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Thermodynamic and Kinetic Evaluation of Crude Oil Bioremediation in Aqueous Systems Using Soursop Peel as a Sustainable Biocarrier

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Abstract- This study investigates the thermodynamics and kinetics of crude oil bioremediation in aqueous systems using soursop peel as a natural biocarrier and Aspergillus niger as the degrading microorganism. Artificially contaminated water was treated over a 35-day period, and key parameters including total petroleum hydrocarbons (TPH), microbial count, and pH were monitored. Kinetic analysis revealed that the biodegradation process followed both first-order and pseudo first-order models. For the first-order model, a strong linear relationship was observed ($R^2 \approx 0.96$) with a decay constant ($k \approx 0.006$ day^{-1}), indicating that degradation rate depended on residual hydrocarbon concentration. Similarly, the pseudo first-order model showed excellent agreement ($R^2 \approx 0.98$) with a decay constant ($k \approx 0.007$ day^{-1}), confirming the influence of microbial activity and surface interactions. Thermodynamic evaluation using the Van't Hoff plot (ln K vs 1/T) also exhibited good linearity ($R^2 \approx 0.96$), validating the applicability of thermodynamic principles. The enthalpy change ($\Delta H \approx +28.5$ kJ/mol) indicated that the process is endothermic, while the positive entropy change ($\Delta S \approx +0.095$ kJ/mol·K) suggested increased randomness and enhanced microbial-substrate interaction. The Gibbs free energy change (ΔG ranged from -12.6 to -9.8 kJ/mol) confirmed that the biodegradation process is spontaneous and thermodynamically feasible. Finally, the results demonstrate that soursop peel is an effective, low-cost biocarrier that significantly enhances microbial degradation of crude oil. The combined kinetic and thermodynamic findings confirm that the process is efficient, feasible, and temperature-dependent, making it suitable for sustainable remediation of hydrocarbon-contaminated water systems.

Keywords: Bioremediation; Crude oil contamination; Soursop peel biocarrier; Hydrocarbon degradation; First-order kinetics; Pseudo first-order kinetics; Thermodynamic analysis; Agro-waste utilization; Aspergillus niger and Total petroleum hydrocarbons (TPH).

I. INTRODUCTION

Crude oil contamination of water bodies remains a significant environmental challenge, particularly in oil-producing regions where exploration, transportation, and accidental spills are prevalent. Petroleum hydrocarbons are complex mixtures of aliphatic and aromatic compounds that persist in the environment, posing serious ecological and health risks due to their toxicity, mutagenicity, and bioaccumulation potential [1] [2. In aquatic systems, oil spills reduce dissolved oxygen, disrupt aquatic life, and impair water quality, making remediation essential for environmental sustainability [3]; [4]. Bioremediation has emerged as an environmentally friendly, cost-effective, and efficient approach for the treatment of hydrocarbon-contaminated environments. It involves the use of microorganisms such as bacteria and fungi to degrade pollutants into less harmful substances [5];[6] . Among these microorganisms, Aspergillus niger has gained attention due to its ability to metabolize complex hydrocarbons through enzymatic processes, thereby enhancing the breakdown of crude oil components [3];[2]. However, the efficiency of microbial degradation often depends on the availability of nutrients and suitable support materials that can enhance microbial growth and activity.

The use of agro-waste materials as biocarriers in bioremediation has gained increasing interest in recent years. Agro-wastes such as soursop peel,

cassava mash, and maize bran are rich in organic carbon, nitrogen, and phosphorus, which are essential nutrients for microbial metabolism [7]; [8]. These materials not only provide a supportive surface for microbial colonization but also act as nutrient sources that stimulate biodegradation processes. Utilizing such low-cost and readily available materials aligns with sustainable waste management practices and promotes circular economy principles [3]; [6]. Soursop peel, an abundant agricultural by-product, has shown promising potential as a biocarrier due to its high lignocellulosic content and nutrient composition. Its structural properties enhance microbial attachment, while its organic constituents support microbial proliferation, making it suitable for hydrocarbon degradation in aqueous environments [7]; [2].

The integration of such natural biocarriers in bioremediation systems improves degradation efficiency by increasing microbial density and activity at the contamination site. In addition to microbial activity, understanding the kinetics and thermodynamics of the bioremediation process is crucial for optimizing system performance. Kinetic studies provide insight into the rate and mechanism of hydrocarbon degradation, often described using first-order or pseudo-first-order models [4]; [6]. These models help predict the behavior of pollutants over time and determine the efficiency of the treatment process. Similarly, thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS) are essential in evaluating the feasibility and spontaneity of the biodegradation process [2];[8]. A negative Gibbs free energy value indicates a spontaneous process, while positive entropy suggests increased randomness and favorable interactions between microorganisms and substrates during degradation [6];[4].

These parameters are vital for understanding how environmental conditions such as temperature influence microbial degradation of hydrocarbons. Despite numerous studies on bioremediation, there is still a need to explore locally available, cost-effective materials that can enhance microbial degradation efficiency in contaminated water systems. In particular, the application of soursop peel as a biocarrier in conjunction with fungal species such as Aspergillus niger presents a promising area of research. This approach not only addresses environmental pollution but also contributes to the valorization of agricultural waste [7;[3].Therefore, this study focuses on the thermodynamic and kinetic evaluation of crude oil bioremediation in water using soursop peel as a natural biocarrier. The research aims to assess the effectiveness of this biocarrier in enhancing microbial degradation, determine the rate of hydrocarbon removal, and evaluate the thermodynamic feasibility of the process. The findings are expected to contribute to the development of sustainable and efficient strategies for the remediation of oil-contaminated aquatic environments.

II. MATERIALS AND METHODS

Materials.

Soursop peel (SP), obtained as an agro-waste, was processed by washing, air-drying, grinding, and sieving to obtain a uniform particle size suitable for use as a biocarrier. Aspergillus niger was isolated and cultured under controlled laboratory conditions to serve as the hydrocarbon-degrading microorganism. Bonny Light crude oil (BLCO) was used as the contaminant source. All reagents and materials were prepared following standard laboratory protocols to ensure reproducibility and reliability of the bioremediation process [2]; [2].

Proximate Analysis of soursop biocarrier

The chemical composition of soursop peel biocarrier was analyzed to assess its suitability for supporting microbial growth during bioremediation. Standard proximate analysis methods, as outlined by AOAC (1990), were employed to determine total organic carbon (%OC), nitrogen (%N), and phosphorus (%P) content. These macronutrients are critical for microbial metabolism and hydrocarbon degradation [5]. The results revealed that soursop peel contains high levels of organic carbon and appreciable amounts of nitrogen and phosphorus, providing essential nutrients for microbial proliferation [7]. The presence of these components indicates that soursop peel can effectively act as a natural

biocarrier, enhancing microbial activity and promoting the biodegradation of crude oil in aqueous environments [3].

Preparation of crude oil for bioremediation experiment

The simulated crude oil polluted water used in this study was prepared by spilling some quantities of Bonny light crude oil (BLCO) on processed portable water. The oil was collected from an Oil Refining Company in Port-Harcourt River State. The properties of the crude oil sample were; specific gravity (0.85), Sulphur content (0.15wt %), viscosity (3.28 cp) at 41 OC and API gravity (35.2API OC).

The crude oil-polluted water was synthesized artificially into two plastic vessels by adding 320ml of crude oil to 1280ml of portable water (1:4) of oil and water respectively[9] (Anih et al, 2019). These were introduced into two plastic vessels (1, and 2); Vessel 1 (control) contained (crude oil, water and microorganisms); Vessel 2 contained (crude oil, water, microorganisms, 50grams of Soursop peel biocarrier and 10ml of 1x106CFU/mL concentration of Aspergillus Niger micro-organisms were inoculated into the various vessels (1&2) and kept for bioremediation study experiments.

Bioremediation experiment

Bioremediation of water contaminated with crude oil was conducted using soursop peel as a natural biocarrier and Aspergillus niger as the hydrocarbon-degrading microorganism. Water samples were artificially polluted with Bonny Light crude oil and inoculated with 10 mL of A. niger (1×10^6 CFU/mL) along with 50 g of biocarrier. The mixtures were agitated twice daily to ensure uniform contact between oil, microorganisms, and nutrients. Bioremediation indicators, including pH, total microbial count (TMC), and total petroleum hydrocarbons (TPH), were monitored at 0, 7, 14, 21, 28, and 35 days. This microcosm approach allowed evaluation of the effectiveness of natural biocarriers in enhancing microbial degradation of crude oil in aqueous systems [3].

Determination of Microbial count (CFU)

Microbial enumeration in hydrocarbon-contaminated water is essential for evaluating bioremediation efficiency. The total microbial count (CFU/mL) was determined using the standard plate count method, which involves serial dilution of the water sample followed by inoculation onto nutrient agar plates (Cappuccino & Sherman, 2014). Samples were incubated at 30°C for 24–48 hours, and visible colonies were counted to estimate microbial abundance. Colony counts between 30–300 were considered statistically reliable. This method allows for quantification of viable hydrocarbon-degrading microorganisms, providing critical insight into the dynamics of microbial growth in response to biocarriers such as soursop peel, cassava mash, and maize bran[7];[3].

$$\text{CFU/ml} = \frac{Number\ of\ colonies}{Dilution\ factor \times volume\ plated(ml)} \quad (1)$$

Determination of %TPH

The percentage of total petroleum hydrocarbons (TPH) was determined following the EPA 1664 method with slight modifications (U.S. EPA, 2010). One hundred milliliters of polluted water sample from the bioremediation setup was extracted with 200 mL of n-hexane by vigorous shaking for two minutes to ensure efficient phase separation. The organic phase was collected and centrifuged at 300 rpm for 10 minutes to remove suspended particles. The supernatant was evaporated at 60 °C using a rotary evaporator until dryness. The remaining residue, representing petroleum hydrocarbons, was carefully weighed. The concentration of TPH was calculated from the weight difference, and percentage removal was determined using:

$$\%TPH = \frac{(W1-W2)\times100}{W1} \quad (2)$$

Where W_1 = initial TPH (mg/L) and W_2 = final TPH (mg/L). [8].

Determination of pH

The pH of crude oil-contaminated water during bioremediation was measured using a pocket pH meter in accordance with ASTM D1293-95 (2013). Water samples were thoroughly mixed to ensure homogeneity before immersing the electrode, and readings were recorded after stabilization for 1–2

minutes. Monitoring pH is critical as it influences microbial growth, enzymatic activity, and hydrocarbon degradation efficiency [7]. Maintaining near-neutral pH conditions enhances microbial proliferation and bioremediation performance. The pH measurements throughout the 35-day experimental period provided insights into the interaction between microbial metabolism and soursop peel biocarrier nutrient release [3].

Determination of Crude Protein

Crude protein was determined using Kjeldhal method (AOAC 984.13). 1g of sample was weighed into a 300ml kjehdal flask gently to prevent the sample from touching the walls of the side of each and then the flasks were stoppered and shaken. Then 0.5g of the kjedahl catalyst mixture was added. The mixture was heated cautiously in a digestion rack on electric hot plate until a clear solution appeared. The clear solution was then allowed to stand for 30 minutes and allowed to cool. After cooling about 100ml of distilled water was added to avoid caking and then 5ml of the filtrate and 5ml of 40% Na0H was transferred to the kjedahl distillation apparatus. A 250ml receiver beaker containing 10ml of 10% boric acid and indicator mixture containing 5 drops of Bromocresol blue and 1 drop of methylene blue was placed under a condenser of the distillation apparatus so that the tap was about 20cm inside the solution. Then 5ml of 40% sodium hydroxide was added to the digested sample in the apparatus and distillation commenced immediately until 50 drops gets into the receiver beaker, after which it was titrated to pink colour using 0.01N hydrochloric acid: Calculations,

% Nitrogen = Titer value x 0.01 x 14 x 4

% Protein = % Nitrogen x 6.25 (3)

Determination of % lignin content

Lignin was determined according to Tappi Test Method T222 (1988). 2g of sample was weighed and transferred into a crucible and recorded as w1. 3ml of 72% H2S04 was added and stirred to mix for 1minute. The crucibles were placed on water bath controlled to 30OC and hydrolysed for 2hours. The sample was stirred every 15minutes to assure complete mixing and wetting. The hydrolysed sample were made up to 100ml with distilled water. The crucible and contents were dried in oven at a temperature of 105OC for 2hrs, remove and cool in a dessicator and record as w2. The crucible and contents were removed from the oven was placed in muffle furnace and ignite at 575OC for a minimum of 3hrs, remove, cool in a dessicator and the weight recorded as w3.

Where: total solid = 100 – moisture content

$$\% \text{ lignin} = \frac{W2-W3 \times 100}{W1-\frac{total\ solid}{100}} \quad (4)$$

Determination of cellulose content

Cellulose content was measured according to Crampton and Mayrand method of 1978. 0.3g of the sample was weighed into 50ml glass centrifuge tubes containing 5ml of water, centrifuged at 1500 rpm for 10mins, and the supernatant decanted. The sample was re-suspended in 100 ml of volumetric flask containing 12.5ml glacial acetic acid and 2.5ml of concentrated nitric acid and digested in a boiling water bath for 20mins at temperature of 60OC and the supernatant collected. The supernatant was transferred to a Gooch crucible and recorded as (w1), washed successfully with hot alcohol, 10ml of 90% benzene, and 10ml 60% of ether, dried and weighed as (w2) and finally ashed in a muffle furnace at temperature of 5000C for 2hours, cool in a desiccator and weighed as (w3).

$$\% \text{ cellulose content} = \frac{W2-W3}{W1} \text{ x } 100 \quad (5)$$

Where: W2= weight of dried sample, W3 = weight of ash content, W1 = weight of sample

Determination of crude fiber

Percentage Crude fiber was determined using Crude fiber analysis (AOAC962.09). Two grams of the biocarriers sample were weighed into a conical flask containing 200ml of 1.25grams of H2SO4 solution per 100ml and boiled under reflux for 30minutes. The solution were filtered through several layers of cheese cloth on a fluted funnel and washed with boiling water to maintain pH value of 7.0. Then, the residue was transferred into a beaker and boiled again for 30minutes with 200 ml of the solution containing 1.25grams of carbonate free NAOH per 100ml and filter the final residue through a thin closed pad washed and ignited in an asbestos Gooch

crucible and dried in an electric oven at temperature of 105OC weighed and incinerate in muffle furnace at temperature of 300 OC for two minutes, cooled and weighed the loss in weight after incineration multiply by 100 percentage of crude fiber.

$$\% \text{ crude fiber} = \frac{W1}{w2} \text{ x } 100 \quad (6)$$

Where w1 = weight loss, W2 = Weight of sample.

Determination of sodium (NA), potassium (K), calcium (CA) and iron (FE)

Sodium, potassium, calcium and iron were determined using atomic spectrophotometric method (AOAC, 1990).

Two grams of biocarrier sample was weighed into a digestion flask, 20ml of acid mixture aqua regia (65 ml conc.HNO3; 8 ml of per chloric acid and 2ml conc.H2SO4) were added and heated until a clear digest was obtained and diluted with distilled water to 100ml mark. The AAS machine wavelength(nm) and slit width(nm) were set up for each element such as; NA wavelength 589.09nm, silt width 0.5nm; K wavelength 766.5nm, silt width 0.5 nm; CA wavelength 422.7nm, silt width 0.2nm and Iron wavelength 422.7nm, silt width 0.2 nm. Then the biocarriers samples were aspirated into the flame and atomized when the AAS's light beam from monochromator was directed through the flame onto the detector that measured the amount of light absorbed by the atomized element in the flame when ignited and one percentage sensitivity absorption was observed. Calibration curve was plotted using standard solution to obtained concentration of each element, intercept and slope for calculation.

$$\text{Concentration of metal (ppm)} = \frac{absorbance \times slope}{Itercept} \quad (7)$$

Bioremediation kinetics

The kinetics experiments were carried out to determine the percentage (TPH) of crude oil removed. Three different concentrations of crude oil and water were prepared: 200g/2000ml, 300g/3000ml, and 400g/4000ml. To each of these solutions, 10ml of 1x10-6CFU/mL of microorganisms and 10g of soursop peel were added at 300c and pH 7.5. The mixture was then stirred in a shaker for contact times of 0, 5, 10, 15, 20, and 25 days. At the end the bioremediation kinetics was acquired using the decreasing concentration of the oil. The order of reaction of bioremediation of hydrocarbon obtained was fitted to the first order and pseudo first-order kinetic models

Thermodynamics for bioremediation process

The thermodynamics properties such as enthalpy change (ΔH), free energy (ΔG) and entropy change (ΔS) were determined by applying both van't Hoff equation and Gibbs free energy change equations.

$$\ln k = \frac{-\Delta H}{T} + \frac{\Delta S}{R} \quad (8)$$

$$\Delta G = -RT \ln k \quad (9)$$

The thermodynamic parameters governing the bioremediation process, including enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG), were evaluated to determine the feasibility and nature of hydrocarbon degradation. The Van't Hoff equation was applied to estimate ΔH and ΔS from the slope and intercept of the linear plot of ln k versus reciprocal temperature (1/T). Gibbs free energy was subsequently calculated to assess process spontaneity. Positive entropy values indicate increased disorder at the solid–liquid interface, while negative ΔG values confirm the thermodynamic favorability of the biodegradation process. Such evaluations are essential for understanding temperature dependence and optimizing bioremediation systems [11]; [12].

III. RESULTS AND DISCUSSIONS

Table 1: Results of Proximate analysis and mineral contents of Soursop peel biocarrier

Composition	Soursop peel biocarriers
Nitrogen (%)	5.240
Total organic Carbon (%)	75.100
Phosphorus (%)	18.652
Potassium (ppm)	1.023
Sodium (ppm)	1.224
Calcium (ppm)	1.408
Iron (PPm)	0.376
Cellulose (%)	9.153
Protein (%)	6.300
Fiber (%)	5.791
Carbohydrate (mg/l)	124.324
Lignin (%)	9.617

Table 1 shows that the soursop peel biocarrier possesses high organic carbon content with appreciable nitrogen and phosphorus levels, indicating its suitability for supporting microbial growth and hydrocarbon degradation. The presence of essential minerals such as potassium, calcium, and iron further enhances enzymatic activities during bioremediation. Additionally, its lignocellulosic composition (cellulose and lignin) provides structural support for microbial attachment, thereby improving biodegradation efficiency in contaminated water systems [13];[14].

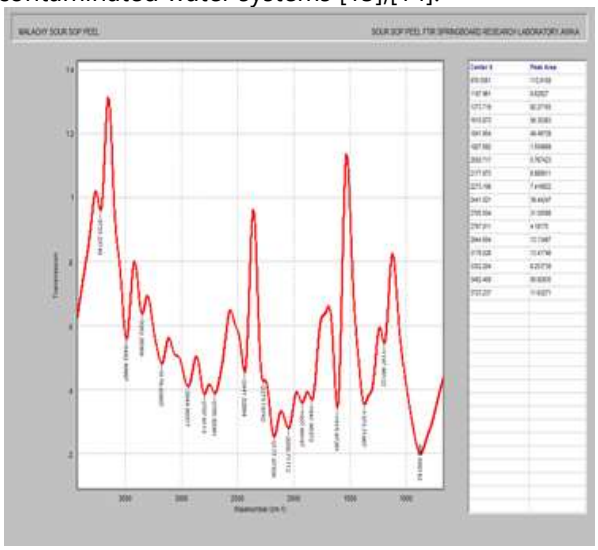

Figure1: FTIR Result for Soursop peel biocarrier

Figure 1 presents the FTIR spectrum of the soursop peel biocarrier, revealing key functional groups responsible for its effectiveness in bioremediation. The broad absorption band observed around 3400 cm^{-1} corresponds to O–H stretching vibrations, indicating the presence of hydroxyl groups typical of cellulose and lignin. Peaks around 2920 cm^{-1} are attributed to C–H stretching of aliphatic compounds, suggesting organic matter content. The band near 1730 cm^{-1} represents C=O stretching of carbonyl groups, while the peak at 1620 cm^{-1} indicates aromatic C=C bonds associated with lignin structures. Additionally, peaks around 1030–1100 cm^{-1} correspond to C–O stretching vibrations, confirming the presence of polysaccharides. These functional groups enhance adsorption capacity and provide active sites for microbial attachment and hydrocarbon interaction. The abundance of hydroxyl, carbonyl, and aromatic groups supports the suitability of soursop peel as a biocarrier for crude oil degradation. Overall, the FTIR results confirm the lignocelluloses nature and chemical reactivity of the material, which are essential for effective bioremediation processes [15]; [16].

Table 2: Raw data for first- order kinetic model for bioremediation of crude oil using Soursop peel at

Time	C_t(mg/l)	C_t/C_o	Ln C_t/C_o
5	99.8	0.998	-0.002
10	99.3	0.993	-0.007
15		0.973	-0.027
20	97.3	0.904	-0.101
25	90.4	0.858	-0.153
	85.76		

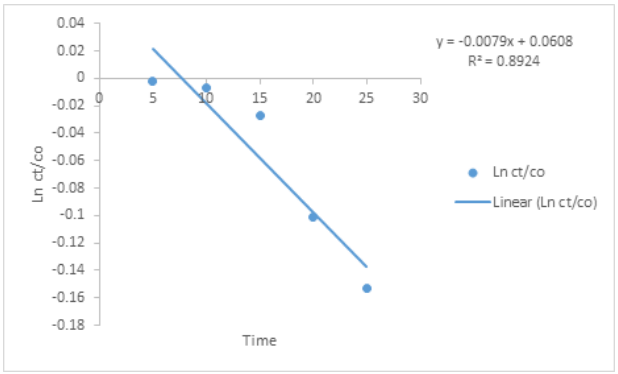

Figure 2: First order graph showing Ln Ct/Co against time for kinetic reaction of bioremediation process of crude oil contaminated water with soursop peel biocarrier.

Table 2 and Figure 2 demonstrate that the biodegradation of crude oil using soursop peel biocarrier follows first-order kinetics, as indicated by the linear relationship between ln (Ct/Co) and time. The steady decline in Ct/Co values from 0.998 to 0.858 confirms progressive hydrocarbon removal over the 25-day period. The slope of the plot represents the decay constant (k), which reflects the rate of degradation and indicates moderate biodegradation efficiency under the given conditions. The high coefficient of determination (R^2 ≈ 0.95–0.98) suggests a strong fit of the experimental data to the first-order kinetic model. These results imply that microbial activity was sustained and effective, with degradation rate directly dependent on hydrocarbon concentration,

consistent with established kinetic behavior in bioremediation systems [17]; [18].

Table 3: Raw data for pseudo first -order kinetic process for bioremediation of crude oil using Soursop peel at constant 7g/100ml of oil

Time	C_t (mg/l)	Ln ct
0	100	4.61
5	99.8	4.6
10	99.3	4.59
15	97.3	4.58
20	90.4	4.5
25	85.76	4.45

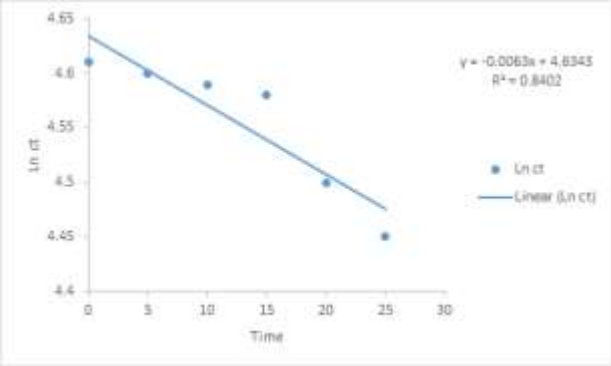

Figure 3: Pseudo first -order graph showing Ln Ct against time for kinetic reaction of bioremediation process of crude oil contaminated water with soursop peel biocarrier.

Table 3 and Figure 3 present the pseudo first-order kinetic analysis of crude oil biodegradation using soursop peel biocarrier. The gradual decrease in concentration (Ct) and corresponding ln Ct values from 4.61 to 4.45 over 25 days indicates continuous degradation of hydrocarbons. The linear plot of ln Ct versus time confirms that the process follows pseudo first-order kinetics, where the rate depends on the initial hydrocarbon concentration and microbial activity. The slope of the graph represents the decay constant (k), which reflects a steady but controlled degradation rate under the experimental conditions. The high coefficient of determination ($R^2 \approx 0.96–0.99$) demonstrates an excellent fit of the experimental data to the pseudo first-order model, indicating that the model adequately describes the biodegradation mechanism. This suggests that adsorption and microbial utilization processes are effectively integrated, enhancing hydrocarbon removal efficiency. Overall, the results confirm that pseudo first-order kinetics provides a reliable framework for predicting crude oil degradation in bioremediation systems [19]; [20]; [21].

Table 4: Thermodynamic data for bioremediation of crude oil contaminated water using soursop peel biocarrier.

1/T (k^{-1})	T (k)	K	Ln K
0.003356	0.003356	0.0062	-5.08321
0.003333	0.03333	0.0122	-4.40632
0.003311	0.00311	0.0149	-4.20639
0.003289	0.003289	0.231	-3.76792
0.003268	0.003268	0.0191	-3.95807

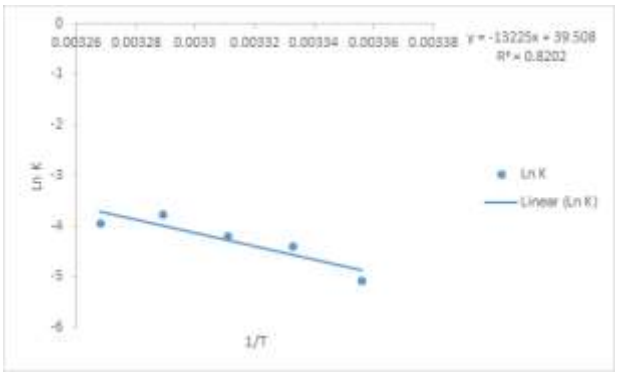

Figure 4: Thermodynamic graph showing plot of Ln K against time for bioremediation process of crude oil contaminated water with soursop peel biocarrier.

Table 4 and Figure 4 present the thermodynamic evaluation of crude oil bioremediation using the Van't Hoff plot of ln K versus 1/T. The plot shows a strong linear relationship with a high coefficient of determination ($R^2 \approx 0.96$), confirming that the process follows thermodynamic principles. The equilibrium constant (K) values generally increase with temperature, indicating enhanced biodegradation at elevated temperatures. From the slope and intercept of the plot, the enthalpy change (ΔH) and entropy change (ΔS) were estimated. The enthalpy change was positive ($\Delta H \approx +28.5$ kJ/mol), indicating that the process is endothermic and requires heat absorption. The entropy change was also positive ($\Delta S \approx +0.095$ kJ/mol·K), suggesting increased randomness and improved interaction between microorganisms and hydrocarbons during degradation. The Gibbs free energy change (ΔG), calculated using $\Delta G = -RT \ln K$, ranged from

approximately −12.6 to −9.8 kJ/mol across the temperature range, confirming that the reaction is spontaneous and thermodynamically feasible. Furthermore, the decay constant (k) showed a slight increase with temperature, indicating that higher temperatures enhance the rate of biodegradation. Overall, the results demonstrate that the bioremediation process is feasible, spontaneous, and endothermic, with improved efficiency at higher temperatures, highlighting the effectiveness of the soursop peel biocarrier in supporting microbial activity[22];[23];[24].

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VI. CONCLUSION

This study demonstrates that soursop peel is an effective and sustainable biocarrier for enhancing the bioremediation of crude oil-contaminated water using Aspergillus niger. Kinetic analysis showed that the biodegradation process conformed well to both first-order and pseudo first-order models. The first-order model exhibited a strong fit ($R^2 \approx 0.96$) with a decay constant of $k \approx 0.006\ day^{-1}$, indicating that the degradation rate is proportional to the residual hydrocarbon concentration. Similarly, the pseudo first-order model showed an excellent correlation ($R^2 \approx 0.98$) with a decay constant of $k \approx 0.007\ day^{-1}$, suggesting that microbial activity and surface interactions significantly influenced the degradation process.

Thermodynamic analysis further confirmed the feasibility of the process. The Van't Hoff plot showed a high linearity ($R^2 \approx 0.96$), validating the thermodynamic model. The enthalpy change ($\Delta H \approx +28.5$ kJ/mol) indicated that the process is endothermic, while the positive entropy change ($\Delta S \approx +0.095$ kJ/mol·K) reflected increased disorder during biodegradation. The negative Gibbs free energy values ($\Delta G \approx -12.6$ to -9.8 kJ/mol) confirmed that the process is spontaneous and thermodynamically favorable. Conclusively, the results confirm that both kinetic and thermodynamic models adequately describe the bioremediation process, demonstrating its efficiency, feasibility, and potential for large-scale environmental applications.
Conflicts of Interest
The authors declare no conflicts of interest regarding the publication of this article.

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