and decrease the Biochemical Oxygen Demand (BOD) loads on rivers and streams around slaughterhouses (Akuma and Durojaye, 2020)

Accordingly, several organic amendments have been used by researchers, namely cow dung and synthetic fertilizer, cow dung and palm kernel

husk ash, bone char from cow bones and goat droppings (Oludele et al. 2021; Akuma and Durojaye, 2020). However, the kinetics of the bioremediation reaction of contaminated soil using liquid biofertilizer from cow dung was not considered. This work seeks to study the kinetics and compare the performance of synthetic fertilizer (NPK) and organic fertilizer (from cow dung in liquid state) for the bioremediation of hydrocarbon-polluted soil. A biodigester was employed to facilitate microbial activity and extract bioactive fluids containing hydrocarbon-degrading bacteria and experimental results used to assess the suitability of pseudo-first-order kinetic model in studying changes in total hydrocarbon concentrations during the treatment process.

2. Materials and Methods

2.1 Materials

Some of the major materials used for this study include drums, PVC pipes and fittings, cow dung, NPK fertilizer, soil samples, and crude oil.

2.2 Methods

2.2.1 Conversion of Cow Dung to Liquid Biofertilizer

i. Construction of Biodigester

A batch-fed biodigester is a device designed to facilitate anaerobic fermentation of cow dung and water, used to process the cow dung for the extraction of microbe-rich fluid, consisting of two cylindrical drums of varying sizes. The larger drum, with a capacity of 220 liters, served as a loading deck for the waste mixture. The smaller drum, functioning as a gas holder with a capacity of 180 liters, prevented atmospheric interference and collected the biogas produced during the fermentation process. A gas outlet was installed on the gas holder to facilitate the extraction of the biogas. Additionally, inlet and outlet pipes, made up of PVC with a diameter of 64 mm, were connected to the bottom of the larger drum for the introduction of waste and water, as well as the removal of liquid biofertilizer (Plate 1).

ii. Cow Dung to Liquid Biofertilizer

A total of 12 kg of cow dung was mixed with 60 liters of water, forming a thick brown slurry, which was then manually loaded into the biodigester. The smaller drum was inverted and placed on top of the larger drum to seal the biodigester. A gas trap, equipped with a pipe and regulator, was installed to allow for the controlled release of biogas. The biodigester operates at a temperature range between 25-33°C which is the temperature range for the region. As it has been widely reported in several literature, the temperature for the optimal operation of biodigester is between 25–40°C, this temperature range accelerates microbial enzymatic activity.

PVC pipes with a diameter of 75 mm were connected to the inlet and outlet holes on the side of the larger drum. Over the 30-day decomposition period, gas formation became evident, accompanied by a rise in the smaller drum. To prevent excessive gas pressure buildup, the gas trap was periodically opened to allow for gas release. While this practice poses environmental risks, it was deemed a safer alternative to the potential dangers of a gas explosion.



Plate 1: Set up for the conversion of cow dung to liquid fertilizer

iii. Harvesting of Liquid Biofertilizer

After 30 days, the outlet line of the biodigester was opened for the collection of biofertilizers

(Aged Biofertilizer) and stored in a plastic container until ready for use (Plate 2). The system was left for another 14 days before the outlet line was opened again for more biofertilizer to be collected, (Fresh Biofertilizer), which was used immediately after it was collected.



Plate 2: Harvested liquid biofertilizer

iv. Preparation of Liquid Synthetic (NPK) Fertilizer

The synthetic (NPK) fertilizer was obtained from a store associated with Indorama Petrochemical Limited, Eleme, a fertilizer-producing company in Nigeria labeled N:P:K (20:10:10). The inorganic fertilizer are white crystals (solid), so there was a need to put both samples of fertilizers in the same physical state. To achieve this goal, 50 g of the NPK fertilizer was weighed out and dissolved in 500 ml of water, resulting in a solution used as the inorganic fertilizer.

2.2.2 Bioremediation Studies

i. Site Preparation and Sample Collection

An area of land was cleared and divided into four (4) portions, labeled samples 1 to 4. The dimension of each portion was 50 cm x 50 cm. After dividing the portions, the collected samples were contaminated with 200 ml of crude oil and mixed thoroughly. The portions were left for a week (7 days) to equilibrate and allow indigenous microorganisms to adapt to the new polluted environment. Then aliquots were collected for baseline analysis. The fertilizers and soil samples were air-dried, gently crushed, and sieved down to 2-mm diameter.

ii. Determination of pH, THC, and THUB

Soil pH is a critical factor in bioremediation, plant growth, and microbial activity. It influences nutrient availability and microbial metabolism; hence, the pH of the soil was determined using a digital soil pH multimeter (Hanna Instruments, USA). The THC of the soil samples was determined using the gravimetric method as reported by Villalobos et al. (2008). The THUB in the samples were recorded with a colony-counting chamber (Osalodion and Ita, 2021; Das and Chandran, 2011).

iii. Determination of Ca^{2+} and K^{+}

Ca^{2+} and K^{+} were extracted with 1 M neutral ammonium acetate ($NH_4CH_3CO_2$). About 5.0 g of sample was mixed with 25 mL of $NH_4CH_3CO_2$ for 30 min and filtered. Ca^{2+} was determined by Atomic Absorption Spectrophotometry (AAS), while K^{+} was determined by flame photometry following the method adopted by Khairo *et al.* (2025).

iv. Determination of phosphorus

Available phosphorus was determined by the Bray 1 method, which is recommended for acidic soils with pH below 6.8. About 2.0g of air-dried sample was mixed with 20 mL of Bray 1 extractant (0.025 M HCl + 0.03 M NH_4F) for 5 min and filtered. Phosphorus in the filtrate was determined by the molybdenum-blue colorimetric method and absorbance was read at 882 nm (Nie *et al*., 2024; Khairo *et al*., 2025).

v. Determination of nitrogen

Nitrate-nitrogen (NO_3-N) was extracted by mixing 5.0 g of the sample with 25 mL of 2 M KCl for 1 hour, followed by filtration. NO_3-N was determined colorimetrically using a continuous-flow analyser as reported by Yu *et al.* (2026).

vi. Determination of SO_4^{2-}

Sulphate was determined by the turbidimetric method (monocalcium phosphate extraction). About 10.0 g of sample was mixed with 25 mL of

0.01 M $Ca(H_2PO_4)_2$ for 30 min and filtered. An aliquot of the extract was treated with $BaCl_2$ to precipitate sulfate as $BaSO_4$, and turbidity was measured at 420 nm as described by Surleva et al. (2025).

vii. Experimental Design and Setup

The Completely Randomized Design (CRD) with four treatment conditions and three replications was implemented as follows:

a) *Treatment 1 (Control):* Contaminated soil without fertilizer amendment.
b) *Treatment 2 (A):* Contaminated soil treated with aged biofertilizer (500 ml).
c) *Treatment 3 (B):* Contaminated soil treated with fresh biofertilizer (500 ml).
d) *Treatment 4 (C):* Contaminated soil treated with synthetic fertilizer solution (500 ml).

viii. Treatment of Hydrocarbon-Contaminated Soil

Each treatment was applied uniformly to the designated cell and thoroughly incorporated into the soil matrix to ensure optimal nutrient-micro-organism contact. The experimental setup were maintained under ambient environmental conditions with natural precipitation and temperature conditions. Aliquots were collected every 7 days for 42 days for analysis to determine the total hydrocarbon content (THC) in each sample. The choice of seven-day intervals for fertilizer application is based on microbial growth cycles, nutrient retention, prevention of toxicity, and practical efficiency. This frequency ensures steady microbial activity, prevents nutrient losses, and optimizes hydrocarbon degradation without overwhelming the system (Nuhu et al., 2020).

ix. Bioremediation Efficiency (BRE)

This is the measure of how much the contamination level has reduced in the soil samples over time due to the treatment applied. The BRE was calculated using equation 1.

$$BRE = \frac{C_o - C_t}{C_o} \times 100\% \quad (1)$$

Where, BRE = biodegradation efficiency (%), Co = the initial concentration of THC (mg/g), Ct = remaining concentration of THC (mg/g) at any time t, and t = remediation time (days).

2.2.3 Determination of the Biodegradation Rate

The basic biodegradation reaction is expressed in equation 2.

$$C_nH_n + O_2 \rightarrow CO_2 + H_2O + Energy \quad (2)$$

The biodegradation reaction rates were obtained using the decreasing concentration of the THC in the soil samples. To determine the biodegradation rate of the THC, the pseudo-first-order reaction kinetic model was fitted to the biodegradation data by employing regression analysis. The well-known pseudo-first-order kinetics is given by equation 3 (Lagergren, 1898).

$$In\frac{C_t}{C_o} = -K_1 t \quad (3)$$

Where, C_0 = initial concentration of THC (mg/g), C_t = remaining concentration of THC (mg/g) at any time, t, K_1 = pseudo-first-order reaction constant (day^{-1}), and t = remediation time (days). K_1 (regression coefficient) was determined by plotting $In\frac{C_t}{C_o}$ against time. To predict C_t, equation 3 was linearized to get equation 4. $In\ (C_O)$ is the intercept on the vertical axis.

$$In\ (C_t) = -k_1 t + In\ (C_O) \quad (4)$$

2.3 Statistical Analysis

All experiments were conducted in triplicate, and results were expressed as mean ± standard deviation. Statistical significance of differences in treatment means was determined using one-way analysis of variance (ANOVA) with significance level set at $p < 0.05$. Kinetic parameters were determined through simple linear regression analysis with coefficient of determination (r^2) used to assess model fitness. ANOVA was performed using Excel-365 (Microsoft Inc., USA).

3. Results and Discussion

3.1 Soil Characteristics

Results from the analysis of the contaminated soil and amendments are presented in Table 1. The results indicated that the biofertilizers (aged and fresh) are rich in potassium, calcium, and phosphorus; this means that there would be an increase in the availability of these nutrients, which would aid remediation of the soil as reported by Igwilo *et al.* (2021) as well as Akuma and Durojaye (2020). In the inorganic (NPK) fertilizer, the potassium and nitrogen contents were relatively high. This explains why NPK fertilizer is widely known to enhance the remediation of contaminated soil.

Table 1: Baseline properties of the soil (7 days after contamination) and the various fertilizers.

S/No.	Property	Contaminated Soil	Aged Biofertilizer	Fresh Biofertilizer	Inorganic Fertilizer
1.	pH	2.80	5.01	4.90	5.10
2.	Phosphorus, P, mg/l	0.51	4.25	3.45	3.07
3.	Sulphate, SO_4^{2-}, mg/l [a]	184.23	1.07	1.11	1.10
4.	Nitrogen, N, mg/l	0.01	0.03	0.03	214.00
5.	Calcium, Ca^{2+}, mg/l	1.40	306.00	325.00	11.65
6.	Potassium, K, mg/l	1.25	674.00	650.00	10,250.00
7.	THUB, Cfu/g [a]	Not Detected	Not Detected	Not Detected	Not Detected
8.	THC, mg/g	110.00	Not Detected	Not Detected	Not Detected

THUB, Total Hydrocarbon-Utilizing Bacteria; THC, Total Hydrocarbon Content

[a] mg/l (milligrams per litre) for liquid samples and Cfu/g (colony forming unit per gram) for solid samples.

3.2 Bioremediation Studies

3.2.1 Changes in the Total Hydrocarbon-Utilizing Bacteria (THUB)

Bioremediation, carried out by THUB, followed an increasing trend for the various soil amendments (Table 2). THUB levels were highest in soil amended with freshly harvested biofertilizer (cell B), reaching 7.5×10^4 CFU/g after seven days of remediation. This likely reflects an active growth phase for THUB in cell B, characterized by high metabolic activity and rapid reproduction. In contrast, bacteria in soil amended with aged biofertilizer (cell A) may have entered a dormant or stationary phase under less favorable conditions, resulting in a lower bacterial count (Osalodion and Ita, 2021). The observed THUB trend in this study was: Cell B > Cell A > Cell C > Control. Overall, THUB increased over time in all the cells (Table 2), consistent with typical increases seen during bioremediation. These results align with reported healthy soil microbial ranges of 10^6–10^9 CFU/g for bacteria and 10^3–10^6 CFU/g for fungi (Das et al., 2011; Tangahu et al., 2017; Ugwoha et al., 2020).

Table 2 further showed that THUB was lowest in the untreated soil (Control) and at higher levels in the portions of soil with treatments (cells A, B, and C). THUB in the samples break down complex hydrocarbon molecules into simpler substances like carbon dioxide and water through biodegradation. They contribute to nutrient cycling in the soil by releasing essential elements like nitrogen, phosphorus, and sulfur, improving soil structure by enhancing aeration and water infiltration and breaking down harmful hydrocarbons, THUB reduce the toxicity of the soil, making it safer for plants and other organisms (Tangahu *et al.,* 2017).

Table 2: Changes in the total hydrocarbon-utilizing bacteria (THUB) days after remediation.

Treatment	Total Hydrocarbon-Utilizing Bacteria (THUB) (cfu/g)					
	7 days	14 days	21 days	28 days	35 days	42 days
Control	2.0×10^4	3.0×10^4	2.0×10^4	4.0×10^4	4.4×10^4	4.50×10^4
A	5.0×10^4	1.7×10^5	1.5×10^5	1.8×10^5	2.2×10^5	2.25×10^5
B	7.5×10^4	1.9×10^5	1.7×10^5	2.0×10^5	3.0×10^5	3.10×10^5
C	4.8×10^4	1.2×10^5	1.4×10^5	1.3×10^5	1.4×10^5	1.30×10^5

A = Aged Biofertilizer**, B** = Fresh Biofertilizer**, C** = Inorganic Fertilizer, **Control** = Contaminated Soil without treatment**.**

3.2.2 Changes in the THC and BRE

THC in hydrocarbon-polluted soil typically decreases over time due to microbial activity. Lighter hydrocarbon components are volatilized, reducing the THC in the soil (Maletic *et al.,* 2009). Table 3 showed that remediation began immediately after the soils were treated from an initial concentration of 110mg/g (see Table 1). After Day 7, cell B showed a reduction from an initial level of 110mg/g in the THC to 95.30mg/g, followed closely by cell A where the THC reduced to 98.54 mg/g. THC in cell C was reduced to 100mg/g. This agrees with the findings of Oludele *et al.* (2021), Johnsen *et al.* (2005), and Lenia *et al.* (2021). The control cell had the lowest biodegradation level because it experienced natural attenuation. The trend in reduction rate continued throughout the bioremediation process of 42 days and the results showed that the biofertilizers had a stronger remediation ability than the inorganic fertilizer. It is important to state that the quality of the biofertilizer produced from the anaerobic degeneration of cow dung may be dependent on the resident time, the shorter the resident time, the better the quality. This is because the freshly harvested biofertilizer outperformed the aged biofertilizer, likely because THUB in cell B were in an active growth phase—exhibiting higher metabolic activity and rapid reproduction—whereas the aged biofertilizer in cell A may have entered a dormant or stationary phase under less favorable conditions, lowering the overall viable count (Osalodion and Ita, 2021; Oludele et al., 2021; Ugwoha et al., 2020).

Table 3: Changes in the THC of the hydrocarbon-contaminated soil days after remediation.

Treatment	Total Hydrocarbon Content (THC) (mg/g)					
	7 days	14 days	21 days	28 days	35 days	42 days
Control	106.00	90.65	85.49	79.65	77.01	72.56
A	98.54	61.87	50.18	47.24	45.09	41.87
B	95.30	57.02	51.10	46.12	42.88	36.50
C	100.00	80.35	72.31	67.28	63.12	54.01

The percentage removal of THC from the hydrocarbon-contaminated soils as illustrated in Figure 1, was in the range of 3.64 - 34.04%, 10.42 - 61.94%, 13.36 - 66.82%, and 9.091 - 50.90% for the control, samples A, B, and C, respectively over the bioremediation period of 42 days. This

range aligns with that reported by Akuma and Durojaye (2020), Oludele *et al*. (2021), and Mbah and Obahiaghon (2018).

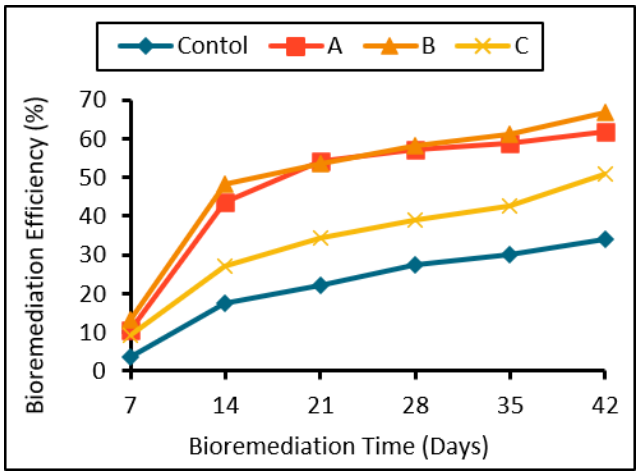


Figure 1: Variation of bioremediation efficiency with time.

3.3 Bioremediation Kinetic Studies

The observed contaminant reduction suggests that the biofertilizer was effective, its performance remained relatively high. In remediation studies, contaminant reduction of ≥90% is typically regarded as highly efficient, whereas reductions of 60–89% are considered moderately efficient, and values below 60% indicate low efficiency and the need for further optimization (Igwilo et al., 2021; Oludele et al., 2021). The results obtained in this study, therefore, showed that the biofertilizer contributed meaningfully to contaminant attenuation. Nevertheless, further improvement may be made by adjusting the biofertilizer application rate, extending the treatment period, optimizing storage or aging conditions, improving amendment delivery, or combining the biofertilizer with other suitable biostimulation or bioaugmentation approaches to enhance contaminant degradation.

The kinetic data of the bioremediation process obtained in this study were assessed by the pseudo-first-order kinetic model in equations 3 and 4 to determine the bioremediation rate constant (K_1) of THC degradation in the various treatment cells. The rate constants of the pseudo-first-order kinetic model for all the treatments are summarized in Table 4. In terms of the reaction rate, a little consideration shows that the treatment cells followed the order: B > A > C > Control. This shows that the fresh biofertilizer degraded the THC faster than any of the other fertilizer variants. This may be attributed to the presence of a relatively large quantity of THUB (7.5×10^5 CFU/g) in cell B (see Table 2) due to the favourable treatment conditions provided by the fresh biofertilizer.

Table 4: Pseudo-first-order kinetic data for the biodegradation of total hydrocarbon content (THC) in the bioremediation of hydrocarbon-contaminated soil using biofertilizer and synthetic (NPK) fertilizer.

S/No.	Treatment	Time (days)	C_t (mg/g)	C_t/C_0	ln (C_t/C_0)	K_1 ($days^{-1}$)
1.	Control (No Fertilizer)	*7*	106.00	0.9636	-0.0371	0.0057
		14	90.65	0.8241	-0.1935	
		21	85.49	0.7772	-0.2521	
		28	79.69	0.7244	-0.3224	
		35	77.01	0.7001	-0.3565	
		42	72.56	0.6596	-0.4161	
2.	A (Aged Biofertilizer)	*7*	98.54	0.8958	-0.1100	0.0196
		14	61.87	0.5625	-0.5754	
		21	50.18	0.4562	-0.7848	
		28	47.24	0.4295	-0.8451	
		35	45.09	0.4099	-0.8918	
		42	41.87	0.3806	-0.9660	

Table 4: *(Continued)*

S/No.	Treatment	Time (days)	C_t (mg/g)	C_t/C_0	ln (C_t/C_0)	K_1 (days^{-1})
3.	B (Fresh Biofertilizer)	*7*	95.30	0.8664	-0.1434	0.0197
		14	57.02	0.5184	-0.6570	
		21	51.10	0.4645	-0.7668	
		28	46.12	0.4193	-0.8692	
		35	42.88	0.3898	-0.9421	
		42	36.50	0.3318	-1.1032	
4.	C (Synthetic Fertilizer)	*7*	100.00	0.9091	-0.0953	0.0151
		14	80.35	0.7304	-0.3142	
		21	72.31	0.6574	-0.4195	
		28	67.28	0.6116	-0.4917	
		35	63.12	0.5738	-0.5555	
		42	54.01	0.4910	-0.7113	

Regression analysis was used to fit the pseudo-first-order kinetic model to the bioremediation data. The plot of ln (C_t/C_o) versus t (time) for the control, illustrated in Figures 2a, gave a linear relationship from where the rate constants (K_1 = 0.0057 day^{-1}), which represents the slope of the line was obtained. The coefficient of determination, r^2 value of 0.9902 was also obtained. This showed that the pseudo-first-order kinetic model did properly fit the experimental data with $r^2 > 0.9$ (Maletic *et al.*, 2009; Maxwell *et al*., 2023). Similarly, plot of ln (C_t/C_0) versus t (time) for sample A (Figure 2b) gave a linear relationship from where the rate constants (K_1) was obtained. A rate constant of 0.0196 day^{-1} and an r^2 value of 0.9143 were obtained for the pseudo-order kinetic model (Figure 2b). With over 90% of explained variance, the pseudo-first-order kinetic model fits the experimental data well, which supports findings in prior studies (Zahed *et al.,* 2011; Kachienga and Momba, 2017; Lenia *et al*., 2021). Furthermore, a similar trend was observed for sample B as presented in Figure 2c, rate constant of 0.0197 day^{-1} and an r^2 value of 0.801 were obtained for pseudo-first-order reaction kinetics. Results showed that over 80% of the variability in the dataset was explained by the model, indicating a good fit (Maletic *et al*. 2009; Amenaghawon *et al.,* 2013; Mbah and Obahioghon, 2018). Additionally, from Figure 2d, a rate constant of 0.0151day^{-}and r^2 values of 0.8296 were obtained for pseudo-first-order reaction kinetics. With high r^2 values, it can be inferred that the biostimulation processes were a pseudo-first-order reaction.

4.0 Conclusions

In this study, liquid biofertilizer from cow dung (Aged and Fresh) and inorganic fertilizer were used in the bioremediation of hydrocarbon polluted soil, and pseudo-first-order kinetic model was used to study the biodegradation of the total hydrocarbon content (THC). Results showed that the THC reductions over the bioremediation period of 42 days were 34.04, 61.94, 66.82, and 50.90% in the Control, A, B, and C cells, respectively. The bioremediation reactions were found to fit the pseudo-first-order kinetic model well with rate constant of 0.0196, 0.0197, and 0.0151day^{-1} for cells A, B, and C, respectively. The cell without treatment (control) had a reaction rate constant of 0.0058 day^{-1}. These results show that hydrocarbon-contaminated soils could be decontaminated using these organic amendments with varied hydrocarbon-degrading abilities proportional to their microbial loads. Thus, the adoption of biofertilizers for the bioremediation of hydrocarbon-contaminated soil could help reduce dependence on chemical fertilizers, support ecological restoration, and contribute to improved food security.

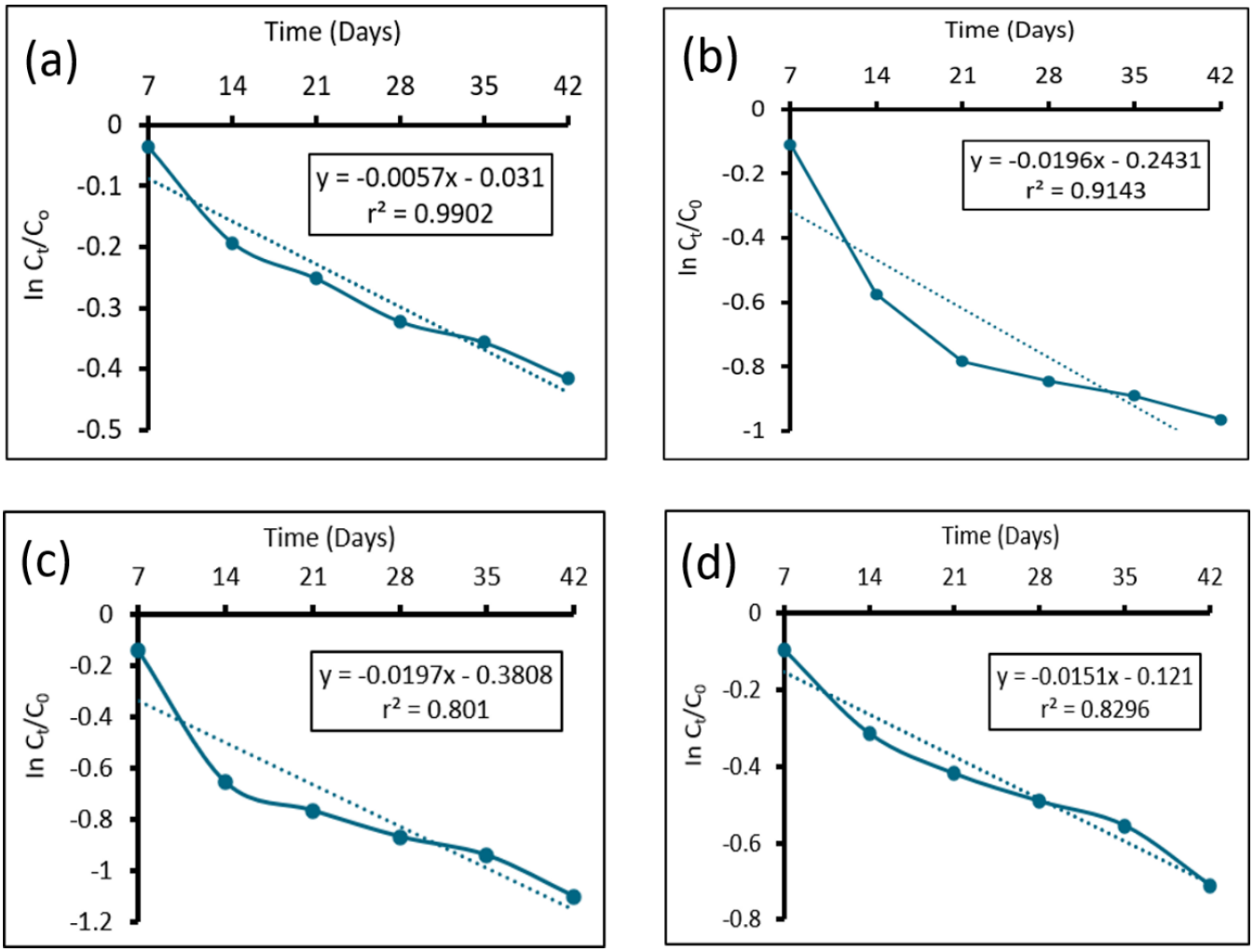


Figure 2: Pseudo-first-order reaction kinetic models for the biodegradation of total hydrocarbon content (THC) in hydrocarbon-contaminated soil for: (a) control cell with no fertilizer, (b) cell A with aged biofertilizer, (c) cell B with fresh biofertilizer, and (d) cell C with synthetic (NPK) fertilizer.

Declarations

Author Contribution

Altraide Ibifuro: Writing the original draft, methodology, investigations, conceptualization.
Akuma A. Oji: writing and data analysis.
Amadi N. Titus: reviewing and editing.
Okparanma N. Reuben: reviewing and editing.

Funding

The authors received no funding from an external source.

Competing Interest

The authors declare no conflict of interest.

Acknowledgements

The Authors are grateful to Engr Durojaye Olalekan S. of the Department of Chemical Engineering, University of Port Harcourt, for his support in the bioremediation process of this study.

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