

Article

Application of Cogon Grass (*Imperata cylindrica*) as Biosorbent in Diesel-Filter System for Oil Spill Removal

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Abstract: *Imperata cylindrica*, often known as cogon grass, is a low-cost and useful sorbent for absorbing oil and optimising processes. The effects of temperature, time, packing density and oil concentration on oil absorption efficiency were investigated and optimised utilising one-factor-at-a-time (OFAT) and response surface methodology (RSM) approaches. Temperature and oil concentration are two important variables in the oil absorption process. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analysis were used to characterise cogon grass. After treatment and oil absorption, the FTIR method indicated new formation and deformation of functional groups, while SEM revealed changes in the surface and texture of cogon grass, including a roughened and jagged surface. Validation of the RSM model yielded 93.54% efficiency with 22.45 mL oil absorbed at 128 °C temperature and 36 (v/v)% oil concentration while keeping packing density and time constant at 30 min and 0.20 g/cm³, respectively. This study may provide an insight into the usefulness of a statistical approach to maximise the oil absorption of cogon grass as an oil sorbent.

Keywords: *Imperata cylindrica*; oil absorption efficiency; one-factor-at-a-time (OFAT); response surface methodology (RSM)

1. Introduction

Oil spills cause serious damage to the environment as they are not zone-free from anthropogenic pollutants. The unfavourable effects of spilled oil on ecosystems as well as the long-term repercussions of pollution demand an efficient clean-up in the affected areas. In response to an oil spill event, the common technologies developed are categorised into four different types, namely chemical methods using dispersants and solidifiers, mechanical recovery such as booms, skimmers and sorption, biological methods or bioremediation, and in situ burning [1,2]. However, most approaches used to date for dealing with oil spills have proven to be less effective.

Nowadays, much focus is drawn on sorption for oil clean up since it has a significant possibility for total oil removal from water and produces no secondary pollution [3]. Natural inorganic, natural organic, organo-mineral and synthetic oil sorbents are the four basic categories of oil sorbent. Good sorbent material should have a high affinity to sorb, hydrophobic and oleophilic properties, be evenly distributed, trap liquid oil within their unique structure and have a low material cost [4]. Recently, agricultural waste has been gaining attention in research as natural sorbent, owing to its high lignocellulosic content, ecologically friendly, non-toxic, degradable, cheap and abundant nature [5,6].

Numerous natural sorbents such as cotton, Kapok fibres, moss, straw, wool, sawdust and peat have been reported to be an excellent alternative to replace commercial products [7–10]. Some of these materials were reported to have a high reusability rate [11]. However, the natural sorbent usually still encounters the drawbacks of dusty, low adsorption capacity and difficulty to be used under windy conditions [12,13]. Some natural organic sorbents absorb both oil and water, causing the sorbents to sink. As a result, the hydrophobicity (water repelling) and oleophilicity (oil attracting) of sorbents, time retention, oil recovery from sorbents, the volume of oil sorbed per unit weight of sorbent as well as the reusability and biodegradability of sorbents are all important elements to consider while collecting oil [14,15].

Cogon grass (CG) is a highly invasive warm-season perennial grass that impacts agriculture and ecosystem health [16]. It can be found on every continent. It grows to a height of 30 to 150 cm and is widely distributed across Asia and the North America, where it has been reported as infesting [17,18]. The grass covers more than 50% of forest land areas throughout moist tropical regions. In reaction to a disturbance like herbicide treatment, fire, mowing, or the first severe frost, CG might begin flowering at other periods of the year [19]. CG is a hardy grass that can withstand drought, shade, salinity and dampness. It thrives in coastal locations, disturbed regions, natural forests, planted forests, range or grasslands, riparian zones, scrub/shrublands, urban areas, and wetlands [20]. Its resistance to heat leads to breakage and it may penetrate the soil up to 4 feet in depth. It may also be used as forage grass and to prevent soil erosion [21].

CG seeds may infiltrate and develop in established native plant communities, choking out even the most hardy native species [16,22]. As a result, natural disasters and human disturbances promote the dissemination of CG and establishment of seed [23]. In Malaysia, CG is abundantly available along the roadside and open areas with no economic value. Without any use, CG ends up as garden waste. Loh et al. [24] reported the compositions of CG consist of 34.1% carbon, 6.6% hydrogen, 1% sulphur, 0.8% nitrogen, 35.1% cellulose, 27.6% hemicellulose and 16.5% lignin.

In the past, CG has been researched as an adsorbent used to remove heavy metals and dyes [25]. The rough and jagged morphology has made the grass suitable for biosorption. A previous study has reported that CG could retain more than 96% of absorbed engine oil, indicating the strong oil retention capacity of the CG [26]. On the other hand, the flower of CG has a high sorptive capacity, which shows attributes of a hydrophobic nature and good oil-wettability [27]. Therefore, the present study aims to investigate the potential of *Imperata cylindrica* for oil spill removal from polluted seawater by using the diesel-filter system. The chemical content of *I. cylindrica* was studied and various parameters affecting oil removal efficiency including temperature, time, packing density, and oil concentration were investigated by means of one-factor-at-a-time (OFAT) and response surface methodology (RSM).

2. Materials and Methods

2.1. Sample Collection and Preparation

Imperata cylindrica grass was collected from an abandoned green compound around Universiti Putra Malaysia (UPM) throughout the study in March–September 2021. The stem, flower and leaf part of grass were manually separated. The stem and flower parts were removed; only leaves were used. Before sun-drying, the leaves were cut into

pieces of 5 cm long and thoroughly washed under running tap water to eliminate dirt and contaminant. The sample was further sun-dried for 8 h for 7 d until reaching constant weight. The dried sample was stored in a zip lock bag until further analysis.

2.2. Diesel-Seawater Mixture Preparation

The diesel (PETRONAS *Dynamic Diesel Euro 5*) used in this experiment was bought from a nearby petrol station, Petronas UPM Serdang. Seawater (salinity: 15–19 ppt, pH: 7.50–8.50) was collected from Pantai Port Dickson, Negeri Sembilan (2.5011° N, 101.8373° E). A mixture consisting of 40 mL diesel and 400 mL seawater was prepared in a 1000 mL beaker for each replicate.

2.3. Experimental Setup

Figure 1 shows the experimental setup for the screening and optimisation process. An opened bottle (400 mL) that acted as a column with 5 cm diameter and 25 cm height was attached to the tripod stands. A holder made of mesh wire (5 cm diameter and 10 cm height) and filled with samples was inserted inside the column. A 500 mL measuring cylinder was placed underneath the column inlet to collect the remaining oil and water effluents after pouring and dripping. The diesel-seawater solution was poured into the opening of the column and left to drip for 10 min. Subsequently, the final weight and volume of oil and water effluents were recorded. All experiment was carried out in triplicates at room temperature of 22 ± 1 °C.

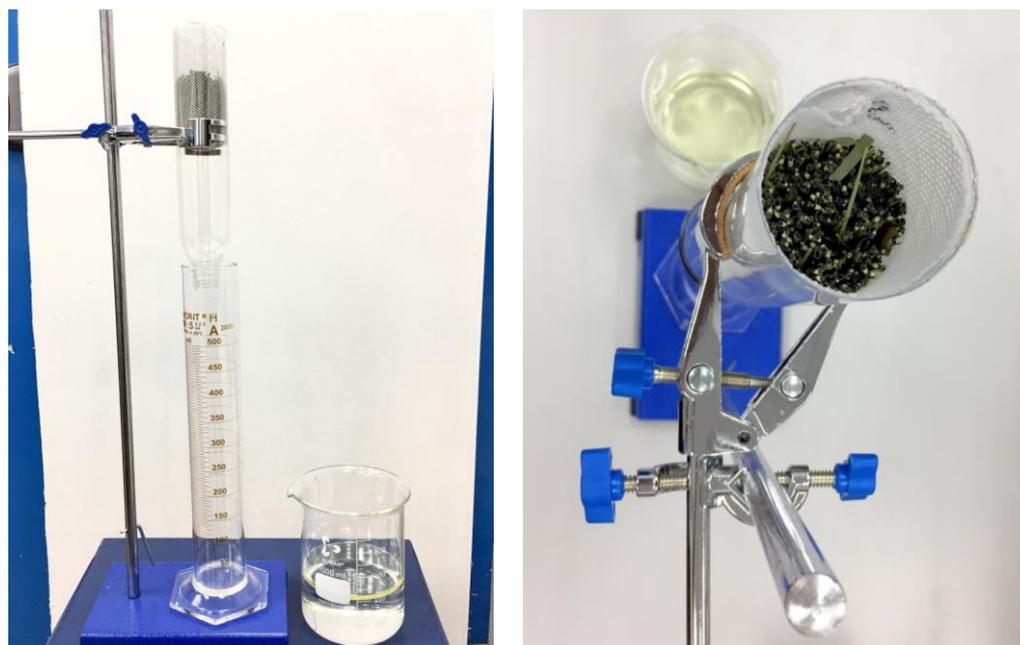


Figure 1. Experimental setup in laboratory for determination of sorption capacity and efficiency of diesel absorption.

2.4. Preliminary Screening of Cogon Grass

About 14 g of untreated and treated CG leaves were tested with diesel-seawater solution (40 mL of diesel and 400 mL of seawater). Treated CG was subjected to heat treatment at 120 °C for 60 min using a laboratory drying oven (forced convection oven) with an accuracy of ± 1 °C (Taisite Lab Sciences Inc., New York, NY, USA). The preliminary screening was carried out as shown in an experimental setup to test the sorption capacity, oil and water absorption efficiency. The sorption capacity (Equation (1)) was determined

following the standard protocol described in the American Society for Testing and Materials (ASTM) F726-99 [28].

$$\text{Oil sorption capacity (g/g)} = \frac{S_i - S_f}{S_i} \quad (1)$$

where S_i is the initial weight (g) of sample before sorption and S_f is the final weight (g) of sample after sorption.

Meanwhile, the efficiency of diesel and seawater absorbed (Equation (2)) was determined using the following formula [26]:

$$\text{Efficiency of diesel/seawater absorbed (\%)} = \frac{D_i - D_f}{D_i} \times 100\% \quad (2)$$

where D_i is the initial volume (mL) of diesel/water before sorption and D_f is the final volume (mL) of diesel/water after sorption.

2.5. One-Factor-at-a-Time (OFAT) Optimisation Approach

The conventional approach, OFAT, was employed to optimise the oil absorption. The parameters were arranged accordingly based on significant importance as they are not dependent on one another: heat treatment (110, 120, 130, 140, and 150 °C), time of heating (15, 30, 45, 60, and 75 min), packing densities (0.12, 0.14, 0.16, 0.18, and 0.20 g/cm³) and oil concentration (5, 10, 15, 20, 25, 30, and 35 (v/v)%). The data of different parameters were subjected to one-way analysis of variance (ANOVA) using GraphPad Prism software (GraphPad Inc., San Diego, CA, USA, version 8.0.2). The significant difference ($p < 0.05$) between means was compared by Tukey's multiple range test.

2.6. Statistical Respond Surface Methodology (RSM) Optimisation

A statistical method using RSM was performed to optimise the treatment process of CG further. In contrast to OFAT, RSM is more likely to be systematic, time-saving, and cost-effective by reducing the number of experimental runs. In this study, Plackett Burman design (PBD) and central composite design (CCD) were used to analyse the experimental data using Design Expert software (Stat-Ease Inc., Minneapolis, MN, USA, version 13.0.5).

2.6.1. Plackett Burman Design (PBD)

Four independent parameters, including temperature, time of heating, packing density and oil concentration, were evaluated at minimum (−1) and maximum (+1) levels (Table 1) through PBD's factorial model. The analysis revealed 18 experimental designs in which the oil absorption efficiency was employed as a response variable for screening significant parameters.

Table 1. Experimental values and levels of independent variables tested in Plackett Burman design (PBD).

Code	Name	Units	Experimental Value	
			Minimum (−1)	Maximum (+1)
A	Temperature	(°C)	110.00	130.00
B	Time	min	30.00	75.00
C	Packing density	g/cm ³	0.14	0.20
D	Oil concentration	(v/v)%	20.00	35.00

2.6.2. Central Composite Design (CCD)

Following PBD, CCD was employed to generate the response surface of the identified significant parameters ($p < 0.05$). Two variables influencing the oil absorption are listed in Table 2 where each factor was studied at five levels with two axial points (+2, −2), two factorial points (+1, −1) and one central point (0). Thus, in 13 experiments run,

two significant variables with five centre points were assessed. Based on a second-order polynomial equation, the quadratic model of CCD (Equation (3)) was developed to describe the relationship between response and independent factors as follows:

$$Y = \beta_0 \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{1 \leq i < j \leq k} \beta_{ij} X_i X_j \quad (3)$$

where Y is the oil absorption (response), β_0 is the model intercept, β_i is the linear coefficient, β_{ii} is the quadratic coefficient, X_i and X_j are the independent variables and k is the number of variables [29]. The significance of the model and regression coefficients was determined using analysis of variance (ANOVA). The interaction among the components was determined using three-dimensional response surface plots based on the statistical parameters collected, including the R^2 and the model's lack of fit. All experiments were performed in triplicate.

Table 2. Experimental values and levels of the selected independent factors for central composite design (CCD).

Code	Variables	Units	Experimental Value				
			(−2)	(−1)	(0)	(+1)	(+2)
A	Temperature	(°C)	101.716	110.00	130.00	150.00	158.284
B	Oil concentration	(v/v)%	20.8579	25	35.00	45.00	49.121

2.7. Chemical Content Analysis and Characterisation of Cogon Grass

2.7.1. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Functional group studies of untreated and treated samples before and after sorption were conducted using FTIR (ALPHA, Bruker Optik GmbH, Ettlingen, Germany). The vibration frequencies of the adsorbents lattice that arise from stretching of bending modes of the functional groups present were determined using the attenuated total reflectance (ATR) method at a spectral range of 4000–500 cm^{-1} with a 4 cm^{-1} resolution.

2.7.2. Scanning Electron Microscope (SEM) Analysis

Morphology of selected samples before and after treatment was observed using Variable Pressure Scanning Electron Microscopy (VP-SEM) (LEO 1455, Carl Zeiss AG, Oberkochen, Germany). The samples were initially mounted on double-sided conductive adhesive carbon tapes adhered to aluminium stubs (1.2 cm diameter) and later sputter-coated with gold for better image quality under SEM using a sputter coater (JEOL JEC-3000 FC, Tokyo, Japan).

3. Results and Discussion

3.1. Screening of Cogon Grass

Figure 2 shows the percentage of oil absorbed by two different samples of CG; untreated and treated before sorption. The percentage of oil absorbed by untreated CG was 34.17% and 40.17% for treated CG, respectively. Due to excessive moisture absorption and low wettability, untreated CG has insufficient adhesion between the fibres and matrix. The graph demonstrated that treated CG absorbed 6% greater oil than untreated CG with 40.16% and 34.16%, respectively. In addition, treated CG has a reduced sorption capacity of 1.01 g/g compared to untreated CG, which has a sorption capacity of 1.06 g/g. However, the amount of water absorbed by untreated CG was higher by 1.64%. The reduced hydrophobicity and oleophilicity of the sorbents may explain this phenomenon. ANOVA analysis showed no significant difference between untreated and treated samples ($p > 0.9999$). Changes in the material's pore structure may have an impact on sorption capacity. Pore size and its distribution have the ability to speed up the oil drops created by capillary action, giving high absorptivity towards oil [30]. Generally, plant fibres showed a

stronger affinity for water than for oil. High water absorption is undesirable as it might induce dimensional instability and potential difficulties in cellulosic products like bowing, cupping and swelling [31,32]. As shown by the result, treated CG absorbed oil better than untreated cogon grass, and thus it was used for subsequent experiments.

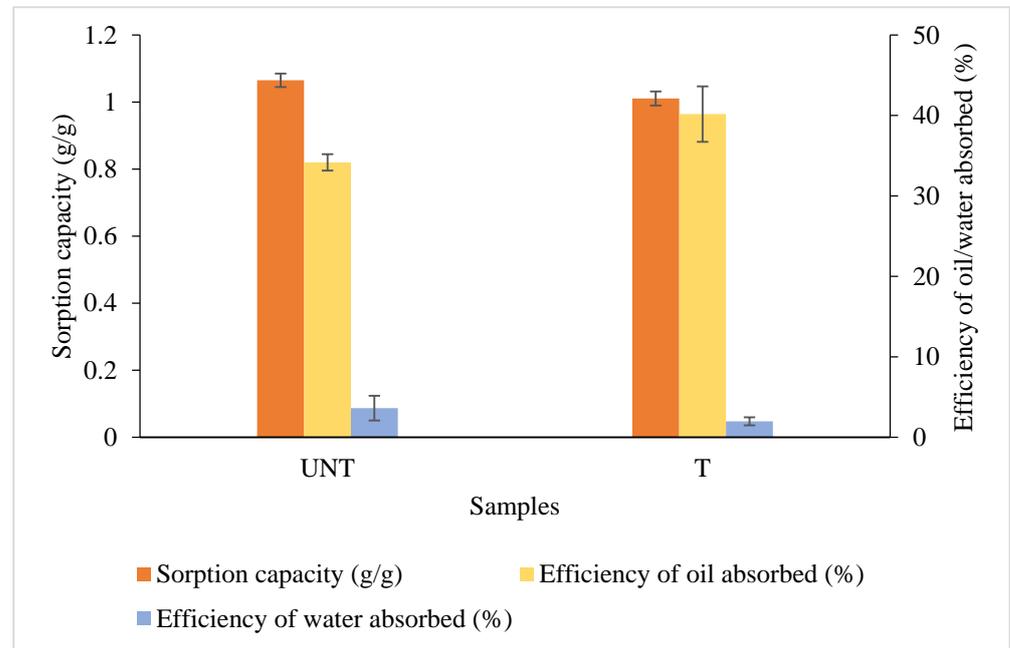


Figure 2. Screening of untreated (UNT) and treated cogon grass (T–120 °C, 60 min) after sorption. Error bars indicates SD for the three replicates.

3.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR infrared spectra were obtained in the range of 4000 to 500 cm^{-1} to detect the presence of functional groups in untreated and treated CG before and after sorption (Figures 3 and 4). Figure 3 shows the acquired spectra for untreated and treated CG before adsorption. The siloxane group linked to the silica backbone was identified at 800 to 1090 cm^{-1} . The C–H group's stretching peaked at 2916.36 cm^{-1} (untreated CG) and thereafter dropped to 2919.80 cm^{-1} (treated CG). As a result of the heating procedure, part of the alkyl chain was damaged. Meanwhile, the aromatic ring of lignin had a peak wavelength of 1400–1600 cm^{-1} while treated CG had a higher reflectance than untreated CG. Stretching of the O–H group, which is derived from cellulose, was discovered in a broad spectrum between wavelengths 3200 and 3600 cm^{-1} . The ether group was also shown to stretch the C–O–C bonds at 1162.66 cm^{-1} in treated CG. Figure 4 shows asymmetric stretching of the Si–O–Si bonds, 1036 cm^{-1} following absorption, corresponding to the symmetric vibration [33]. At wavelength 2850–2922 cm^{-1} , the C–H group detected a similar stretching pattern, which is more obvious than in Figure 3 since it is caused by adsorbed oil. After sorption, the functional group on the surface of CG was seen at a shifted wavelength from 3280 to 3330 cm^{-1} , where the hydrogen bond O–H stretched again.

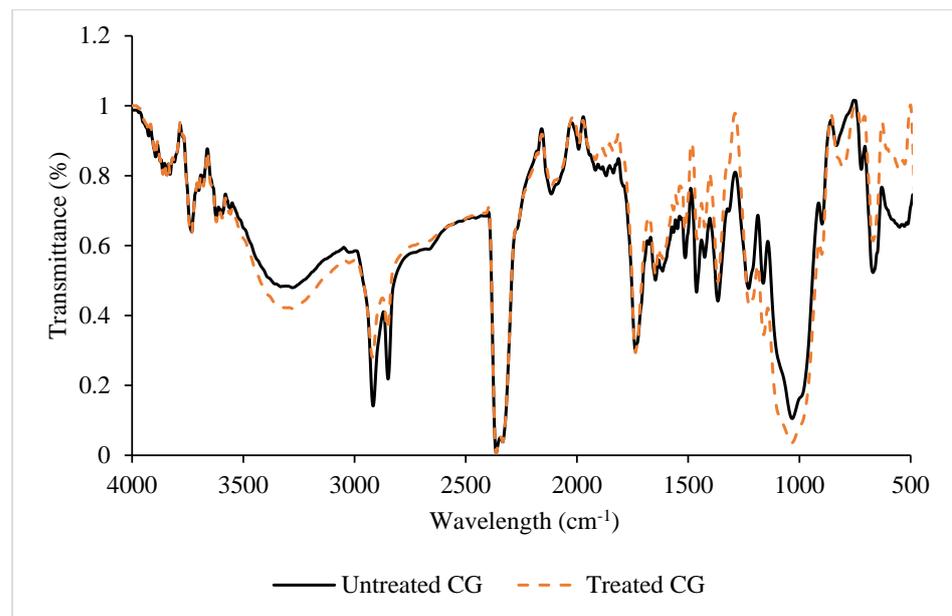


Figure 3. Attenuated total reflectance–Fourier transform infrared (ATR-FTIR) spectra of untreated and treated cogon grass before sorption. Treated cogon grass was heated at 120 °C for 45 min.

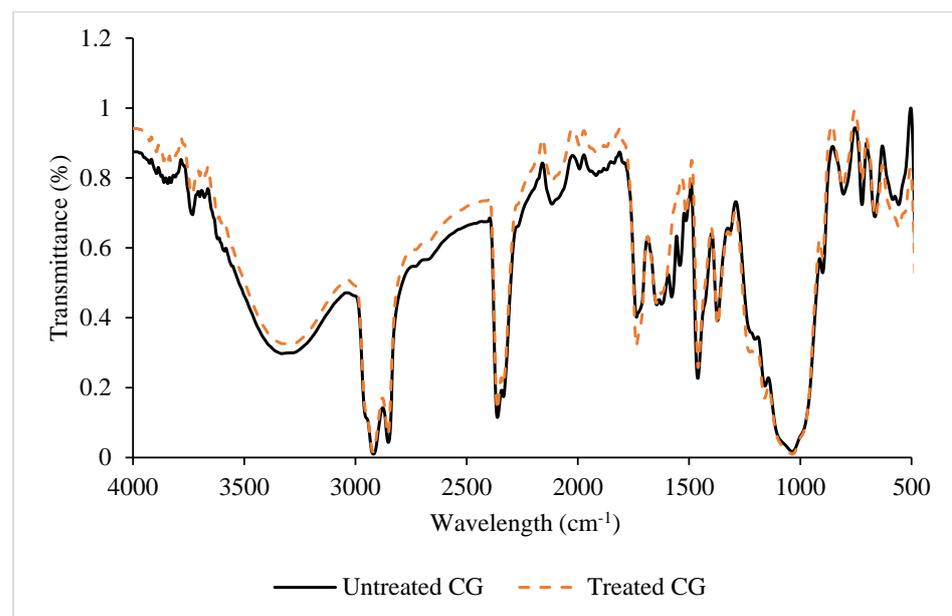


Figure 4. ATR-FTIR spectra of untreated and treated cogon grass after sorption. Treated cogon grass was heated at 120 °C for 45 min.

3.3. Scanning Electron Microscope Analysis

The morphology of CG by SEM micrograph of 250× magnification is shown in Figure 5. Figure 5a,c show SEM pictures of the changes in surface and texture of CG after 45 min of heating at 120 °C. Untreated CG showed a flat, smooth and continuous surface, whereas treated CG had a rough, porous and uneven surface. The finding was explained by the fact that untreated CG was unexposed to any chemical or treatment. Haque et al. [34] reported a similar finding using a different temperature and time, 105 °C and 10 min, respectively. In addition, the rough surface resulted in greater oil absorption. Figure 5b,d indicate that after sorption, a portion of the CG was coated with oil, and broken fibres were present due to the heat treatment. As the sample was exposed to oil, empty spaces and holes between the fibres appeared and became larger [35].

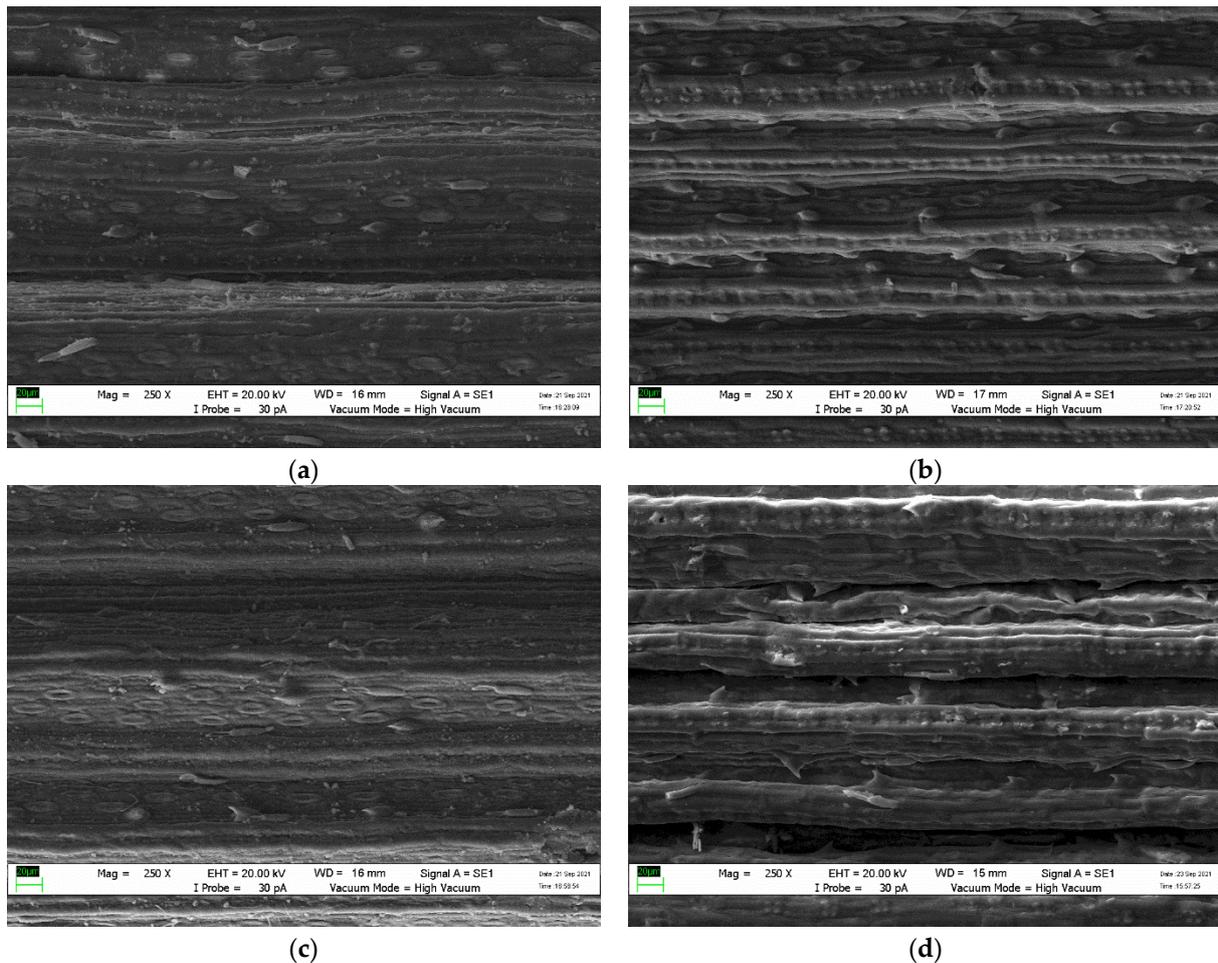


Figure 5. Scanning electron microscopy (SEM) micrograph of (a) untreated cogon grass before sorption; (b) treated cogon grass before sorption; (c) untreated cogon grass after sorption; and (d) treated cogon grass after sorption at magnifications 250 \times . Treated cogon grass was heated at 120 $^{\circ}$ C for 45 min.

3.4. One-Factor-at-a-Time (OFAT) Optimisation

3.4.1. Effects of Temperature

As seen in Figure 6, the temperature has a minimal effect on oil absorption. One-way analysis of variance (ANOVA) was used to determine the effect of temperature on the efficiency of oil absorption. The amount of water absorbed at various heating temperatures was also shown to select the oil that absorbed the most at a given temperature while absorbing the least amount of water. A low water absorption indicates a high selectivity of the sorbent for oil. Figure 6 shows that 120 $^{\circ}$ C has the maximum oil absorption efficiency of 40.17%, coupled with 1.98% of seawater absorbed and 1.01 g/g sorption capacity, whereas 110 $^{\circ}$ C has the lowest at 30.00% with 1.8% water absorbed and 1.05 g/g sorption capacity. Oil absorption was low (30% to 32%) when the temperature was raised over 120 $^{\circ}$ C. The efficiency of oil absorbed was significantly different for varying heating temperatures ($F_{5,12} = 4.943$, $p = 0.0109$). The result was the opposite for water absorbed, with no significant difference in heating temperatures ($F_{5,1} = 0.09734$, $p = 0.9761$). Further analysis of ANOVA showed sorption capacity that has a significant difference between the treatments of CG ($F_{5,12} = 7.016$, $p = 0.028$). A previous study reported heat treatment removed the waxy coating on the leaves, allowing the medium to easily reach the cellulose fibres [36]. Apart from contaminants, waxy compounds on the surface of CG caused poor surface wetting and decreased fibre-matrix bonding [37]. High temperatures help develop surface roughness, and a rough surface improves the adhesive ability of the oil [38].

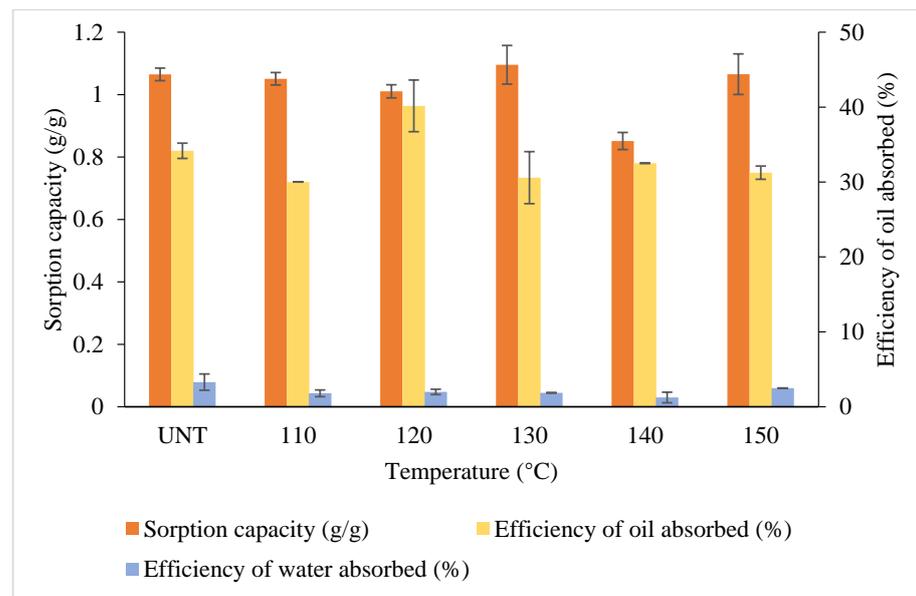


Figure 6. Effect of varying temperature (°C) on sorption capacity and oil/water absorption efficiency. Error bars indicates SD for the three replicates.

3.4.2. Effects of Time

Treatment factors such as time, temperature and concentration are critical for maximising the efficiency of natural sorbent in oil absorption. OFAT optimisation was further continued with the second factor, time. Treatment of cogon grass resulted in the maximum oil absorption efficiency of 37.5% and the lowest water absorption efficiency of 1.54% at 45 min (Figure 7). On the other hand, while having a high sorption capacity at 75 min, the oil absorption efficiency was only 25.83%, and the value for absorbed water was relatively high, 2.33%. There was no significant difference between the sorption capacity and efficiency of water absorbed values ($F_{5,12} = 0.4407, p > 0.05$; $F_{5,12} = 1.986, p = 0.1532$). In contrast, there was a significant difference across the time intervals ($F_{5,12} = 14.66, p < 0.0001$) in terms of oil absorption. Therefore, the ideal time to proceed to the next single component was 45 min.

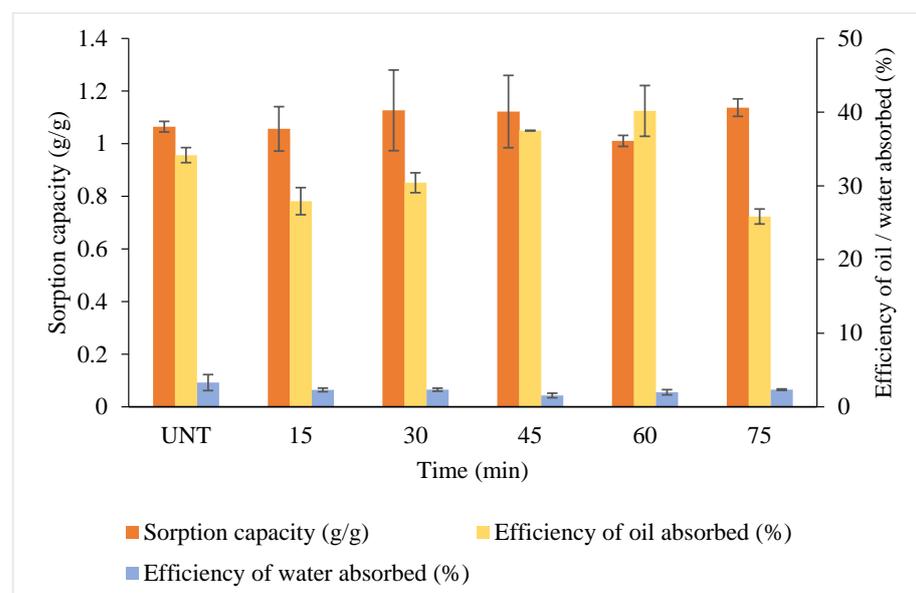


Figure 7. Effects of varying time (min) on sorption capacity and oil/water absorption efficiency. Error bars indicates SD for the three replicates.

3.4.3. Effects of Packing Density

The sorption capacity of sorbent and oil absorption efficiency was studied using a range of packing densities. The findings are shown in Figure 8, which shows oil content as a function of packing density. The amount of oil absorbed increased with packing density, as predicted. Figure 8 shows that sorption capacity and oil absorption efficiency rose gradually from packing density of 0.14 g/cm³ to 0.18 g/cm³, before declining with a packing density of 0.2 g/cm³; hence, the oil absorption between different packing densities has no significant difference ($F_{5,12} = 13.13$, $p = 0.0002$). However, with packing densities 0.14 g/cm³ and 0.18 g/cm³, respectively, a significant increase in oil absorbed was observed from 25% to 38%. Packing density of 0.14 g/cm³ was significantly different to the other values ($p = 0.0478$) while the rest showed no significant difference ($p = 0.0181$). Moving on to the sorption capacity values, there was no significant difference between the packing densities ($F_{5,12} = 4.285$, $p = 0.0181$) as displayed in Figure 8. The highest oil absorbed, 40% was achieved by packing density of 0.18 g/cm³, combined with the highest sorption capacity (1.19 g/g) and an average value of seawater absorbed (2.5%). With a higher packing density, 36.6% of the oil was absorbed, 1.17 g/g of sorption capacity was achieved, and 3.83% of water was absorbed. Interestingly, it was found that there was a significant difference in the efficiency of water absorbed where $F_{5,12} = 12.62$ and $p = 0.0002$. A lower fibre packing density would aid the development of inter-fibre porosity. However, the quantity of inter-fibre pores accessible for oil sorption decreased as the packing density of the fibre assembly increased, resulting in a substantial reduction in oil sorption capacity. A study conducted by Xu et al. [39] showed lower packing density correlated with increased porosity, which increases surface area and results in rapid oil sorption. Another study also proved that the oil sorption capacity might be increased by increasing the surface area, which is possible at low packing density. Furthermore, the considerable drop in oil flow in densely packed CG was mostly due to the narrowing of channel flow diameters, which resulted in a prolonged saturation period [40].

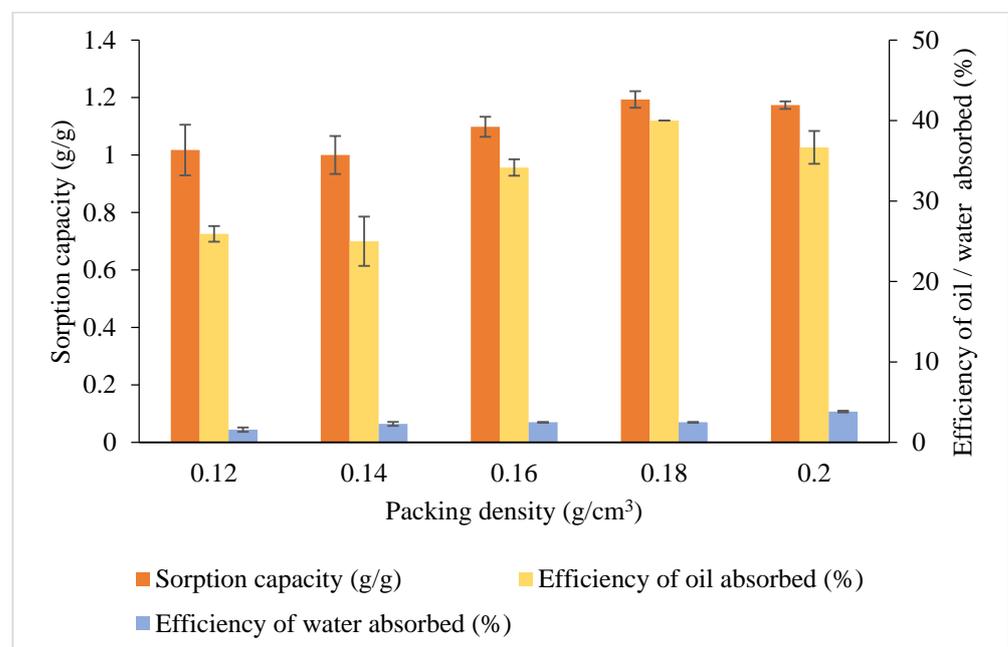


Figure 8. Effects of varying packing densities (g/cm³) on sorption capacity and oil/water absorption efficiency. Error bars indicates SD for the three replicates.

3.4.4. Effects of Oil Concentration

The effects of oil concentration on oil absorbed by CG were also studied (Figure 9). It was evident that with increasing oil concentration, the efficiency of oil absorbed by CG increased. ANOVA analysis showed significant differences in sorption capacity ($F_{6,14} = 9.049$,

$p = 0.0004$) and absorbed water ($F_{6,14} = 4.319$, $p = 0.0113$) across the oil concentration. The highest oil absorbed was observed at an oil concentration of 30 (v/v)% and decreased at a higher concentration. The oil absorbed at 30 (v/v)% was significantly different from 35 (v/v)% ($p < 0.0001$) but was not significantly different from other concentrations ($p > 0.05$). Sorption capacity and oil absorption were the highest at 1.32 g/g and 19.07 mL at an oil concentration of 30% compared to other concentrations. This indicates that oil absorption was greatly affected by different oil concentrations. However, sorption capacity was affected by the increasing oil concentration, which significantly increased at 25 (v/v)%. Baiseitov et al. [41] reported that the speed of active sorption started to reduce once the ideal sorption time was achieved through the desorption process and sorbent's oil saturation. The findings showed that the saturation of sorbent occurred at 30% oil content. The increase in oil adsorption capacity was due to the adsorption of oil at hydrophobic reactive sites and diffusion into the pores or hollow lumen of the sorbents. Meanwhile, the decrease might be caused by increased pressure and desorption in oil-saturated reactive sites [42].

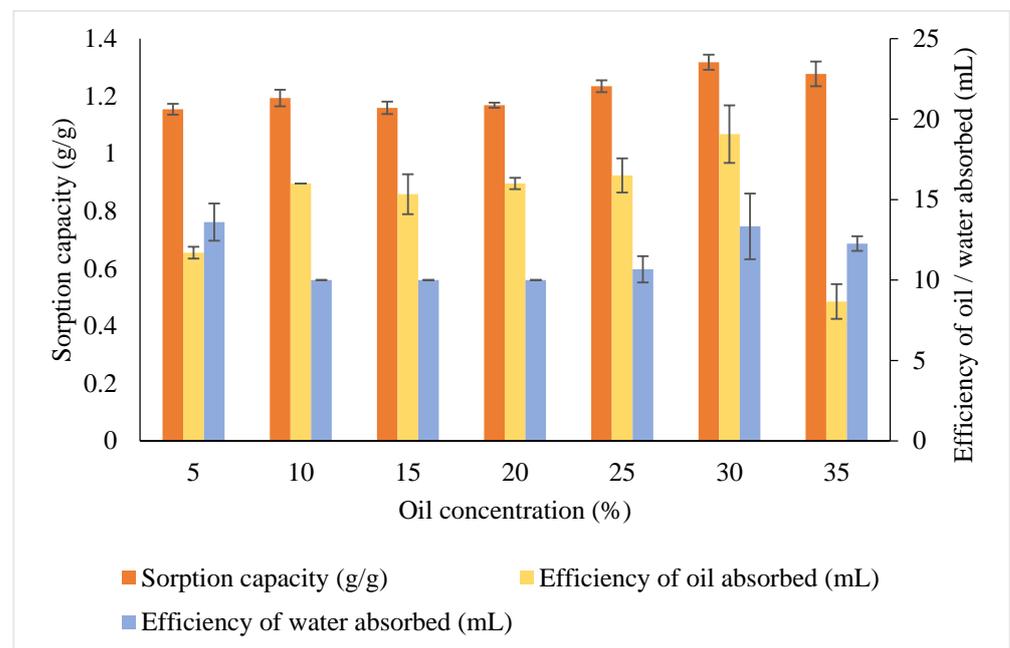


Figure 9. Effects of varying oil concentrations (v/v)% on sorption capacity and oil/water absorption efficiency. Error bars indicates SD for the three replicates.

3.5. Response Surface Methodology (RSM) Optimisation

3.5.1. Plackett Burman Design

In the 18 runs of the Plackett Burman design used to improve the performance of CG, oil absorption ranged from 7.57 to 26.67 mL, respectively (Table 3). At 110 °C for 30 min with packing density and oil concentration of 0.2 g/cm³ and 20%, maximum oil absorption (run 6) was obtained. At 130 °C, 75 min and packing density and oil concentration of 0.14 g/cm³ and 20%, the lowest oil absorption (run 8), was recorded.

ANOVA (Table 4) confirmed that temperature (A), time (B), packing density (C) and oil concentration (D) were the significant factors affecting oil absorption by CG. The model was identified to be significant ($p < 0.0001$) and highly reliable.

Table 3. Secondary screening of significant parameters affecting diesel sorption using Plackett Burman design for cogon grass (SD, $n = 3$).

Run	A	B	C	D	Oil Absorption (mL)
1	120	52.5	0.17	27.5	22.33
2	110	75.0	0.14	35.0	13.33
3	130	75.0	0.20	20.0	18.33
4	120	52.5	0.17	27.5	22.33
5	120	52.5	0.17	27.5	22.33
6	110	30.0	0.20	20.0	26.67
7	130	30.0	0.14	20.0	17.33
8	130	75.0	0.14	20.0	7.57
9	120	52.5	0.17	27.5	22.33
10	120	52.5	0.17	27.5	22.33
11	130	75.0	0.14	35.0	10.50
12	130	30.0	0.20	35.0	22.83
13	110	30.0	0.14	35.0	15.33
14	110	30.0	0.14	20.0	20.67
15	120	52.5	0.17	27.5	22.33
16	130	30.0	0.20	35.0	22.83
17	110	75.0	0.20	35.0	19.10
18	110	75.0	0.20	20.0	24.33

A: Temperature ($^{\circ}\text{C}$); B: Time of heating (min); C: Packing density (g/cm^3); D: Oil concentration (v/v)%.

Table 4. Analysis of variance (ANOVA) of the Plackett Burman design (PBD) model used to identify the factor significantly influencing diesel absorption.

Source	Sum of Squares	df	Mean Square	F-Value	p -Value
Model	2095.69	4	523.92	34.49	<0.0001 ***
A-Temperature	198.73	1	198.73	13.08	0.0035 ***
B-Time	533.33	1	533.33	35.11	<0.0001 ***
C-Packing density	1295.15	1	1295.15	85.27	<0.0001 ***
D-Oil concentration	68.48	1	68.48	4.51	0.0552 *
Residual	182.26	12	15.19		
Lack of Fit	182.26	6	30.38		
Pure Error	0.0000	6	0.0000		
Cor Total	2689.13	17			
Std. Dev.	3.90		R^2	0.9200	
Mean	49.07		Adjusted R^2	0.8933	
C.V.	7.94		Predicted R^2	0.7649	
			Adequate Precision	20.9006	

A: Temperature ($^{\circ}\text{C}$); B: Time of heating (min); C: Packing density (g/cm^3); D: Oil concentration (v/v)%; * $p < 0.05$, *** $p < 0.001$.

3.5.2. Central Composite Design

Following identification of the significant parameters in PBD, CCD was conducted to study the interactions between the significant factors and determine the optimal conditions for oil absorption by cogon grass. The initial model with four significant parameters was shown to be insignificant; thus, CCD was repeated. Table 5 shows the results of the second CCD's experimental runs with two significant factors: temperature ($^{\circ}\text{C}$) and oil concentration (v/v)%, as well as the experimental and predicted values. The levels of oil absorption ranged between 14.00 to 22.17 mL. The model was highly significant ($p < 0.0001$) according to ANOVA (Table 6) and was based on a quadratic model.

Table 5. Optimisation of parameters for diesel degradation using central composite design (CCD) (SD, $n = 3$).

Run	A	D	Oil Absorption (mL)	
			Experimental Value	Predicted Value
1	130.0	35.0	22.17	22.17
2	130.0	35.0	22.17	22.17
3	150.0	45.0	22.00	20.82
4	150.0	25.0	14.00	13.79
5	130.0	35.0	22.17	22.17
6	130.0	20.9	14.00	13.97
7	101.7	35.0	22.00	22.60
8	110.0	45.0	21.50	20.40
9	110.0	25.0	19.83	19.70
10	158.3	35.0	18.00	18.71
11	130.0	35.0	22.17	22.17
12	130.0	35.0	22.17	22.17
13	130.0	49.1	18.1	19.44

Table 6. Analysis of variance (ANOVA) of the central composite design (CCD) model used to identify the factor significantly influencing oil absorption.

Source	Sum of Squares	df	Mean Square	F-Value	p-Value
Model	108.05	5	21.61	28.50	0.0002 ***
A-Temperature	15.10	1	15.10	19.91	0.0029 **
B-Oil concentration	29.90	1	29.90	39.43	0.0004 ***
AB	10.03	1	10.03	13.23	0.0083 **
A ²	3.98	1	3.98	5.25	0.0557 *
B ²	51.89	1	51.89	68.45	<0.0001 ***
Residual	5.31	7	0.76		
Lack of Fit	5.31	3	1.77		
Pure Error	0.0000	4	0.0000		
Cor Total	113.36	12			
Std. Dev.	0.8707		R ²	0.9532	
Mean	20.02		Adjusted R ²	0.9197	
C.V.	4.32		Predicted R ²	0.671	
			Adequate Precision	14.8900	

A: Temperature (°C); B: Oil concentration (v/v)%; * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

Design Expert Software version 13.0.5 was used to plot the three-dimensional response surfaces to visualise the interaction effects between two pairs of variables while keeping the other variables constant. The highest oil absorption was predicted at the highest point of the 3D surface plot in which the optimal values of the parameters were determined. The highest oil absorbed was observed at the oil concentration between 20 to 22 mL and temperature of 110–130 °C (Figure 10). The absorption of the oil on the sorbents was affected by temperature. The increase in oil absorption might be attributed to the formation of additional active sites on the sorbent due to the removal of certain surface components after heating [43,44]. Besides temperature, oil concentration also influences the rate and absorption of the sorbent. The response increased as oil concentration (B) increased, likely due to the driving force from a greater concentration [31].

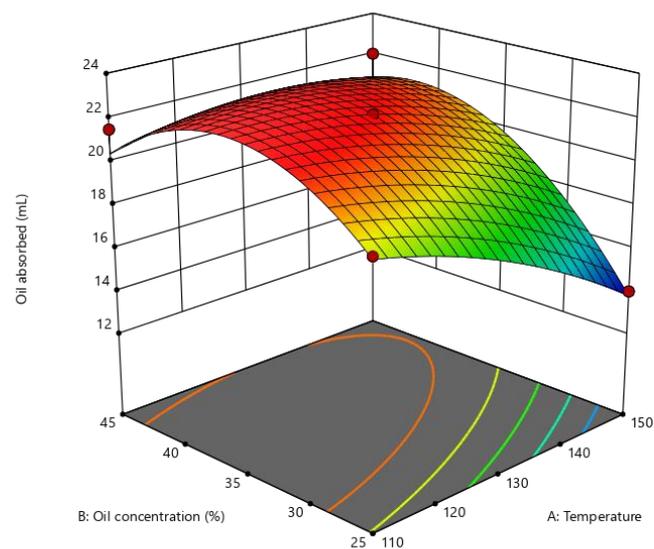


Figure 10. Three-dimensional contour plots generated by Design Expert (Stat Ease, Inc.) of the significantly interacting model terms A: Temperature ($^{\circ}\text{C}$) and B: Oil concentration ($v/v\%$).

3.5.3. Model Validation Experiment

To experimentally evaluate the predicted value of oil absorption, a combination of the two significant variables was kept at optimal values of 128°C and $36 (v/v)\%$, as shown in Table 7. According to the analysis of the RSM fitting model, the predicted value was 22.45 mL. The experimental value of 24 mL oil absorption was close to the model's prediction, thus confirming model validity. Therefore, the RSM model was able to predict the efficiency of oil absorbed by CG.

Table 7. Model validation of predicted optima values.

Optimised Parameters	Value	Predicted Value	Experimental Value	Efficiency
Temperature	128°C	22.45 mL	24 mL	93.54%
Oil concentration	$36 (v/v)\%$			

4. Conclusions

This study examined CG as a natural sorbent for oil spill clean-up. CG is inherently hydrophobic and oleophilic in the actual scenario, meaning it absorbs both oil and water. Optimisation aids in the improvement of CG performance by maximising the quantity of oil absorbed while minimising the amount of water absorbed. The modification of CG was easy and affordable, and the result was a product with high stability, high crude oil capacity, low water retention and high reusability. The optimal condition of 128°C temperature and $36 (v/v)\%$ oil concentration using the RSM model outperformed OFAT and improved the performance of CG by 93.54% efficiency with 22.45 mL of oil absorbed through CCD. CG may be less efficient than other natural sorbents, but owing to its oil/water selectivity properties, it becomes a cost-effective method with high potential to combat oil spills.

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