

Optimisation of Crude Oil Adsorbent Developed from a Modified Styrene Kenaf Shive

Zwahruddeen Muhammad Salisu^{1*}, Ishiaku S. Umaru², Danladi Abdullahi²,
Mohammed Kabir Yakubu², Diya'uddeen Bashir Hasan³

¹National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria

²Department of Polymer and Textile Engineering, Ahmadu Bello University (ABU), Zaria, Nigeria

³Center for Energy Research and Training (CERT), Ahmadu Bello University (ABU), Zaria, Nigeria

Email: *ruddeen.zms@gmail.com

How to cite this paper: Salisu, Z.M., Umaru, I.S., Abdullahi, D., Yakubu, M.K. and Hasan, D.B. (2019) Optimisation of Crude Oil Adsorbent Developed from a Modified Styrene Kenaf Shive. *Journal of Materials Science and Chemical Engineering*, 7, 38-51.

<https://doi.org/10.4236/msce.2019.72004>

Received: November 1, 2018

Accepted: February 25, 2019

Published: February 28, 2019

Copyright © 2019 by author(s) and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

A new kind of hydrophobic crude oil sorbent was successfully developed by grafting kenaf shive with styrene monomer. In this paper, crude oil sorbents were developed through regeneration method by varying the initiator concentration, monomer ratio and particle sizes in the range of 0.5 - 2.5 wt%, 0.5 - 2.0 wt % and 125 - 1000 μm respectively. This research approach for the development of crude oil sorbent from graft modified kenaf shive/core and the aforementioned variable optimization has not been reported. The effect studies of the individual and combine factors were carried out using a statistical experimental design matrix using five-level central composite design (CCD). Respond surface methodology (RSM) was used to optimise and develop equations of the aforementioned variables (initiator concentration, monomer ratio and particle sizes). The optimal swelling capacity of 616% and 267% lower retention were achieved at initiator concentration, monomer ratio and particle size of 12.5 wt%, 1.50 wt% and 562 μm respectively. TGA-DTA, XRD and BET analysis were carried out on optimised sample and, FTIR was carried on both unmodified (UG) and optimized sorbent. Further computations were done for grafting efficiency (GE), homopolymers and density. The findings display the effect of the three variables and navigation equations were generated for further investigations on them. However, the results show the feasibility and robustness of facile oil sorption.

Keywords

Sorbent, Initiator, Crude Oil, Kenaf Shive, Respond Surface Methodology (RSM)

1. Introduction

Crude oil spillage is the release of a liquid petroleum hydrocarbon into the environment due to human activity, and is a form of pollution. The term often refers to marine oil spills, where oil is released into the ocean or coastal waters. Oil spills include releases of crude oil from tankers, offshore platforms, drilling rigs and wells, as well as spills of refined petroleum products (such as gasoline, diesel) and their by-products, and heavier fuels used by large ships such as bunker fuel, or the spill of any oily white substance refuse or waste oil. Spills may take from a month up to years to clean up. Oil also enters the marine environment from natural oil seeps.

Crude oil is one of the major sources of income bestowed under the earth's crust of many countries; Nigeria is one of the most endowed countries with this resource. But because of environmental issues associated with exploration, transportation and refining of the crude oil, this very important revenue earner becomes a menace for most of developing countries mainly due to spillage. [1] [2] reported that oil spills cost Nigeria more than 1.89 million barrels annually from more than 10,000 accidental spills which are less than 4% and 22.5% as a result of tanker accidents and operational discharge respectively. [3] reports Tokyo oil spill incident—where about 4 million gallons was spilled out—many lives were lost. Apart from the attendant loss in revenue, aquatic organisms also suffer a lot from this oil spills.

Oil spills is considered as one of the most serious disasters that is threatening the marine ecosystem [4] [5] [6] [7]. Many techniques have been devised to combat this problem [5].

Oil spill has a great negative influence on the ecosystem by putting the marine lives at high risk. However, the extent of risk is dependent on the type and volume of the oil in addition to other abiotic factors such as the sensitivity limit of the marine habitat. Oil spill on river or sea envelopes the water surface and consequently, shields the diffusion of sunlight that enhances photosynthesis. Aquatic lives rely mainly on Phytoplankton and seaweed for existence. Majority of crude oil discharge occurred in the water ways. About 5 millions tons of unrefined oil products are transported per annum averagely across the ocean globally [8] [9]. Oil consists of wide range of organic (hydrocarbon) based constituents which might be crude oil, refined, edible and non-edible oil. However, crude oil may contain other elements such as sulphur, hydrogen, sulphide and oxygen [10].

Methods of Combating Crude Oil Spillage

In the past, containment and recovery measures have been utilized for oil spill mitigation. The conventional techniques include: containment and mechanical recovery; burning; bioremediation; chemical dispersant and the use of absorbent. The recovery techniques are dependent on various factors such as weather conditions, sea condition, oil type and environmental considerations, which

could necessitate the combinations of these measures for clean-up. These techniques include: burning *in situ*, bioremediation, chemical dispersion and synthetic sorbents in spite of their secondary effect of nondegradability [4]. The most widely accepted by many researchers and industries is the one prepared from polypropylene fibres and is now being considered hazardous [9] [11] [12].

Nanocellulose aerogel, carbon nanotubes are the recent ones that gave high absorbency capacity (g/g), but these cannot be sustained because of the high cost of raw materials and processing [8] [13] [14]. Most recent research discovery shows that natural materials are the best for oil cleaning-up [4]. Moreover, cotton and kapok are the best amongst the green plants. This is because of their higher oil sorption capacity, biodegradability and recyclability which are preeminent materials for oil spill cleanup. Cotton has loose fibers, which presumably limited their application [4]. The problem with cotton necessitated the use of kenaf shive as a possible alternative, it has other advantages over cotton which has to be converted into pads in the preparation sequence consequently reducing the diameter of the capillaries also has collapsing lumens [15]. Kenaffibres is used in producing bags for agricultural packaging and, by utilizing its shives makes a lot of economic sense since it is normally thrown away [4].

There are many techniques which were employed to combat oil spillage in the past and the present. Each of these techniques has its peculiar hinges and bottlenecks. These methods were broadly divided into: mechanical/physical methods e.g. Oil booms/adsorbents, Chemical e.g. dispersants, biological e.g. micro-organisms [9] [16] [17]. Amongst these techniques the one that was considered as very promising, eco-friendly and viable to mention but a few, is the physical methods *i.e.* adsorbents.

Adsorbents are further classified into three, depending on the raw material sources. Synthetic sorbents has been widely used because of its high sorption capacity alas, non-biodegradable. Example of this is foams of polyurethane, urea formaldehyde, polypropylene materials [18]. The second class is inorganic material sorbents which were reported and has its moderate sorption capacity but less abundant and not easily recyclable [12] [19]. The promising and the robust class is natural organic sorbents. Natural materials though with its hydrophilic property can be modified for oil adsorption [3] [13]. Some of its preeminent qualities are: availability, eco-friendly, Cost effective, ease of application, oil retention, rate of adsorption or absorption, re-usability (Recycling) [20].

Hydrophobic properties are conferred to natural materials by either creating surface roughness e.g. sol-gel, nanoparticle deposit, chemical vapour or by regeneration/fragmentation e.g. electrospinning, cellulose composites, grafting [5] [19].

Being kenaf shive one of the most abundant cellulosic sources with less usage in both industries and household, the research was deemed important to add value to it and solve one of the most disastrous menace that bothers environmental ecological system. Furthermore, kenafbastfibre is used for agricultural

packages and many more but the shive/core that is about 60% - 70% of the plant has no economic value. Modifying its shive to obtain the performing properties can be easily achieved by graft-co-polymerisation with hydrophobic monomer e.g. styrene.

2. Materials and Methods

2.1. Materials and Chemical Preparation

All chemicals are analytical grades and used how it was received without further purification, except for the monomer (styrene) which inhibitors were removed. Dried Kenaf stalks were obtained from National Research Institute for Chemical Technology (NARICT), Zaria.

2.2. Source of Crude Oil

The crude oil sample used for the sorption test was obtained from Petroleum Research Laboratory, Warri, Delta state, Nigeria. The raw crude oil was kept at room temperature and the adsorption test was carried out at 40°C after sorbent development through grafting styrene monomer onto the kenaf shive.

2.3. Experimental Procedures

The obtained dried kenaf stalks were subjected to chemical retting, 1% w/v NaOH for 2 hrs in order to extract its shive from the two components (shive and bastfibres). The product was washed with distilled water until neutrality was achieved and further drying took place for 72 hrs at room temperature. The extracted shive was ground into different particle sizes as prescribed by the DoE software.

Synthesis of the grafted sorbent was done by soaking requisite quantity (1.00 g) of kenaf shive in 5 mls of distilled water for 24 hrs. The mixture was transferred to reaction kettle and 1.00 ml of 2% acetic acid, 10.00 ml of 0.4 M of nitric acid and 0.5 ml of the weight percent of the requisite quantities of initiator as well as monomer concentration as in **Table 2** were added, however, the monomer was added after purging nitrogen gas for 5 min. The reaction continued for 3 hrs at 60°C. The sample was then washed, filtered and oven dried at 40°C.

Three neck flask was quarterly filled with about 25 ml of acetone for homopolymers removal. The initial weight of the thimble was taken after which the thimble plus grafted shive was noted. The latter was inserted into the extractor for the extraction process. This was done at 60°C for 24 hrs in which the homopolymers weight was calculated as in **Table 2**. The experimental processes were repeated for twenty samples using requisite regressors as in **Table 2**.

The extracted grafted sorbents were tested for crude oil sorption using requisite quantity of the sorbent (0.10 g) into watch glass containing 5 mls of the oil. This was done at 40°C for 5 mins to achieve proper sorption.

2.4. Analytical Test

Infrared spectra of the sorbent in KBr pellets is analysed and scanned from 4000

- 400 cm^{-1} using Shimadzu FTIR-8400S and PerkinElmer FTIR spectrometer Spectrum RX1. This test was carried out on the optimized sorbents to confirm the modifications by taking the advantage of their analyzed functional groups. BET, XRD and DTA-TGA were carried out ascertain the obtained result from FTIR, in addition, to elucidate the properties of the developed sorbent.

2.5. Experimental Design, Data Analysis and Process Optimisation

There are several variables which potentially affects the grafting efficiency and absorption. Response surface method (RSM) would be of tremendous important in the analysis of such multivariate system. The objective of using RSM is to get a quick insight in the interaction amongst the investigated variables, facilitate the optimisation conditions and locate optimal response in the region of interest [21]. For these purpose, a reduction empirical model describing the process was developed for predicting and determining future responses in such system. The generated results of the responses from the experimental runs would be obtained by employing Equation (1) through fitting with a second-polynomial equation was used to predict the studied variable factors as independent variable and interaction between them:

$$Y = b_0 + \sum_{i=1}^k biXi + \sum_{i=1}^k biiX^2i + \sum_{i=1}^k \sum_{j=2}^k bijXiXj + \varepsilon \quad (1)$$

where, Y is the predicted dependent variable, b_0 is constant coefficient, bi , bii are regression coefficient, i and j are index numbers, k is number of patterns, X 's are independent variables and ε is the random error. The analysis of variance (ANOVA) was used to assess the significance and adequacy of the model. The fitness of the polynomial model was express by coefficient of determination, R^2 , R_{adj}^2 and R_{pred}^2 . The main indicators that were used to show the significance of the model were Fisher Variation Ratio (F -value), probability value ($\text{Prob} > F$) with 95% confidence level and adequate precision. The final model for each response was obtained after elimination of insignificance term ($p > 0.05$) based on F -test and 3D plots were presented. In addition, the optimum values of the independent variables were identified and further development of the absorbent was carried out at this condition to confirm the regression models.

3. Results

3.1. The Crude Oil Sample Was Characterised Using Rheometer Instrument

Experimental Designs and ANOVA Analysis

The obtained results from the absorbent experiments and predicted values by the developed model for the studied dependents variables are presented in **Table 3**.

From the interaction results of the variables, two multivariate models were derived to describe the cleaning accompanying the sorbent developed (Equation (2) and (3)).

$$\begin{aligned} \text{Grafting Efficiency (ST)} = & -15.2541 + 49.35873*(A) + 0.68243*(B) \\ & - 0.023632*(C) + 0.26812*(A)*(B) \\ & - 0.015626*(A)*(B) + 0.000762975*(B)*(C) \\ & - 14.32115*(A)^2 - 0.039564*(B)^2 + 0.000033766*(C)^2 \end{aligned} \quad (2)$$

$$\begin{aligned} \text{Oil sorption (ST)} = & -221.52117 + 888.78619*(A) - 18.98705*(B) \\ & - 0.024291*(C) + 2.83508*(A)*(B) \\ & - 0.5119*(A)*(C) + 0.044332*(B)*(C) \\ & - 214.81519*(A)^2 + 0.019518*(B)^2 + 0.000274144*(C)^2 \end{aligned} \quad (3)$$

3.2. XRD Plot of Optimized Styrene/Kenaf Shive Sorbent

Figure 1 shows is a plot which indicates the crystallinity properties of the sorbent. It is obvious that there are two plateaus which attributes to the crystalline region at 16° and 22°. Generally speaking, the graph shows the sample is amorphous. This is of advantage in the reaction actualization as it comes prone to the reactants, however, gives it more ability to for adsorption.

4. Discussions

4.1. Analysis of Variance (ANOVA)

The properties of the crude oil used in this experimental runs was displayed in **Table 1**. Based on the kinetic viscosity and density it shows that oil is of high viscose with the nomenclature Ruby (RB) oil. The major properties which affect the oil sorption onto the regenerated sorbent are oil viscosity and modification efficiency as shown in **Table 1**. The functional group which was displayed is a great indication for the modification feasibility.

The synergistic and antagonistic effects are shown by the positive and negative signs in the equations respectively. Based on these models, grafting efficiency and absorption can be predicted as a function of particle sizes, monomer ratio and initiator concentration.

Experimental runs of the studied variables according to central composite design (CCD) results and corresponding values for both experimental and predicted were captured in **Table 2**. The table includes some vital information which were determined during the experiments such as; sorbents densities and extracted homopolymers. The effect of variables under study was translated in surface responses both 3D and contour as shown in **Figure 2** and **Figure 3**.

The models were found statistically significant ($p < 0.05$) and therefore included in the models, analysis of variance (ANOVA) was performed (**Table 3**). Based on the results, it is seen that the p -values for both responses were both less than 0.05 (<0.0001), this indicates that is significance and both could be used for response prediction. Regression coefficient R^2 , adjusted R^2 and predicted R^2 were used to evaluate the quality of the developed equations. The adjusted R^2 values

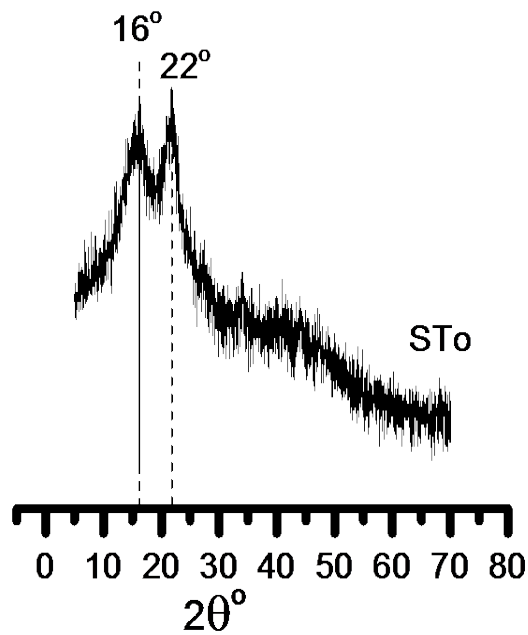


Figure 1. XRD plot of optimized styrene/kenaf shive sorbent.

Table 1. Specifications of crude oil samples (Petroleum Research Laboratory, Warri, Delta state, Nigeria).

Sample	Viscosity (m ² /s)	Speed (m/s ²)	Torgue (Nm)	Temp. (°C)	Density (g/cm ³)
Crude oil	1.33	30.00	0.10	24.5	0.8965
	0.67	60.00	0.00	24.5	

that display the total variation of the response were 0.9092 and 0.8670 for grafting efficiency and adsorption, respectively. The R^2 values close to 1.000 is desirable as it shows the acceptable adjustment of the suggested model with experimental data. The grafting and adsorption efficiency of the regression coefficient ($R^2 = 0.8469$ and 0.8179) and predicted ($R^2 = 0.8397$ and 0.7983) indicated that the models are highly reliable in terms of repetition of the experiments and also adequate in the actual relationship between the responses and the variables. Furthermore, the adj- R^2 and pre- R^2 are in good agreement where the difference between them was less than 0.2 [22]. However, the adequate precision that is signal to noise ratios were 8.3520 and 7.9870 respectively, which are greater than 4.0 (desirable value). This indicates adequate signals that show the models could be used to navigate the design space. The “lack of fit” shows the variation around the fitted model. In the adsorption is 0.1480 implies that the “lack of fit” is in significant relative to the pure error. The functional groups were displayed in **Table 4** indicating the feasibility of the modification. The insignificant “lack of fit” was good and it showed that this model was good to predict the amount of adsorption within the studied range of variables. On the contrary, the lack of fit was significant (F -value was 0.0001) for the graft efficiency, the model could still be used for design space navigation defined by the central composite design

Table 2. Design matrix for the modified styrene crude oil sorbent.

Run no	Results								
	Experimental design					Experimental		Predicted	
	Monomer ratio (%) A	Particle size (μm) B	Initiator conc. (%) C	Density (g/cm^3)	Homopolymer (g)	Grafting efficiency	% swelling	Grafting efficiency	% swelling
1	5	1000.00	0.50	0.075	0.021	8.78	637.20	8.013	675.74
2	5	125.00	2.50	0.068	0.049	24.18	326.30	23.32	312.75
3	12.5	562.50	1.50	0.088	0.036	4.47	474.30	5.36	383.75
4	20	125.00	0.50	0.106	0.027	14.63	342.90	16.07	307.71
5	5	125.00	0.50	0.140	0.004	11.70	305.00	15.41	322.16
6	20	125.00	2.50	0.120	0.026	15.18	453.90	16.61	415.70
7	5	1000.00	2.50	0.058	0.054	13.57	365.10	12.79	400.63
8	12.5	562.50	1.50	0.072	0.045	4.67	365.10	5.36	383.75
9	12.5	562.50	0.50	0.078	0.012	11.52	516.70	5.71	482.30
10	12.5	562.50	1.50	0.071	0.058	4.67	365.10	5.36	383.75
11	12.5	562.50	2.50	0.102	0.010	4.99	365.70	8.36	398.74
12	20	1000.00	2.50	0.074	0.001	3.69	389.70	0.70	372.88
13	12.5	1000.00	1.50	0.085	0.019	2.29	501.70	5.53	430.56
14	12.5	562.50	1.50	0.083	0.042	4.57	365.10	5.36	383.75
15	12.5	125.00	1.50	0.079	0.034	22.86	205.40	17.18	275.18
16	20	562.50	1.50	0.074	0.022	2.72	304.50	1.51	380.82
17	12.5	562.50	1.50	0.083	0.042	4.17	365.10	5.36	383.75
18	20	1000.00	0.50	0.075	0.032	1.72	516.70	3.30	530.59
19	12.5	562.50	1.50	0.083	0.042	4.37	365.10	5.36	383.75
20	5	562.50	1.50	0.073	0.044	8.45	479.60	7.22	401.92

Table 3. Analysis of variance (ANOVA) for the modified styrene sorbent-sorption process.

Source	Sum of squares	Degrees of freedom	Mean square	F-ratio	p-value (Prob > F)
Grafting efficiency					
Model	442.41	3	147.47	6.11	0.0057
Residual	386.25	16	24.14	-	-
Lack of fit	386.04	11	35.09	822.52	0.0001
Pure error	0.21	5	0.043	-	-
Cor total	828.66	19	-	-	-
Adsorption					
Model	1.297E5	6	21609.49	5.38	0.0054
Residual	52241.38	13	4018.57	-	-
Lack of fit	42304.18	8	5288.02	2.66	0.1480
Pure error	9937.20	5	1987.44	-	-
Cor total	1.819E5	19	-	-	-

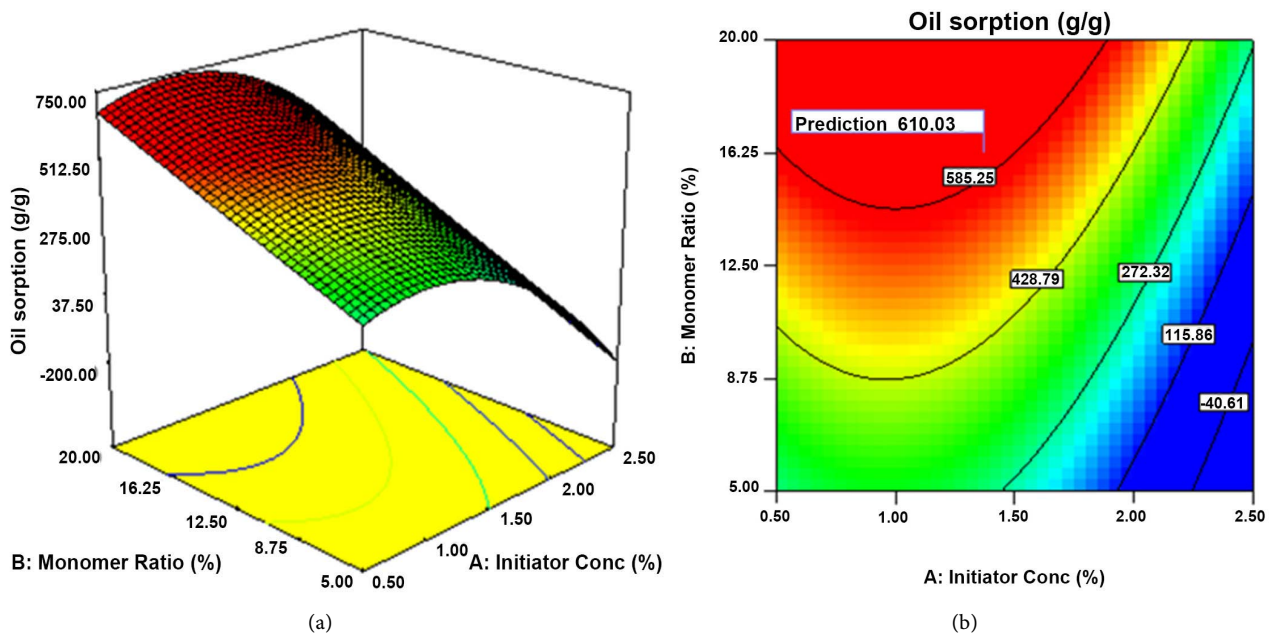


Figure 2. Response surface (a) and contour plots (b) for oil sorption as function of particle sizes and monomer ratio.

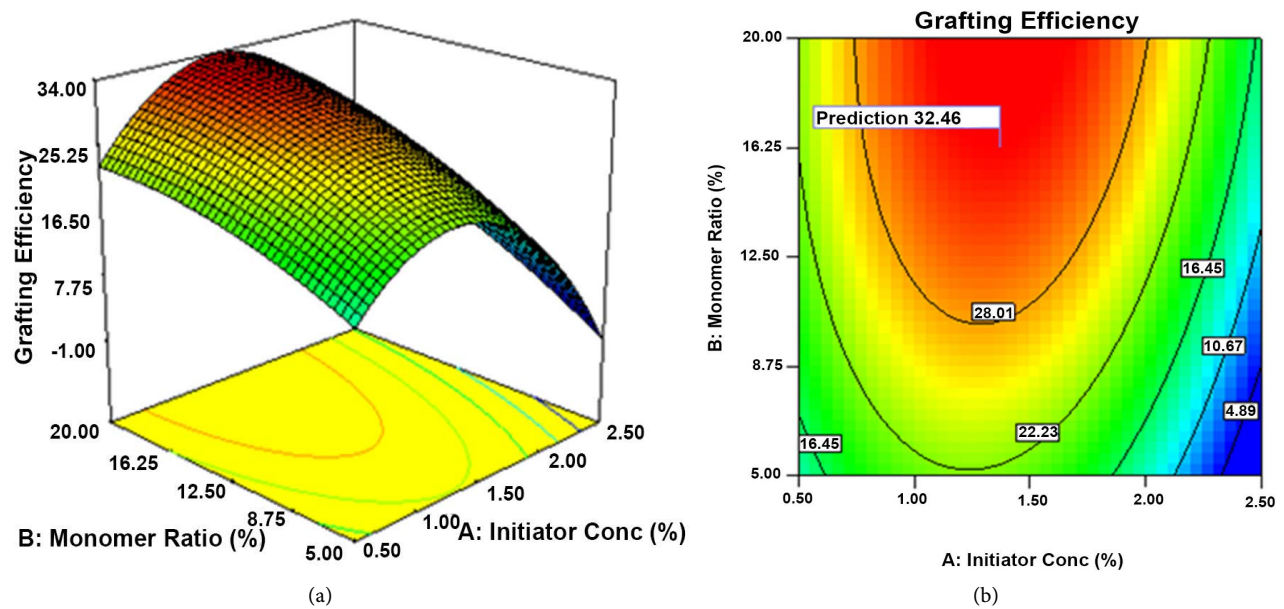


Figure 3. Response surface (a) and contour plots (b) for grafting efficiency as function of particle sizes and monomer ratio.

(CCD), due to good agreement between the adjusted and predicted R^2 values [13] [22].

It is obvious that **Table 5** shows the effect of particle size without the effect of any modifier on the kenaf shive sorption capacity. It is observed that particle size (1000 μm) has highest swelling capacity but with high retention. The difference of swelling and retention results to the oil recovery capacity by the shive. The least particle size (125 μm) in **Table 5** shows a negative sign in the retention column this might be due to the method in recovering the adsorbed oil consequently, resulting to escape of the shive particle with oil.

Table 4. FTIR results for styrene grafted modification.

WAVE NUMBER (cm ⁻¹)	VIBRATION	STRUCTURE
2950 - 2907	δ_s (CH ₃)	-CH ₃
3500 - 3338	δ_s (OH)	-OH
2650 - 2113	δ_{as} (CH ₂)	-CH ₂
1750 - 1722	δ_{as} (CO)	-C=O
1457 - 1400	δ_s (CH)	-CH ₃ -H
1250 - 1159	V _s (CO)	-C-O-

δ_{as} —Asymmetrical stretch, δ_s —symmetrical stretch, V_s—symmetrical vibration.

Table 5. Control (Unmodified kenaf shive).

Particle Size (μm)	Mass of Sorbent before sorption (g)	Mass of Sorbent after sorption (g)	Mass of Sorbent after squeezing (g)	Oil sorption (g)	% Swelling	% Retention
1000	0.1	0.625	0.506	0.119	525	406
562	0.1	0.580	0.312	0.268	480	212
250	0.1	0.548	0.397	0.151	448	297
125	0.1	0.123	0.079	0.044	23	-21

4.2. FTIR Spectrum

The optimised absorbent (STo) one was subjected to FTIR analysis as shown in **Figure 4**, where by following peaks are boldly displayed. The peaks at about 2950, 3500, 2975, 2736, 1650, 1220, 1010 cm⁻¹ that were, respectively, assigned to -CH₃, -OH, -CH₂, -C=O, -CH₂-H and -C-O- as shown in **Table 4** and **Figure 4**. From this result it shows the elements of monomer functional group and the parent chain of the kenaf shive. The spectrum also proves the feasibility of the treatment as when compared with the unmodified (UG) shive because of the cementing materials increases the transmittance [23]. The peaks at 1734, 1593 and 1503 indicates the vibration of -C=O and -CH₃.

4.3. DTA-TGA

The adsorption optimization shows increase in monomer and initiator concentration close to one gives the highest oil sorption within the studied range. To the graft efficiency, it shows that increase in initiator concentration and monomer ratio at 1.50% and 16.5% yields the best result. This is also attributed to particle sizes of 560 μm as it is closer to the original length of the kenaf shive [24]. The grafting efficiency was computed using the following relation:

$$\%E = \left[\frac{(w_3 - w_1)}{(w_2 - w_1)} \right] \times 100\%$$

%E is the efficiency percentage, w₁ is the weight of the original grafted shive, w₂ is the weight of the grafted product after copolymerization, and w₃ is the weight of the grafted product after copolymerization and purification (extraction) [23].

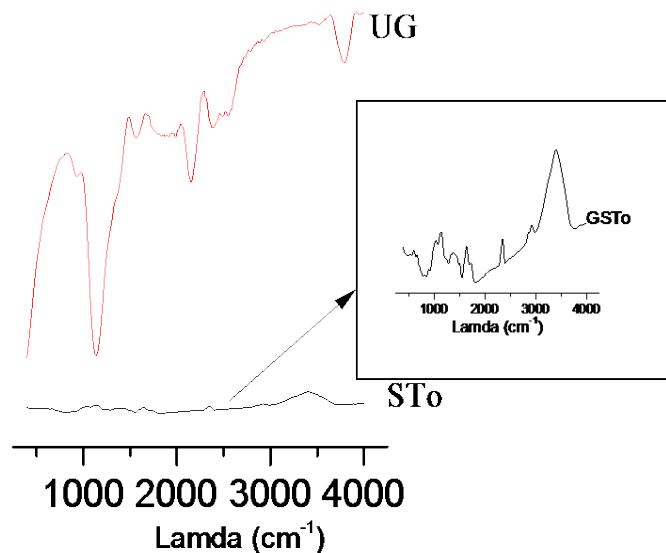


Figure 4. FTIR spectra of the modified and unmodified kenaf shive.

$$%S = [(w_2 - w_1)/(w_1)] \times 100\%$$

$%S$ is swelling percentage; w_1 is the weight of sorbent before sorption w_2 is the weight sorbent after sorption.

It is observed that the variables have important role in the above results *i.e.* percentage swelling and grafting efficiency. The swelling factor also depends on grafting efficiency for oil sorption to some extent until when it becomes saturated.

Figure 5 showed that DTA transition which is an indication of the water evaporation, crystallization, pyrolysis and decompositions at about 110°C, part W, X, Y and Z respectively.

On the other hand, TGA plot shows that at ambient temperature there is little indication of weight loss but not obvious this indicates the hydrophobic nature of the sorbent and this is proved from the DTA plot [8] [23]. The major weight loss was shown at part label X and Z where there were, respectively, weight loss of 25% and 50%. Afterwards, there was continuous degradation living about 5% residue. This is an indication of its degree of organic property.

4.4. Sorption Properties

Table 2 shows the swelling capacities of the modified shive in which the highest is 637% and the lowest [25] is 205% while **Table 5**, the control *i.e.* unmodified shive is having 525 as the highest and 23% as the lowest. However, this is not the yardstick for the best between the two because we have to consider percentage retention that is the determining factor for the oil recovery. In a nutshell, the grafted shive is preeminent properties for the high oil sorption and recovery, consequently, low retention and high swelling percentage than the ungrafted ones.

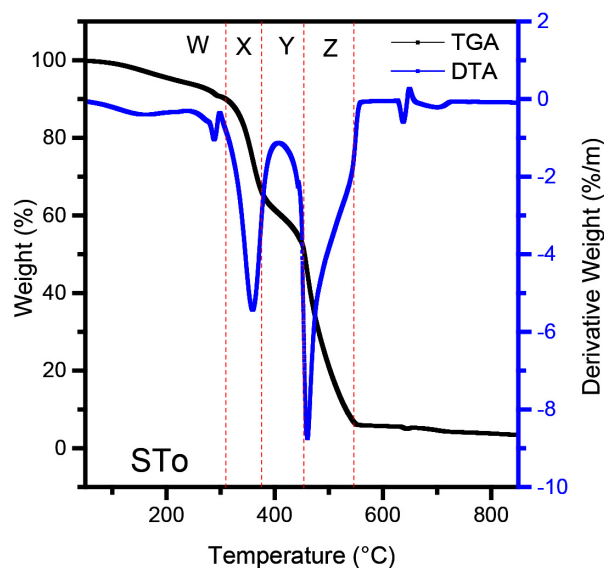


Figure 5. Effect of temperature on the optimized modified styrene sorbent.

4.5. BET Analysis

Brunure-Emmitt-Teller (BET) gives the pore sizes as it indicates the plot as type IV according to the IUPAC nomenclature [4]. This is not abrupt to have this type, as styrene is hydrophobic in nature. The developed sorbest has 301.1 cm²/g, 393.3 cm²/g, 36.75 nm, 23.49 cm³/g, 17.85 cm³/g and 5.64 cm³/g as single and multiple surface area, radius in nanometer, total volume, micro and meso volume respectively. These were obtained using appropriate methods as recommended by [7]. The pore size properties prove to the large different in oil adsorption between the modified and unmodified kenaf shive by about 600% - 700% of same kind.

5. Conclusion

An alternative means of developing crude oil sorbent was successfully achieved from kenaf shive by chemical modification. Effect of three important variables in the modification was studied: monomer ratio, particle size and initiator concentration based on the statistically designed experimental matrix. These effects were investigated using 5-level central composite design (CCD) and response surface methodology (RSM) was used for the process optimisation. FTIR result also indicates the modification achievement, where the expected peaks were obviously shown. This succeeded optimized sorbent was tested for oil recovery; 7.2 g/g was achieved fitting the Langmuir isotherm model. This sorption capacity when compared with the control (ungrafted) and other cellulosic sorbents was very excellent and robust. The modified kenaf shive shows a low retention and high swelling while the unmodified has high retention which is an indication for poor recovery. Based on the studied variables for the sorbents, the sorbent with 562 μm, 16.5%, 1.50% w/v of particle sizes, monomer ratio and initiator concentra-

tion, respectively, gives the higher oil sorption of (516%, swelling capacity and lower retention of 267%). This perhaps due to presence of homopolymers as the research also investigated on its positive effect. The sorbent has preeminent properties of low density, robust and facile. BET shows the pore size property which prove that is majorly of mesopores $2\text{ nm} < \text{size} < 50\text{ nm}$ and XRD indicates that the sorbent is amorphous. DTA-TGA indicates the ash content which is invariably proving the organic nature of the sorbent and eco-friendliness. Burial test which was not captured here for brevity, proved that 50.46% of sorbent was degraded within two months.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Adelana, S.O., Adeosun, T.A., Adesina, A.O. and Ojuroye, M.O. (2011) Environmental Pollution and Remediation: Challenges and Management of Oil Spillage in the Nigerian Coastal Areas. *American Journal of Science and Industrial Research*, **2**, 834-845.
- [2] Osakue, I.Y. and Amenaghawon, N.A. (2018) Response Surface Methodology for Optimizing Alkaline Hydrogen Peroxide Pretreatment of Corn Stover. *Nigerian Research Journal of Engineering and Environmental Sciences*, **3**, 118-124.
- [3] Arfaoui, M.A., Dolez, P.I., Dube, M. and David, E. (2017) Development and Characterization of Hydrophobic Treatment for Jute Fibres Based on Zinc Oxide Nanoparticles and a Fatty Acid. *Applied Surface Science*, **397**, 19-29. <https://doi.org/10.1016/j.apsusc.2016.11.085>
- [4] Singh, V., Kendall, R.J., Hake, K. and Ramkumar, S. (2014) Crude Oil Sorption by Raw Cotton. *Industrial & Engineering Chemistry Research*, **52**, 6277-6281. <https://doi.org/10.1021/ie4005942>
- [5] Nguyen, S.T., Feng, J.D., Le, N.T., Le, A.T.T., Hoang, N., Tan, V.B.C. and Duong, H.M. (2013) Cellulose Aerogel from Paper Waste for Crude Oil Spill Cleaning. *Industrial and Engineering Research*, **52**, 18386-18391.
- [6] Viet, H.P. and James, H.D. (2014) Superhydrophobic Silanized Melamine Sponges as High Efficiency Oil Absorbent Materials. *American Journal of Science and Industrial Research*, **6**, 14181-14188.
- [7] Bhairavi, D., Mika, S. and Simo, K. (2018) A Review of Bio-Based Materials for Oil Spill Treatment. *Journal of Water Research*, **135**, 262-277. <https://doi.org/10.1016/j.watres.2018.02.034>
- [8] Al-Majed, A.A., Adebayo, A.R. and Hossain, M.E. (2012) A Sustainable Approach to Controlling Oil Spills. *Journal of Environmental Management*, **113**, 213-227. <https://doi.org/10.1016/j.jenvman.2012.07.034>
- [9] Bayat, A., Aghamiri, S.F., Moheb, A. and Vakili-Nezhaad, G.R. (2005) Oil Spill Cleanup from Sea Water by Sorbent Materials. *Chemical Engineering & Technology*, **28**, 1525-1528. <https://doi.org/10.1002/ceat.200407083>
- [10] Wang, D. (2007) Superabsorbent Polymers Derived from Kenaf. 2007 *International Symposium on Kenaf and Allies Fibres*, Xiamen, 19-21 June 2007, 9-11.

- [11] Lv, N., Wang, X.L., Peng, S.T., Zhang, H.Q. and Luo, L. (2018) Study of the Kinetics and Equilibrium of the Adsorption of Oils Onto Hydrophobic Jute Fiber Modified via the Sol-Gel Method. *International Journal of Environmental Research and Public Health*, **15**, 969.
- [12] Jamaliah, I., Eyu, G.D., Ahmad, Z. and Chukwuekezie, C.S. (2014) Oil Spills and Sustainable Cleanup Approach. *Australian Journal of Basic and Applied Sciences*, **7**, 272-280.
- [13] Feng, Y., Liu, S., Liu, G. and Yao, J. (2017) Facile and Fast Removal of Oil through Porouscarbon Spheres Derived from the Fruit of *Liquidambar formosana*. *Chemosphere*, **170**, 68-74.
- [14] Gui, X.C., Li, H.B., Wang, K.L., Wei, J.Q., Jia, Y., Li, Z., Fan, L.L., Cao, A.Y., Zhu, H.W. and Wu, D.H. (2011) Recyclable Carbon Nanotube Sponges for Oil Absorption. *Acta Materialia*, **59**, 4798-4804. <https://doi.org/10.1016/j.actamat.2011.04.022>
- [15] Maleki, H. (2016) Recent Advances in Aerogels for Environmental Remediation Application: A Review. *Chemical Engineering Journal*, **300**, 98-118. <https://doi.org/10.1016/j.cej.2016.04.098>
- [16] Gürdag, G. and Sarmad, S. (2013) Cellulose Grafting Copolymers: Synthesis, Properties and Application. Polysaccharide Based Graft Copolymer, Springer-Verlag, Berlin, Heidelberg.
- [17] EPA (2017) Oil Spill Response Techniques, EPA's Response Techniques. <https://www.epa.gov/emergency-response/epas-response-techniques>
- [18] Yuan, X. and Chung, T.C.M. (2012) Novel Solution to Oil Spill Recovery: Using Thermodegradable Polyolefin Oil Superabsorbent Polymer (Oil-SAP). *Energy Fuels*, **26**, 4896. <https://doi.org/10.1021/ef300388h>
- [19] Korhonen, J.T., Kettunen, M., Ras, R.H.A. and Ikkala, O. (2011) Hydrophobic Nanocellulose Aerogels as Floating, Sustainable, Reusable, and Recyclable Oil Absorbents. *ACS Applied Materials & Interfaces*, **3**, 1813. <https://doi.org/10.1021/am200475b>
- [20] Romero, I.C., Toro-Farmer, G., Diercks, A.R., Schwing, P., Muller-Karger, F., Murawski, S. and Hollander, D.J. (2017) Large-Scale Deposition of Weathered Oil in the Gulf of Mexico Following a Deep-Water Oil Spill. *Environmental Pollution*, **228**, 179-189. <https://doi.org/10.1016/j.envpol.2017.05.019>
- [21] Diya'uddeen, B.H., Abdul Aziz, A.R. and Daud, W.M.A.W. (2011) Oxidative Mineralisation of Petroleum Refinery Effluent Using Fenton-Like Process. Institute of Chemical Engineers, Elsevier, Amsterdam.
- [22] Diya'uddeen, B.H., Pouran, S.R., Abdul Aziz, A.R. and Daud, W.M.A.W. (2015) Fenton Oxidative Treatment of Petroleum Refinery Wastewater: Process Optimization and Sludge Characterisation. *Royal Society of Chemistry Advance*, **5**, 68159-681668.
- [23] NurAzmyra, A., Aznizam, A., Azman, H. and Nurulhusna, A. (2014) Synthesis of Chitosan-Grafted-Poly(Methyl Methacrylate) with Fenton's Reagent (Fe^{2+} - H_2O_2) as a Redox Initiator. *Malaysian Journal of Analytical Sciences*, **18**, 415-422.
- [24] Taylor, S.C. (2004) Kenaf—New Crop Fact Sheet. Kenaf International Ltd., McAllen. <http://www.hort.purdue.edu/newcrop/CropFactSheets/kenaf.html>
- [25] Mitul, Z. (2004) Absorbency Characteristics of Kenaf Core Particles. M.Sc. Thesis, Department of Textile Apparel Technology and Management, College of Textiles North Carolina State University, Raleigh.