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Removal of Total Petroleum Hydrocarbons from Simulated Crude Oil Contaminated Seawater Using Plantain Stem Derived Biosorbent

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ABSTRACT

This study investigated the application of plantain stem biosorbent for the removal of total petroleum hydrocarbons (TPH) from simulated crude-oil-polluted seawater. The prepared contaminated seawater exhibited a slightly acidic condition (pH 6.47), salinity of 8.51 ppt, and an initial TPH concentration of 213.48 mg L^{-1}. The biosorbent was characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and Brunauer–Emmett–Teller (BET) analysis to evaluate its surface properties and adsorption potential. The results confirmed the presence of oxygen-containing functional groups, porous morphology, and carbon-rich composition suitable for hydrocarbon adsorption. A three-factor Box–Behnken design was employed to optimize the effects of adsorbent dosage, adsorption time, and particle size on TPH removal. The quadratic model was statistically significant (F-value = 109.02, $p < 0.0001$) with a high coefficient of determination ($R^2 = 0.9929$), indicating good agreement between predicted and experimental values. The optimum conditions were obtained at an adsorbent dosage of 2 g L^{-1}, contact time of 20 min, and particle size of 70 μm, achieving a predicted TPH removal efficiency of 95.63%. Adsorption equilibrium analysis showed that the Langmuir model provided a better fit than the Freundlich model, suggesting monolayer adsorption on the biosorbent surface. The study demonstrates that plantain stem, an abundant agricultural residue, is a promising low-cost and sustainable biosorbent for petroleum hydrocarbon remediation in contaminated seawater.

1. Introduction

Petroleum hydrocarbon contamination of marine environments remains a significant global environmental challenge, particularly in regions associated with crude oil exploration, production, transportation, storage, and accidental release. Offshore activities and oil spill incidents introduce complex mixtures of hydrocarbon compounds into aquatic systems, creating persistent pollution problems due to the chemical stability and hydrophobic nature of petroleum-derived substances [1,2]. Crude oil consists of a diverse range of organic components, including saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes, whose distribution and persistence determine their environmental behavior and potential toxicity [3,4]. Among the different indicators used for petroleum contamination assessment, total petroleum hydrocarbons (TPH) are widely applied because they provide an overall measurement of hydrocarbon concentrations present in contaminated environmental matrices [5].

The introduction of petroleum hydrocarbons into seawater can significantly disrupt marine ecosystems by altering physicochemical properties of water, limiting oxygen exchange, and affecting the survival and reproductive performance of aquatic organisms. Persistent hydrocarbon compounds may accumulate within marine organisms and subsequently enter the human food chain through the consumption of contaminated seafood, creating potential ecological and public health concerns [6,7,8]. Due to the complex composition and persistence of petroleum pollutants, effective remediation strategies are required to minimize their long-term environmental impacts.

Several techniques have been employed for petroleum hydrocarbon removal from contaminated aquatic environments, including mechanical recovery, chemical dispersion, thermal treatment, and biological degradation. Although these approaches have demonstrated effectiveness under specific

conditions, their practical application is often restricted by operational complexity, high treatment costs, incomplete pollutant removal, and the possibility of generating secondary environmental impacts [9,10,11]. Consequently, increasing research attention has been directed toward the development of efficient, economical, and environmentally compatible treatment technologies.

Adsorption has emerged as a promising remediation technique for removing petroleum pollutants from water due to its operational simplicity, high removal efficiency, and adaptability to different contamination conditions. The process occurs through the accumulation of pollutants on the surface of an adsorbent material, facilitated by interactions such as hydrophobic attraction, van der Waals forces, pore filling, and surface chemical interactions [12]. Although conventional adsorbents such as activated carbon and synthetic polymer-based materials have been widely investigated for hydrocarbon removal, their application may be limited by production costs, regeneration challenges, and restricted accessibility, particularly in developing regions [13]. These limitations have encouraged the exploration of naturally occurring biomass materials as alternative adsorbents.

Agricultural residues have received considerable attention as potential biosorbents because of their abundance, renewability, biodegradability, and chemical composition. Many plant-based materials possess lignocellulosic structures containing cellulose, hemicellulose, lignin, and various oxygen-containing functional groups that provide active sites for pollutant interaction and adsorption [14,15]. Beyond their remediation capability, the utilization of agricultural waste materials contributes to circular economy principles by transforming discarded biomass into valuable environmental treatment resources rather than allowing uncontrolled disposal [16].

Plantain stem represents one such agricultural residue with considerable potential for biosorption applications. In many tropical agricultural regions, particularly across Africa, large quantities of plantain stems are generated after fruit harvesting and are commonly discarded without significant utilization, contributing to biomass waste management challenges [17]. However, plantain stems are composed primarily of lignocellulosic materials with naturally occurring porous structures and surface functional groups that may facilitate interactions with petroleum hydrocarbon molecules [18,19]. Their availability, low cost, and renewable nature make them attractive candidates for developing sustainable biosorbent materials for marine pollution control.

Previous studies have investigated various agricultural wastes for petroleum contaminant removal [19] however, the application of plantain stem-derived biosorbent for TPH removal from saline aquatic environments remains insufficiently explored. Considering the increasing need for low-cost remediation technologies suitable for oil-producing regions, converting plantain stem waste into an effective biosorbent may provide both environmental and waste-management benefits. Such an approach supports sustainable resource utilization while addressing petroleum contamination challenges.

Therefore, this study aims to characterize plantain stem biosorbent and evaluate its effectiveness for the removal of total petroleum hydrocarbons from simulated crude-oil-polluted seawater. The influence of adsorption conditions on hydrocarbon removal performance is investigated to assess the suitability of plantain stem as a sustainable alternative biosorbent for marine oil pollution remediation.

3.1 Materials and Equipment

The materials used in this study included plantain stem biomass, simulated crude-oil-polluted seawater, and analytical-grade chemical reagents. Plantain stems were collected, processed, and prepared as biosorbent materials for the removal of total petroleum hydrocarbons (TPH) from contaminated seawater. The chemical reagents used during biosorbent preparation and analysis included sodium hydroxide (96% purity, CDH, New Delhi, India), sulphuric acid (98% purity, Fisons, Loughborough, England), nitric acid (99.8% purity, JHD, Shantou, China), and hydrochloric acid (37% analytical grade, Loba Chemie, India). The experimental procedures were carried out using standard laboratory equipment, including measuring cylinders, beakers, conical flasks, separating funnels, magnetic stirrer, vacuum drying oven, autoclave, muffle furnace, and orbital shaker. A MS300 constant-temperature magnetic stirrer (B. Brian, England), Vacutherm VT 6025 air-dry vacuum oven (Thermo Scientific, USA), SX-5-12 electric muffle furnace (PEC Medical, USA), and HY-4A orbital shaking vibrator (Jinotec Scientific, China) were used during biosorbent preparation, treatment, and adsorption experiments.

3.2 Preparation of Simulated Crude-Oil-Polluted Seawater

Simulated crude-oil-polluted seawater was prepared by introducing petroleum crude oil into a saline aqueous medium under controlled laboratory conditions. The saline solution was prepared by dissolving sodium chloride (NaCl) in distilled water, after which 5% (w/v) crude oil was added to the solution to represent petroleum contamination. The resulting crude oil saline water mixture was subjected to continuous agitation using a magnetic stirrer for 90 min to achieve proper dispersion of the oil phase and obtain a homogeneous simulated polluted seawater sample before adsorption experiments.

3.3 Characterization of Simulated Crude-Oil-Polluted Seawater

The initial physicochemical characteristics of the simulated crude-oil-polluted seawater were evaluated before treatment with the plantain stem biosorbent. The prepared samples were collected in clean 2.0 L plastic containers and immediately transported for laboratory analysis. The measured parameters included total dissolved solids (TDS), salinity, electrical conductivity (EC), turbidity, dissolved oxygen (DO), pH, chemical oxygen demand (COD), and total petroleum hydrocarbon (TPH) concentration. These parameters were determined to establish the baseline quality characteristics of the contaminated seawater and provide reference values for assessing the efficiency of the biosorbent during hydrocarbon removal.

3.4 Characterization of Plantain Stem Biosorbent

The prepared plantain stem biosorbent was characterized using Brunauer–Emmett–Teller (BET) surface area analysis, Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM). These analytical techniques were employed to evaluate the surface properties, functional groups, morphological characteristics, and thermal stability of the biosorbent. The characterization results provided insight into the structural features responsible for the adsorption of total petroleum hydrocarbons from contaminated seawater.

3.5 Experimental Design and Batch Adsorption Studies

The adsorption experiments were designed to evaluate the influence of operational parameters on the removal of total petroleum hydrocarbons (TPH) from simulated crude-oil-polluted seawater using plantain stem biosorbent. Three independent variables were investigated: adsorbent dosage, adsorption time, and biosorbent particle size. The selected experimental ranges were established

based on preliminary investigations and adsorption behavior reported for lignocellulosic-based biosorbents. The design factors and their corresponding experimental levels are presented in Table 1.

Table 1: Experimental design factors and levels

Factor	Parameter	Minimum	Maximum	Coded Low	Coded High	Mean
A	Adsorbent dosage (g/L)	1.00	3.00	−1 (1.00)	+1 (3.00)	2.00
B	Adsorption time (min)	10.00	30.00	−1 (10.00)	+1 (30.00)	20.00
C	Adsorbent particle size (µm)	40.00	100.00	−1 (40.00)	+1 (100.00)	70.00

Batch adsorption experiments were conducted using 250 mL conical flasks containing 100 mL of simulated crude-oil-polluted seawater. A predetermined quantity of plantain stem biosorbent was introduced into each flask according to the experimental design conditions. The mixtures were agitated at 150 rpm using an orbital shaker for the specified adsorption periods. After treatment, the samples were separated by filtration, and the filtrates were analyzed to determine the residual TPH concentration. The percentage removal efficiency of total petroleum hydrocarbons was calculated using Equation 1

$$TPH\ removal\ (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

Where C_o and C_f are the initial and final TPH concentration in mg/l, respectively

The adsorption capacity of the plantain stem biosorbent was determined using Equation 2

$$q = \frac{(C_o - C_f) \times V}{m} \quad (2)$$

Where V is the volume of produced water in litres, and m is the adsorbent dose in grams.

3.6 Adsorption Isotherm Studies

The equilibrium adsorption behavior of total petroleum hydrocarbons (TPH) onto the plantain stem biosorbent was evaluated using Langmuir, Freundlich, and Temkin adsorption isotherm models. The models were applied to the equilibrium adsorption data to determine the interaction between TPH molecules and the biosorbent surface and to identify the model that best describes the adsorption process.

The Langmuir model assumes monolayer adsorption onto a homogeneous surface with a finite number of adsorption sites, while the Freundlich model describes adsorption on heterogeneous surfaces [20]. The Temkin model considers adsorbate–adsorbent interactions and the variation of adsorption heat with increasing surface coverage.

The experimental equilibrium data were fitted to the linearized forms of the three models, and the suitability of each model was evaluated using the coefficient of determination (R^2). The model with the highest R^2 value was considered the best fit for describing the adsorption equilibrium behavior of TPH onto the plantain stem biosorbent.

4. Results and discussion

4.1 *Physicochemical Properties of Simulated Crude-Oil-Polluted Seawater*

The physicochemical characteristics of the simulated crude-oil-polluted seawater are presented in Table 2. The measured parameters provide important information regarding the initial quality of

the contaminated seawater and establish baseline conditions for evaluating the performance of the plantain stem biosorbent during TPH removal.

The measured pH value of 6.47 indicates a slightly acidic condition. This deviation from the typical alkaline nature of natural seawater may be attributed to the presence of petroleum hydrocarbons and the formation of acidic intermediates during hydrocarbon oxidation. Changes in pH can influence adsorption behavior by affecting the surface charge of the biosorbent and the interaction between hydrocarbon molecules and active adsorption sites [21].

The total dissolved solids (TDS) and electrical conductivity (EC) values were recorded as 4753 mg/L and 9506 μS/cm, respectively, with a corresponding salinity value of 8.51 ppt. These values indicate a saline environment with lower ionic strength compared with typical open seawater, which generally exhibits higher dissolved salt concentrations [22]. The reduced salinity may be associated with the simulated preparation conditions and dilution effects within the aqueous medium.

The dissolved oxygen (DO) concentration of 3.20 mg/L indicates oxygen depletion within the contaminated water system. This reduction may result from the presence of petroleum hydrocarbons, which promote oxygen consumption during microbial degradation and oxidation processes. The elevated chemical oxygen demand (COD) value of 58.4 mg/L and total organic carbon (TOC) concentration of 35.2 mg/L further indicate the presence of significant organic pollutants capable of consuming dissolved oxygen.

The initial total petroleum hydrocarbon (TPH) concentration was measured as 213.48 mg/L, confirming successful preparation of the crude-oil-polluted seawater. The elevated hydrocarbon concentration provides a suitable contamination level for evaluating the adsorption efficiency of

the plantain stem biosorbent. High TPH concentrations are associated with reduced water quality and potential ecological risks due to the persistence and toxicity of petroleum-derived compounds.

Overall, the physicochemical characteristics confirm that the prepared seawater sample contained significant petroleum contamination and provided an appropriate medium for assessing the hydrocarbon removal capability of the developed biosorbent.

Table 2: Physicochemical Properties of Sea Water

Property	**Value**
pH	6.47
TDS (ppm)	4753
EC (µS/cm)	9506
Salinity (ppt)	8.51
DO (mg/L)	3.20
COD (mg/L)	58.4
TOC (mg/L)	35.2
TPH Content (mg/L)	213.48

4.2 Characterization of Plantain Stem Biosorbent

4.2.1 Fourier Transform Infrared (FTIR) Analysis

The FTIR spectrum of the plantain stem biosorbent is presented in Figure 1. The observed absorption bands indicate the presence of several functional groups associated with lignocellulosic biomass, which contribute to the adsorption of petroleum hydrocarbons from contaminated seawater.

A broad absorption band observed at 3572.74 cm^{-1} corresponds to the stretching vibration of hydroxyl groups (–OH) present in cellulose, hemicellulose, and lignin structures. These hydroxyl-containing groups provide active surface sites capable of participating in intermolecular interactions with adsorbed hydrocarbon molecules.

The absorption peak at 1636.33 cm^{-1} can be attributed to carbonyl (C=O) stretching vibrations of carboxyl-containing compounds and bending vibrations of absorbed water molecules within the biomass structure. The presence of these oxygen-containing functional groups contributes to surface polarity and enhances interactions between the biosorbent and contaminant molecules.

The band observed at 1424.98 cm^{-1} is associated with C–H bending vibrations of aliphatic structures, while the peak at 1098.67 cm^{-1} corresponds to C–O stretching vibrations from alcohol, ether, and glycosidic linkages within the cellulose and hemicellulose components. These structural features are characteristic of plant-based lignocellulosic materials.

The weaker absorption bands detected at 881.29 cm^{-1} and within the lower wavenumber region (approximately 500–400 cm^{-1}) are related to C–H deformation and skeletal vibrations of the biomass matrix. The presence of these functional groups confirms the lignocellulosic nature of the plantain stem biosorbent.

Overall, the FTIR analysis demonstrates that plantain stem contains hydroxyl, carbonyl, and ether functional groups that may contribute to TPH adsorption through surface interactions, hydrogen bonding, and physical retention within the biomass structure. In addition, the lignin-rich components provide hydrophobic regions that can enhance affinity toward non-polar petroleum hydrocarbon molecules. These structural characteristics support the application of plantain stem as a sustainable biosorbent for crude-oil-contaminated seawater remediation.

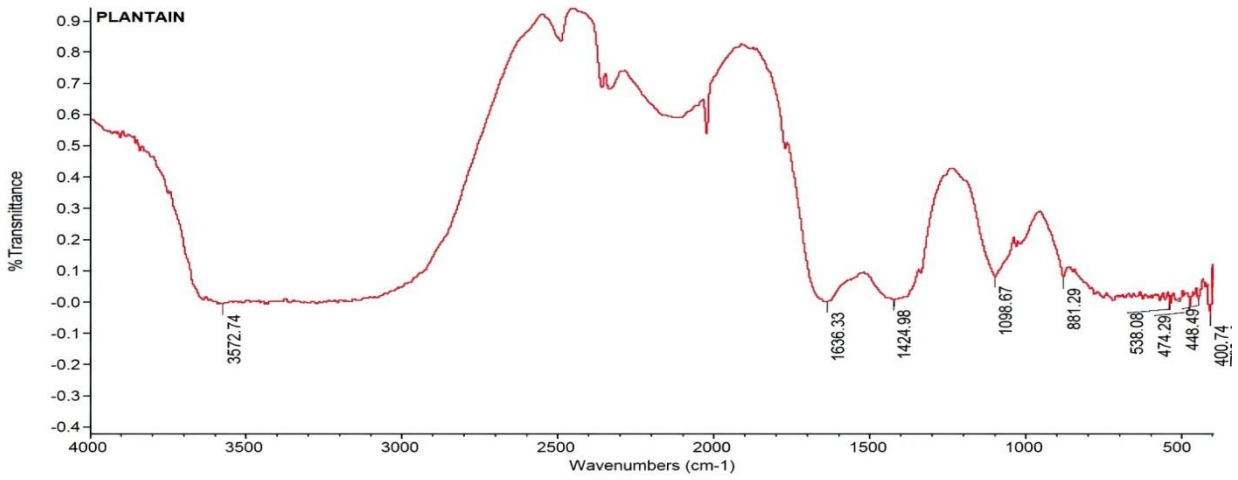


Figure 1: Fourier transform infrared (FTIR) analysis of adsorbent

4.2.2 Scanning Electron Microscopy (SEM) Analysis

The SEM images of the plantain stem biosorbent at different magnifications revealed a heterogeneous, rough, and porous surface morphology as shown in figure 2. At 500× magnification, the surface exhibited irregular layers, fibrous structures, and surface cracks, indicating the presence of external sites available for pollutant interaction.

Increasing the magnification to 1000× and 1500× revealed a more detailed surface structure consisting of irregular particles, cavities, and micro-porous regions. These morphological features increase the accessible surface area and provide potential adsorption sites for petroleum hydrocarbon molecules.

The observed rough texture and porous structure are characteristic of lignocellulosic biomass and contribute to adsorption through physical trapping and surface interactions. The SEM results

confirm that plantain stem possesses suitable morphological characteristics for application as a biosorbent in the removal of total petroleum hydrocarbons from contaminated seawater.

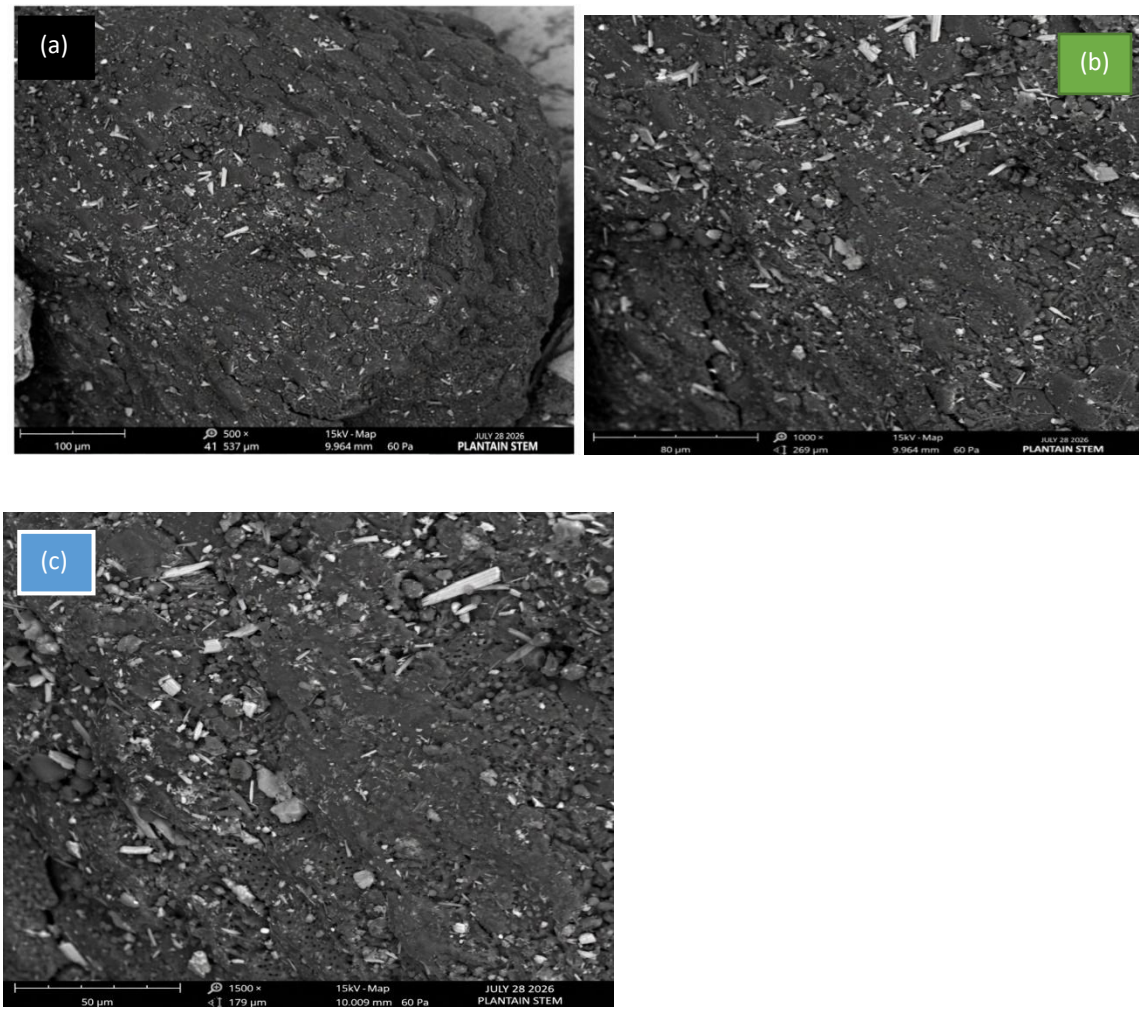


Figure 2: SEM analysis of Adsorbent at different magnifications: (a) 500x,(b) 100x, and (c) 1550x

4.2.3 Energy Dispersive Spectroscopy (EDS) and Elemental Composition

The elemental composition of the plantain stem biosorbent was analyzed using EDS, and the results are presented in Figure 3 and Table 3. The spectrum shows a carbon-rich structure, confirming the lignocellulosic nature of the biomass.

Carbon was the dominant element, with an atomic concentration of 69.68% and weight concentration of 48.94%, indicating the presence of an organic matrix composed mainly of cellulose, hemicellulose, and lignin. Oxygen was also detected, which is associated with oxygen-containing functional groups present in plant-based materials.

In addition to carbon and oxygen, inorganic elements including sodium (Na), calcium (Ca), aluminium (Al), silicon (Si), phosphorus, magnesium, zinc, iron, chlorine, and potassium were detected in varying concentrations. These mineral constituents are commonly associated with natural plant biomass and may influence the surface properties of the biosorbent.

The high carbon content of the plantain stem provides a suitable hydrophobic framework for interaction with petroleum hydrocarbon molecules, while the presence of oxygen-containing components contributes additional active sites for adsorption. The EDS results therefore confirm the suitability of plantain stem as a lignocellulosic biosorbent for TPH removal from contaminated seawater.

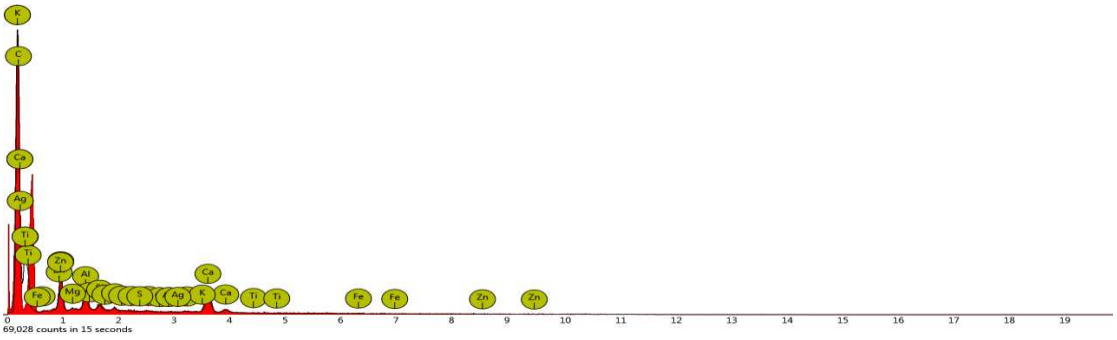


Figure 3: EDX spectrum of Adsorbent

Table 3: Quantitative Elemental Composition

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	69.68	48.94
11	Na	Sodium	15.08	20.28
20	Ca	Calcium	7.44	17.44
13	Al	Aluminium	4.79	7.56
14	Si	Silicon	1.18	1.93
15	P	Phosphorus	0.64	1.16
12	Mg	Magnesium	0.54	0.77
30	Zn	Zinc	0.19	0.73
26	Fe	Iron	0.17	0.56
17	Cl	Chlorine	0.17	0.36
19	K	Potassium	0.12	0.28

4.3 Modeling and Optimization of Seawater Treatment

The experimental results obtained from the Box–Behnken Design (BBD) for the optimization of total petroleum hydrocarbon (TPH) removal using plantain stem biosorbent are presented in Table 4. The design evaluated the effects of three independent variables: adsorbent dosage (A), adsorption time (B), and particle size (C) on TPH reduction.

The experimental runs showed considerable variation in TPH removal efficiency, indicating that the selected operating parameters significantly influenced the adsorption process. The highest TPH

reduction of 96.834% was obtained at the central experimental condition of 2 g/L adsorbent dosage, 20 min contact time, and 70 μm particle size. The repeated centre-point experiments produced similar removal values, demonstrating good reproducibility and stability of the experimental system.

The adsorption performance decreased under extreme operating conditions. The lowest TPH reduction (34.251%) was observed at 2 g/L dosage, 10 min contact time, and 40 μm particle size, suggesting that insufficient contact time limited interaction between the biosorbent surface and hydrocarbon molecules. Similarly, reduced efficiency at some high dosage conditions indicates that excessive biosorbent addition does not necessarily improve removal, possibly due to particle aggregation and reduced effective adsorption sites [23,24].

The results further indicate that intermediate particle size (70 μm) provided better adsorption performance compared with smaller or larger particles. This may be attributed to improved accessibility of adsorption sites and favourable surface interaction between the biosorbent and petroleum hydrocarbons [25,26].

Overall, the BBD experimental matrix demonstrates that adsorbent dosage, contact time, and particle size collectively influence TPH removal efficiency. The obtained dataset provides a suitable basis for developing a second-order response surface model and determining the optimum conditions for crude-oil-polluted seawater treatment using plantain stem biosorbent.

Table 4: Experimental Design Values

Run	Adsorbent dosage (g/L)	Contact time (minute)	Particle size (μm)	TPH Reduction (%)

1	2	20	70	90.834
2	2	20	70	96.834
3	1	20	40	49.098
4	2	20	70	96.834
5	2	10	100	61.901
6	2	20	70	96.834
7	1	20	100	56.745
8	2	30	40	68.372
9	3	20	40	43.895
10	1	30	70	51.298
11	2	20	70	96.834
12	2	30	100	72.265
13	3	30	70	73.622
14	3	10	70	43.539
15	2	10	40	34.251
16	3	20	100	76.784
17	1	10	70	46.812

4.3.1 Analysis of Variance (ANOVA) of the Quadratic Model for TPH Reduction

The ANOVA results for the quadratic model of TPH reduction are presented in Table 5. The model was statistically significant (F-value = 109.02, $p < 0.0001$), indicating a strong relationship between the experimental variables and TPH removal efficiency. All linear, interaction, and quadratic terms were significant ($p < 0.05$), confirming their influence on the adsorption process.

The model showed good agreement with the experimental data, with $R^2 = 0.9929$, adjusted $R^2 = 0.9838$, and predicted $R^2 = 0.9418$. The non-significant lack-of-fit ($p = 0.4341$) confirms the adequacy of the model, while the high adequate precision value (28.9167) and low coefficient of variation (4.06%) indicate good reliability and reproducibility. Therefore, the quadratic model was considered suitable for predicting and optimizing TPH removal from simulated crude-oil-polluted seawater using plantain stem biosorbent.

Table 5: ANOVA Quadratic Model of TPH Reduction

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	7488.06	9	832.01	109.02	< 0.0001	Significant
A-Adsorbent dosage	143.54	1	143.54	18.81	0.0034	
B-Adsorption time	781.19	1	781.19	102.36	< 0.0001	
C-Adsorbent Particle	649.42	1	649.42	85.10	< 0.0001	
AB	163.80	1	163.80	21.46	0.0024	
AC	159.29	1	159.29	20.87	0.0026	
BC	141.10	1	141.10	18.49	0.0036	
A^2	2073.53	1	2073.53	271.70	< 0.0001	
B^2	1621.60	1	1621.60	212.49	< 0.0001	
C^2	1190.08	1	1190.08	155.94	< 0.0001	
Residual	53.42	7	7.63			

Lack of Fit	24.62	3	8.21	1.14	0.4341	not significant
Pure Error	28.80	4	7.20			
Cor Total	7541.48	16				
	R^2	0.9929	Adjusted R^2	0.9838	Predicted R^2	0.9418
	Adequate Precision	28.9167	Std. Dev.	2.76	Mean	68.04
	C.V. %	4.06				

4.4 Response Surface Plots of TPH Removal from Polluted Seawater

The three-dimensional response surface plots generated from the quadratic model illustrate the combined effects of adsorbent dosage, adsorption time, and particle size on TPH removal efficiency. The curved surfaces observed in the plots confirm the significance of the quadratic terms identified in the ANOVA analysis, indicating nonlinear interactions among the process variables. The response surfaces show that maximum TPH removal occurs within intermediate operating conditions, while extreme factor combinations result in reduced adsorption efficiency. This behavior suggests that excessive or insufficient levels of the variables may limit pollutant removal due to reduced mass transfer, site saturation, or particle interaction effects.

4.4.1 Effect of Adsorbent Dosage (A) and Adsorption Time (B)

The response surface plot showing the interaction between adsorbent dosage and adsorption time, with particle size maintained at its central level, is presented in Figure 4. The surface exhibits a curved profile, indicating significant interaction between the two factors.

Low adsorbent dosage and short contact time resulted in lower TPH removal, while increasing both variables improved adsorption efficiency. The highest removal efficiency was obtained around 2 g/L adsorbent dosage and 20–25 min contact time, where sufficient adsorption sites and adequate interaction time promoted hydrocarbon uptake.

The decline in removal efficiency beyond the optimum region indicates the presence of quadratic effects, suggesting that further increases in dosage or contact time provide limited improvement due to possible saturation of adsorption sites and reduced adsorption efficiency [27,28]. The positive interaction between dosage and contact time demonstrates that effective TPH removal depends on the combined contribution of available adsorption sites and sufficient contact duration [29,30].

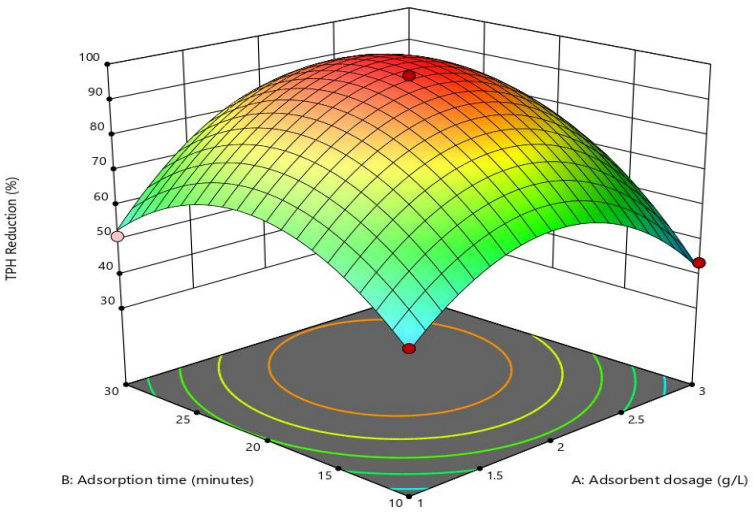


Figure 4: Interaction of adsorption dosage (A) and adsorbent time (B) on TPH removal

4.4.2 Effect of Adsorbent Dosage (A) and Particle Size (C)

The response surface plot illustrating the interaction between adsorbent dosage and particle size, with adsorption time maintained at the central level, is presented in Figure 5. The plot shows that maximum TPH removal occurs near the optimum conditions of 2 g/L adsorbent dosage and 70 µm particle size.

Reduction in removal efficiency was observed at very low or high dosage levels and at extreme particle sizes (40 and 100 µm). This behavior indicates that intermediate particle size provides better accessibility of adsorption sites, while excessive dosage or unsuitable particle size may reduce adsorption efficiency due to particle aggregation or diffusion limitations [31,32].

The observed interaction between dosage and particle size confirms that both factors collectively influence the adsorption performance of plantain stem biosorbent. An optimum balance between available adsorption sites and surface accessibility is therefore required for effective TPH removal.

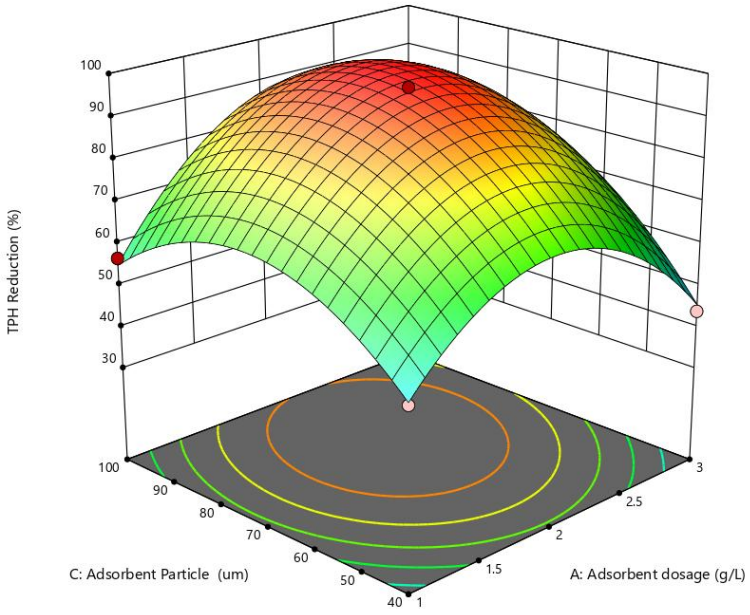


Figure 5: Interaction of adsorbent dosage (A) and adsorbent particle size (B) on TPH removal

4.4.3. Effect of Adsorption time (B) and Adsorbent particle size (C)

The response surface plot illustrating the combined effect of adsorption time and particle size, with adsorbent dosage maintained at the central level, is presented in Figure 6. The plot shows maximum TPH removal near the optimum conditions of 20–25 min contact time and 70 µm particle size.

Lower removal efficiency was observed at short contact times and extreme particle sizes (40 and 100 µm). Increasing contact time improved hydrocarbon uptake by allowing greater interaction between the pollutant molecules and available adsorption sites. However, intermediate particle size provided the best performance, as very small particles may promote aggregation [33] while larger particles reduce accessible surface area and diffusion efficiency [34]. The observed response pattern confirms the significant quadratic and interaction effects of adsorption time and particle size on TPH removal. An appropriate balance between contact duration and particle size is therefore essential for achieving efficient adsorption using plantain stem biosorbent.

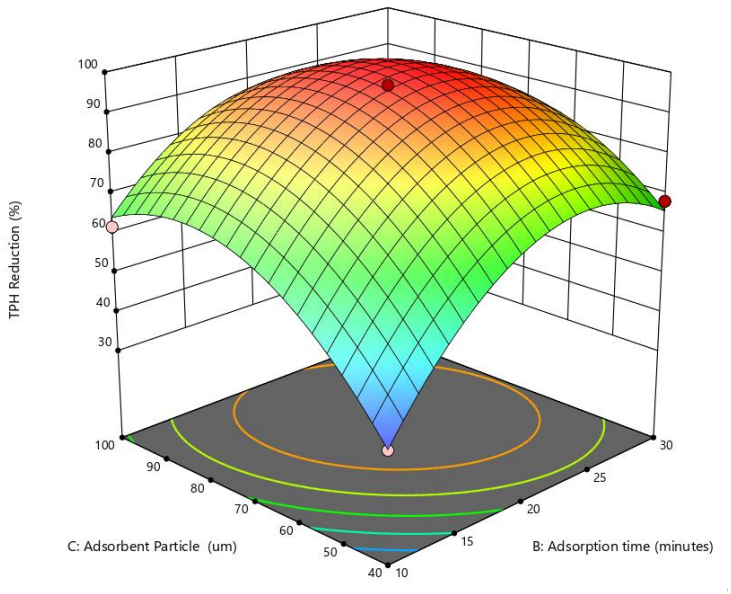


Figure 6: Interaction of adsorption time (B) and adsorbent particle size (C) on TPH removal

4.5 Parity Plot of Predicted and Actual TPH Reduction

The parity plot comparing the predicted and experimental TPH reduction values is presented in Figure 7. The data points are closely distributed around the ideal regression line (y = x), indicating strong agreement between the model predictions and the experimental results.

The minimal deviation between the predicted and actual values confirms the accuracy of the quadratic model in describing the effects of adsorbent dosage, adsorption time, and particle size on TPH removal. This observation agrees with the high statistical performance obtained from the ANOVA analysis (R^2 = 0.9929, adjusted R^2 = 0.9838, predicted R^2 = 0.9418), confirming the reliability of the model for predicting TPH reduction using plantain stem biosorbent.

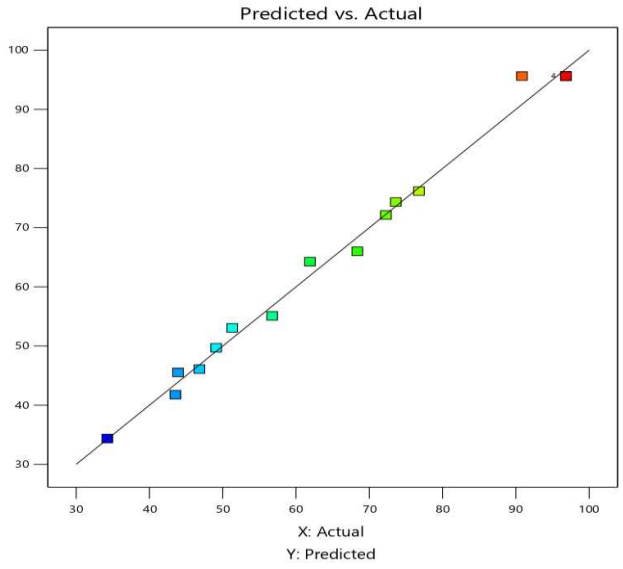


Figure 7: Parity plot of predicted and actual TPH removal percentage

4.6 Optimum Conditions for TPH Removal from Seawater

The optimum operating conditions for TPH removal using plantain stem biosorbent were determined using the Box–Behnken Design optimization model as shown in Figure 8. The predicted optimum conditions were obtained at an adsorbent dosage of 2 g/L, adsorption time of 20 min, and particle size of 70 µm.

Under these conditions, the model predicted a maximum TPH reduction of 95.634%, which is comparable with the experimental maximum removal value of 96.834%. The selection of intermediate values for all three variables indicates that the adsorption process is influenced by the balance between available adsorption sites, contact duration, and surface accessibility [35].

The optimum response obtained at the central region of the design space agrees with the significant quadratic effects observed in the ANOVA results. Deviations from these conditions resulted in reduced TPH removal, confirming that the selected operating parameters provide the most favorable conditions for efficient crude-oil removal from seawater using plantain stem biosorbent.

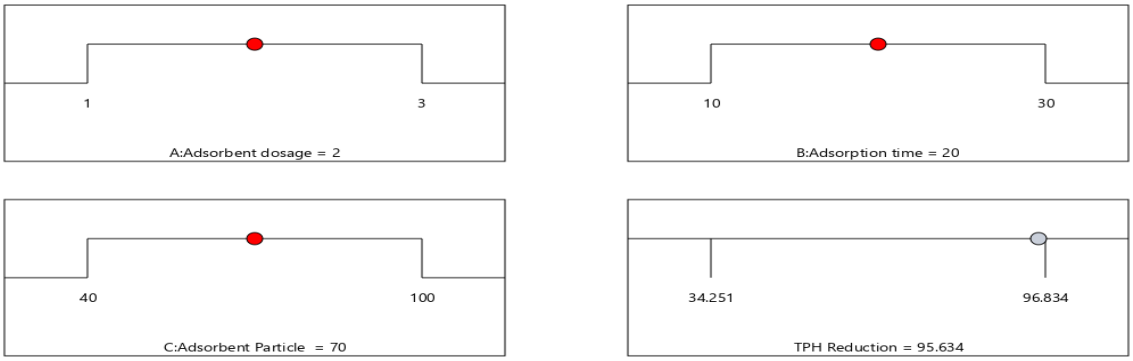


Figure 8: Ramp Plot of TPH Removal

4.7 Langmuir I and Freundlich Isotherm

Figure 9, shows the linear Langmuir isotherm plot of Ce/qe versusCe for TPH adsorption. The data points align closely along the fitted straight line $\frac{C_e}{q_e}$=0.0151 Ce+0.2835 with a high coefficient

of determination (R^2=0.9921). This excellent linearity confirms that the adsorption process follows the Langmuir model, indicating monolayer coverage on a homogeneous adsorbent surface with a finite number of identical active sites and negligible interaction between adsorbed molecules.

From the slope and intercept, the maximum adsorption capacity (qm) and Langmuir constant (K_L) can be readily calculated, further supporting the favourable and well-defined nature of TPH uptake under the studied conditions [36].

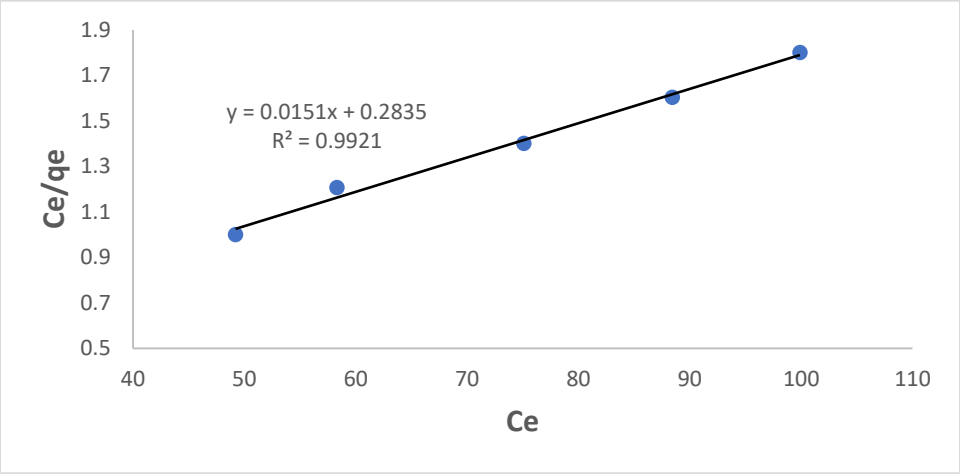


Figure 9: The Langmuir Isotherm Plot

Figure 10, presents the linear Freundlich isotherm plot of log qe versus log Ce for TPH adsorption. The data points yield the fitted equation: log qe =0.2092 logCe+1.3299, with a coefficient of determination R^2=0.8788. Although a moderate linear trend is observed, the relatively lower R^2 value (compared with the Langmuir plot, R^2=0.9921) indicates that the Freundlich model provides a poorer description of the equilibrium data. The slope ($^1/_n = 0.2092$) suggests favourable adsorption (n>1), yet the overall fit confirms that TPH uptake is better represented by monolayer coverage on a homogeneous surface (Langmuir) than by multilayer adsorption on a heterogeneous surface (Freundlich).

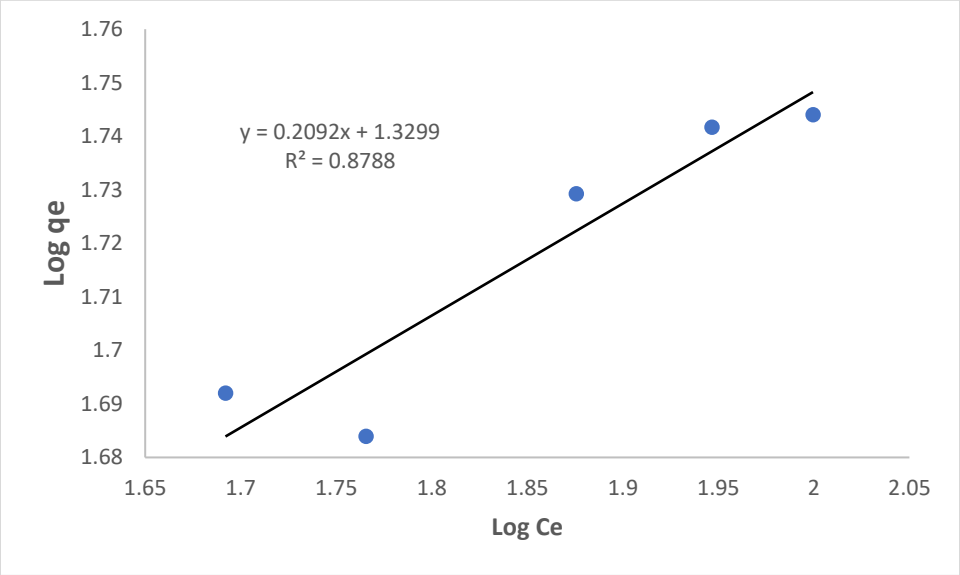


Figure 10: The Freundlich Isotherm Plot

5. Conclusion

This study demonstrated the effectiveness of plantain stem-derived biosorbent for the removal of total petroleum hydrocarbons from simulated crude-oil-polluted seawater. Characterization analyses using FTIR, SEM, EDS, and BET confirmed the presence of functional groups, carbon-rich composition, and favorable surface characteristics that support hydrocarbon adsorption.

The Box–Behnken Design model effectively described the adsorption process, showing that adsorbent dosage, adsorption time, and particle size significantly influenced TPH removal. The optimum conditions were obtained at 2 g/L adsorbent dosage, 20 min contact time, and 70 µm particle size, with a predicted TPH reduction of 95.634%, closely agreeing with the experimental result.

The findings confirm that plantain stem waste can serve as a low-cost and sustainable biosorbent for petroleum hydrocarbon remediation in contaminated seawater. Further investigations on regeneration potential and application under real marine pollution conditions are recommended.

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Authors Contributions

Rockson-Itiveh, David Emoefe: Conceptualization, Literature review, Formal analysis, writing original draft, Writing review and editing**. Marcel Ajogri:** Literature review, Formal analysis, Writing review and editing. **Mabel Keke:** Literature review, Data curation, Writing review and editing. **Anakpoha Cyril:** Literature review, Formal analysis, Writing review and editing. **Fabian Ozioko Chidiebere:** Literature review, Writing review and editing. **Okpo Onoriode Samson:** Literature review, Data curation, Writing review and editing. **Wisdom Ulakpa:** Literature review, Writing – review and editing.

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Data availability

The data used during the current study are present in the manuscript.

Declarations

Ethical approval

Not Applicable. This study does not involve human research participants or live vertebrates.

Consent to participate

Not applicable. This study does not involve human research participants.

Consent to publish

Not applicable. This study does not involve participants whose personal data or information require consent for publication.

Competing interests

The authors declare no competing interests.

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