

Recovery of Crude Oil from Aqueous Medium by Optimised Styrene/Kenaf Shive Graft-Based Sorbent Via Regeneration Method: Study of the Equilibrium, Kinetics and Activation Energy

Salisu Z. M., Ishiaku S.U., Abdullahi D, Yakubu M.K., Diya Uddeen B.H.

Abstract— The area of research that cast the mind of many environmentalist is remediation of oil spilled environments. This paper addresses the development of new bio-based sorbent through ceric induced grafting. The effect studies of the individual and combine factors was 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 variables (initiator concentration, monomer ratio and particle sizes). To the optimized sorbent, unmodified kenaf shive was compared with, it reveals a positive hydrophobic shift. However, instrumental analysis such as: XRD, FTIR, BET and DTA-TGA were carried out on the optimized sorbent. In addition, the capability of the oil sorption in water was reported and the kinetics and equilibrium isotherms employed fits respectively, the pseudo-second order and Langmuir isotherm with regression coefficient $R^2=0.9822$ and $R^2=0.9900$. The sorption property was found to be spontaneous and exothermic, however, the activation energy studies shows physic-sorption phenomenon with 25.6kJmol^{-1} and $R^2=0.9847$.

Index Terms— kenaf shive, design matrix, grafting, kinetic, isotherm, physic-sorption.

I. INTRODUCTION

Highlight Crude oil is one of the major sources of income bestowed under the earth's crust of most developed countries. 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, 10, 14, 26].

Oil spills is considered as one of the most serious disasters that is threatening the marine ecosystem [18, 20-24]. Many techniques have been devised to combat this problem [3]. These techniques include: burning in situ, bioremediation, chemical dispersion and synthetic sorbents in spite of their secondary effect of non-degradability [3, 5-6, 23]. The most widely accepted by many researchers and industries is the one

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prepared from polyurethane and polypropylene fibres and is now being considered hazardous [2, 16, 22]. Owing to the cost implication associated to incineration of these synthetic and the preparation of nanocellulose sorbents lead to the revolution of natural sorbents.

The two preeminent properties which were lacking in natural (cellulosic) sorbents: hydrophobicity and oleophilicity are now improved via surface coating or/and regeneration [11, 17-24].

This paper addresses the oil spill clean-up using ceric induced grafting methods (regeneration) on kenaf shive that is sustainable, cost effective and eco-friendly. Kenaf plant is one of the fast growing plant which adapts to different climatic changes. The shive constitutes about 60-70% of the plant, however, have little or no economic importance and available at our door step. Styrene being hydrophobic was used to incorporate the hydrophobic properties that inturn enhanced the oleophilicity.

II. MATERIALS AND METHODS

All chemicals are analytical grades and used how it was received without further purification, except for the monomer (acrylonitrile) which inhibitors were removed by washing it severally with 5% concentration of NaOH. However, stabilizers removal for Acrylic acid and Acrylamide was achieved by vacuum distillation and recrystallization with acetone, respectively. Dried Kenaf stalks were obtained from National Research Institute for Chemical Technology (NARICT), Zaria

A. 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. However, the adsorption test for modified and unmodified kenaf shive in preliminary runs was carried out at 40°C. Table 1 shows the significant properties of the oil that perhaps affect the oil sorption.

B. Experimental Procedures

The obtained dried kenaf stalks were subjected to chemical retting, 1% w/v NaOH for 2hrs in order to extract its shive from the two components (shive and bast fibres). The product was washed with distilled water until neutrality was achieved

Recovery of Crude Oil from Aqueous Medium by Optimised Styrene/Kenaf Shive Graft-Based Sorbent Via Regeneration Method: Study of the Equilibrium, Kinetics and Activation Energy

and further drying took place for 72hrs at room temperature. The extracted shive was ground into different particle sizes as prescribed by the DoE software result sheet.

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

Three neck flask was quarterly filled with about 25ml 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 24hrs in which the homopolymers weight were calculated as in Table 3. The experimental processes were repeated for twenty samples using requisites regressors as in Table 1.

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

Adsorption capabilities of both optimized extracted and unextracted homopolymer sorbents were compared.

C. Characterisations

Infrared spectra of the sorbent in KBr pellets is analysed and scanned from 4000 – 400 cm⁻¹ using Shimadzu FTIR-8400S. This test was carried out on the optimized unextracted sorbent –that has the highest oil sorption– to confirm the modifications by taking the advantage of their analyzed functional groups. The sorbent crystallinity was determine using Shimadzu XRD 6000 (Tokyo, Japan) with CuK α radiation ($\lambda = 1.542 \text{ \AA}$) operated at 30 kV and 30 mA. Surface area was determined using Brunauer, Emimett and Teller(BET) technique by (Quantachrome Instruments, Model Nova1000e series, USA), however, the heat properties was not set aside but determine using DTA-TGA60 Shimadzu, Japan.

D. Adsorbability Measurement

Oil adsorption capability for both preliminaries and the optimized extracted as well as unextracted sorbent of the modified kenaf shive fibers was investigated. According to ASTM F-726-12, the adsorption capacity formula is expressed as follows [7,15]:

$$S_w = \frac{S_{wt} - S_o}{S_o} \text{ ----- (1)}$$

where Sw is the sorption rate (g (liquid)/g (sorbent)), So is the quality of the shive fibre before sorption, and Swt is the quality of the kenaf shive fiber after sorption. We took 1 g of raw and modified shive fibres, immersed them in a beaker, and took measurements every 5 min. According to ASTM F-726-12, the test measures the rapid adsorption

capacity (15 min soaking) and 24 h adsorption capacity. The sea water used for this test is a natural seawater not simulated.

E. Batch Experiments

Equal mixture of 15mL petroleum ether and 1mL of 1+1 sulfuric acid were shaken in a reparatory funnel for 15mins. The lower aqueous organic layer was released after settling for about 10min. The organic layer was poured into a beaker containing 1.2g of drying agent (anhydrous sodium sulfate), then the mixture was drain into glass funnel. Consequently, the solution was filtered into the colorimeter coupled with 25mL of petroleum ether (this was repeated with the same quantity of petroleum ether). The residual oil concentration was determined by filtering the sorbent and analysed using UV-Vis spectroscopy.

Adsorption kinetics were performed by immersing 1g of developed sorbent a mixture of oil/sea water at room temperature. Samples and crude oil concentration were, respectively, weighed and measured at different time interval, between 1-90min.

Isotherm studies was carried out at room temperature (298K) by varying the initial concentrations 5-30g/L at interval of 5g/L using the aforementioned procedure.

The adsorption thermodynamics and activation energies (Ea) were determined via the batch experiments at different temperatures (298, 303, 313 and 323K).

The crude adsorption capacity at equilibrium (Q) is calculated by the following formula:

$$Q = \frac{(C_o - C_e)V}{S} \text{ ----- (2)}$$

Where, Co and Ce are, respectively, the initial and equilibrium concentrations of crude oil (g/L) at any time t. V is the volume of the solution (L), and S is the mass of the adsorbent (g).

2.6 Adsorption kinetics

2.6.1 Pseudo first-order model

The pseudo-first-order model is represented by the following equation [7,11]:

$$\frac{dQ_t}{dt} = K_1(Q_e - Q_t) \text{ ----- (3)}$$

When boundary conditions are reached, t = 0, Q = 0 and t = t, Q = Qt, the equation can change to:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \text{ ----- (4)}$$

this is simplified as:

$$Q_t = Q_e(1 - e^{-K_1 t}) \text{ ----- (5)}$$

Where, k₁ is the pseudo first-order rate constant; Q_e and Q_t are the adsorption capacities of the adsorbent at equilibrium.

2.6.2 Pseudo second-order model

The pseudo second-order model is represented as follows [17,19]:

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \text{ ----- (6)}$$

The linearized-integrated form of the equation is:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \text{ ----- (7)}$$

where k₂ is the pseudo second-order rate constant.

2.6.3 Intraparticle diffusion model

The intraparticle diffusion model can be used to analyze the removal of pollutants by an absorbent during a diffusion

process. This is expressed as the following equation [7, 20]:

$$Q_t = k_p t^{0.5} + C \dots\dots\dots (8)$$

where k_p is the intraparticle diffusion rate constant; and C is a constant related to the bounding layer thickness.

F. Adsorption Isotherm

Langmuir isotherm model

The Langmuir isotherm model assumes that adsorption occurs at a specific uniform location on the adsorbent surface. According to this model, the adsorbent forms a molecular monolayer.

The equation is as follows [7, 12, 16]:

$$Q_e = \frac{k_1 Q_0 C_e}{1 + k_1 C_e} \dots\dots\dots (9)$$

where Q_0 is the maximum adsorption capacity of the adsorbent (g/g); and K_1 is the Langmuir constant of equilibrium adsorption.

2.7.2 Freundlich isotherm model

The Freundlich isotherm model assumes that multilayer adsorption takes place at heterogeneous surfaces with different adsorption energies and characteristics. Here, the adsorption of the surface is calculated by the following equation [16]:

$$Q_e = k_2 C_e^{1/n} \dots\dots\dots (10)$$

where K_2 (mg/g)(L/mg) $1/n$ is the Freundlich constant; and n is the adsorption intensity.

G. Adsorption Thermodynamics

The adsorption thermodynamics of the diesel adsorption process need to be further investigated. Various thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) can be obtained by isothermal adsorption studies [7- 9, 25]. ΔG of adsorption can be represented by the classical van't Hoff equation:

$$\Delta G = RT \ln K_0 \dots\dots\dots (11)$$

where K_0 can be calculated by the following equation:

$$K_0 = Q_e / C_e$$

The apparent enthalpy (ΔH) of adsorption and the entropy (ΔS) are calculated as follows:

$$\ln \left(\frac{Q_e}{C_e} \right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (12)$$

where ΔG is in (kJ/mol); ΔH is in (kJ/mol); ΔS is in (kJ/(molK)); R is the universal gas constant (8.314 J/mol); T is the adsorption temperature (K).

H. Activation energy

The activation energy can be determined from the change of the absorption rate constant, k with temperature, $T(K)$ using the Arrhenius equation [7, 12-13].

$$\ln k = \ln A - \frac{E_a}{RT} \dots\dots\dots (13)$$

Where A is the pre-exponential factor obtained from the intercept plot of $\ln k$ versus $1/T$ and R is the gas constant (8.314 J/mol K). By plotting $\ln[k]$ against $1/T$, E_a can be calculated from the slope. Plots of kinetic rate constants of the best fitted model versus $1/T$ were obtained.

I. Characterisation

[1] Infrared spectra of the sorbent in KBr pellets is analysed and scanned from 4000 – 400 cm^{-1} using Shimadzu FTIR-8400S. This analysis was carried out on the raw kenaf shive (unmodified) and the optimized developed sorbent. Further characterization were conducted on the developed sorbents; X-ray diffraction analysis using a Shimadzu XRD 6000 X-ray diffractometer (Tokyo, Japan), DTA-TGA and BET.

III. RESULTS AND DISCUSSIONS

A. The crude oil sample was characterised using Rheometer instrument.

Table 1- Specifications of crude oil samples

Sample	K. (m ² /s)	Viscosity	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	

In Table 1, the physical properties of the used crude oil was expatiated. Hence, viscosity and density played a vital role in adsorption. However, different crude oil physical properties were recorded and is one of yardstick used in it distinguishing. This is in side of the heavy crude oil. This has some difficulties in penetrating through the sorbent than the medium or light crudes [21].

Table 2- Design matrix for crude oil styrene (ST) modified sorbents

Results									
Run no	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	5.00	125.00	0.50	0.075	0.021	10.48	176.20	6.012156	78.7694
2	5.00	125.00	2.50	0.068	0.049	17.67	472.08	17.57742	467.8264
3	12.50	1000.00	1.50	0.088	0.036	30.91	457.80	30.16935	483.3463
4	20.00	562.50	0.50	0.106	0.027	7.33	419.08	7.928607	253.4254
5	5.00	562.50	0.50	0.140	0.004	3.99	101.60	4.080156	135.5976
6	20.50	1000	2.50	0.120	0.026	12.47	224.60	16.19304	284.4126

Recovery of Crude Oil from Aqueous Medium by Optimised Styrene/Kenaf Shive Graft-Based Sorbent Via Regeneration Method: Study of the Equilibrium, Kinetics and Activation Energy

7	5.00	562.50	2.50	0.058	0.054	4.95	98.96	1.972666	76.74213
8	12.50	562.50	1.50	0.072	0.045	31.88	479.70	23.50816	400.0642
9	12.50	562.5	0.50	0.078	0.012	5.43	110.98	8.229856	193.4136
10	12.50	1000.00	1.50	0.071	0.058	32.46	567.90	30.16935	483.3463
11	12.50	125.00	2.50	0.102	0.010	23.06	414.20	23.2454	422.7043
12	20.00	125.00	2.50	0.074	0.001	25.30	421.64	24.46244	379.7779
13	12.50	1000.00	1.50	0.085	0.019	29.92	479.57	30.16935	483.3463
14	12.50	125.00	1.50	0.083	0.042	24.56	286.69	29.77302	421.7279
15	12.50	1000.00	1.50	0.079	0.034	31.11	487.96	30.16935	483.3463
16	20.00	562.50	1.50	0.074	0.022	29.68	480.30	25.21781	481.3391
17	12.50	562.50	1.50	0.083	0.042	30.85	482.65	23.50816	400.0642
18	20.00	562.50	0.50	0.075	0.032	6.95	106.78	7.928607	253.4254
19	12.50	562.50	1.50	0.083	0.042	12.27	404.01	23.50816	400.0642
20	5.00	562.50	1.50	0.073	0.044	9.90	231.09	17.34756	320.9851

B. Structural Characterisation

In Figure 1 is the FTIR spectra indicating peaks of the raw (unmodified) and, modified (optimized sorbent) kenaf shive. The results are fully discussed in [14] for succinctness is not discussed herein. The Brunure-Emmitte-Teller (BET) result is briefly discussed here. The BET results indicates an increase in surface area from 100 to 301.1m²/g. This attributes to the high crude oil sorption of the optimized sorbent than the unmodified shive. Couple with the cementing materials effect which was vividly shown in Figure 1.

The DT-TGA spectra indicates the heat behavior and state transition of the optimized sorbent. The TG thermogram

indicates four decomposition and weight loss labelled W, X, Y and Z at corresponding temperatures of 185, 355, 415 and 475°C respectively. The weight loss 10% at W was as a result of dehydration and pyrolysis in the sample via endothermic heat exchange. This phenomenon was proved by DT thermogram. The second stage exothermic heat was observed resulting to weight losses at X, Y and Z corresponding to 25, 10, 50% respectively leaving 5% residue, these indicate the sorbent degradation. This attribute indicates the optimized sorbent is highly organic and decomposability consequently, eco-friendly.

Table 3- Crude oil adsorption of Raw, Unextracted, Extracted and Optimised Styrene Grafted kenaf shive/core at 40°C for 5mins [14].

Sample	Crude oil Recovered (g/g)
Raw Kenaf Shive	3.20
Unextracted Styrene Grafted Shive (UxGST)	6.76
Extracted Styrene Grafted Shive (XGST)	5.43
Optimised Styrene Grafted Shive (GSTo).	8.03

Table 4: Comparative adsorption capacities of different sorbents for crude oil

Adsorbents	Maximum Sorption Capacity (g/g)	References
Crosslinked-1-Octene/styrene/DVB terpolymer	40	[25]
Carbon fibre aerogel	115	[23]
Graphene coated melamine sponge	165	[22]
Silanized melamine sponge	163	[4]
Polypropylene	15	[13, 26]
Banana skins	5-7	[3]
Silanized cellulose aerogel from paper waste	24.4	[5]
Acrylic acid modified kenaf shive	7	[26]
Styrene modified kenaf shive	8.03	This work

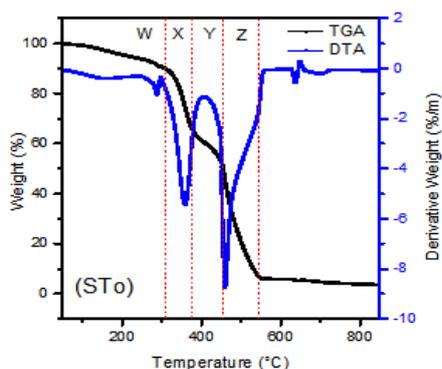


Figure 2: DTA-TGA thermogram for optimized styrene grafted shive (STo)

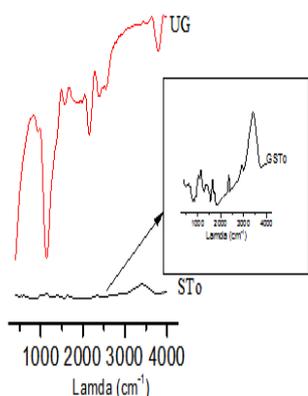


Figure 3: FTIR spectra for modified and unmodified kenaf shive

C. Adsorption Kinetics

Adsorption kinetics curve for the modified and optimized Kenaf Shive sorbent was exemplified in Figure 3. The relationship for the adsorption per unit time was tested in oil-water system. The slope at each point indicates the instantaneous sorption capacity. The adsorption capability increases rapidly at the initial stage i.e. 0-5min. A slow increase in adsorption was observed up to 30min, after, the curve flattens indicating equilibrium adsorption. This phenomenon was attributed to the increase in pore size of the optimized sorbent which was justified by the BET results analysis. Hence, the used oil is hydrophobic and viscose which made it slightly soluble in water, then couple with hydrophobic nature of the modifier leads to the high adsorption capability. The diffusion becomes slow when the pore sizes reduce this contributes to the slowness and little increase in sorption capacity after 30min.

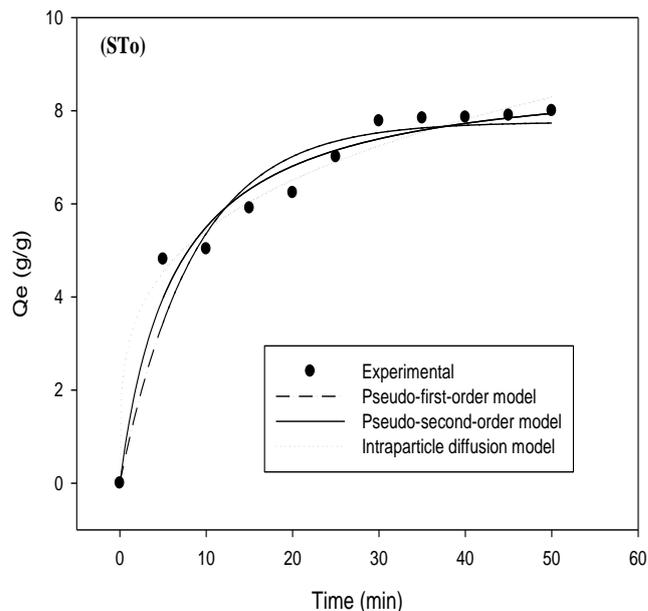


Figure 4: Kinetics of crude oil sorption on modified and optimized kenaf shive sorbent

This study shows that out of the three (pseudo-first-order, pseudo-second-order and intraparticle diffusion) kinetic models used the behavior that best fits the sorption capacity of this modified and optimized sorbent is pseudo-first-order. This was proven by correlation coefficient (R^2) of the three said models. The R^2 of pseudo-first-order is 0.9502 with sorption capacity 7.82g/g. The corresponding R^2 and sorption capacities were shown in Table 5.

Table 5: Kinetic parameters for modified/optimized kenaf shive sorption in oil/water system

Kinetic Model	Paramet	Val
	ers	ue
Pseudo-first-order	Q_e	7.9
	K_1	900
	R^2	0.0
Pseudo-second-order	Q_e	142
	K_2	0.7
	R^2	453
Intraparticle diffusion	Q_e	8.0
	K_3	100
	R^2	1.2
		757
		0.9
		603
		0.0
		581
		5.7
		325
		0.8
		489

D. Adsorption Isotherm

Sorption isotherms describe the equilibrium existence between the liquid and solid phase, however, shows the interrelation between solute and sorbent. It is therefore, important in the sorbent optimization. Besides, it also gives the capacity of the sorbent and the equilibrium relationships between sorbent and sorbate. In other words, the ratio between the quantity sorbed and the remaining in solution at fixed temperature at equilibrium. In this study the data are fitted into prominent models; Langmuir and Freundlich isotherms. These isotherm models were depicted in Figure 4.9.3 whose constant values express the affinity of sorbate to surface of sorbent.

The Langmuir Isotherm model was developed to describe a monolayer sorption onto a solid surface of specific finite number of identical binding sites. This model shows the equilibrium distribution of sorbate onto solid or liquid sorbents with the assumption of monolayer formation on homogenous energy surface [7, 15, 18]. The sorption mechanisms in this model involve three steps: the diffusion of ions residue to the external surface of sorbent; the diffusion into the pores of sorbent; and the sorption of the residue on the internal surface of sorbent [16].

Initial concentration and contact time are the basic factors that affect the first part of this model and the final part is considered as rate determining step that is relatively quick process. Linearized form of Langmuir equation was used in this studies.

The Freundlich isotherm model is applied in the intensity estimation of sorbent towards sorbate. One major characteristic of the Freundlich isotherm, though not based on a theoretical background, is its ability to give a good representation of equilibrium data over a restricted range of concentration. The model assumes that the removal of crude oil molecules occurs on a heterogeneous sorbent surface and can be applied to multilayer sorption [3, 19]. The equilibrium data were treated with the linearized Freundlich isotherm equations.

The mathematical model for the adsorption isotherm for modified kenaf shive in an oil/water mixture at 313 K is presented. The results are shown in Figure 4 and Table 5. Comparison of the R² values (Table 5) reveals that the Langmuir model is the best fitting to explain the adsorption of crude oil from the optimized kenaf shive sorbent(GSTo).

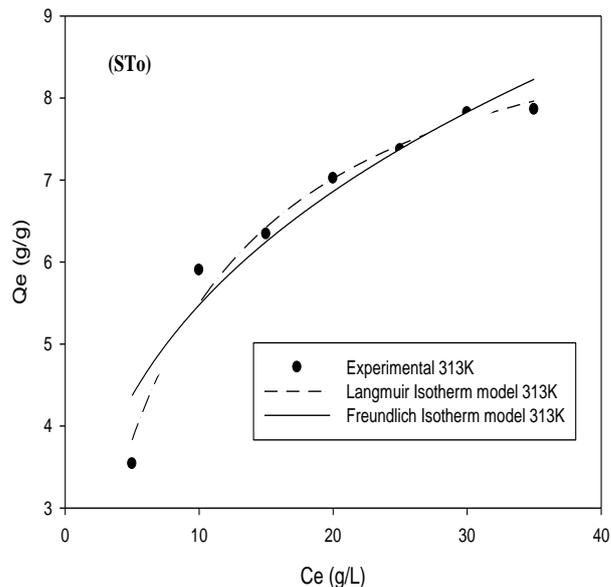


Figure 5: Isotherm of crude oil sorption on modified and optimized kenaf shive sorbent (STo)

Table 6: Thermodynamic parameters for the sorption of crude oil onto optimized kenaf shive sorbent

Isotherm Model	Isotherm Constants	Temperature (313K)
Langmuir	Q_0	10.4743
	K_1	0.0804
	R^2	0.9003
Freundlich	n	0.4812
	K_2	0.1943
	R^2	0.8224

3.5 Thermodynamic Studies

The thermodynamic parameters, values ΔG and ΔH can be calculated by plotting $\ln(Q_e/C_e)$ versus $1/T$ (Figure 4.9.4 and Table 4.9.2). The ΔG values of the developed sorbent ranges between approximately -20 to 82 kJ/mol at temperatures of 303, 313, 323, 333K, indicates that in the adsorption process, crude oil molecules are spontaneously adsorbed from the mixture of the oil/water to surface of modified sorbents. This appeared for the sorbents having a negative ΔG_s , however, for those sorbents having positive ΔG appeared to be nonspontaneous. It also observed that as the temperature increases ΔG reduces, in other words is inversely related with temperature. Consequently, higher temperatures leads to weaker driving force of adsorption, in addition, lead to more difficult sorption of the oil [2, 7, 15]. If $\Delta S < 0$, then the oil molecules movement in the developed sorbent is said to be limited and show a level of orderliness as well as decrease in randomness at the solid–mixture interface during the adsorption of crude oil from water due to the highly ordered crude oil molecules in the hydrophobic layer of the sorbents at adsorption equilibrium.

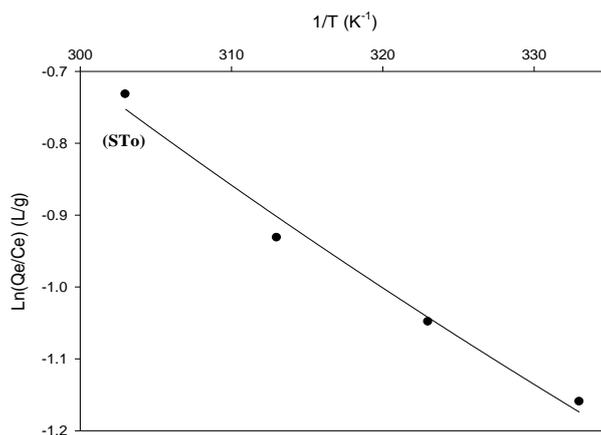


Figure 6: Plot of $\ln(Q_e/C_e)$ against $\frac{1}{T}$ for crude oil adsorption of optimized kenaf shive sorbent for thermodynamics parameters

Table 7: thermodynamics parameters for crude oil sorption on optimized kenaf shive sorbent

T (K)	ΔG (kJ.mol ⁻¹)	ΔH (kJ.mol ⁻¹)	ΔS (J.mol ⁻¹ .K ⁻¹)	Ea (kJ.mol ⁻¹)	R ²
303	49.04				
313	49.49	-35.36	45.16	25.64	0.9847
323	49.94				
333	50.40				

3.6 Activation Energy

Activation energy, Ea is an important thermodynamic parameter which must be overcome by a sorbate before sorption interaction occur with the functional groups of the sorbent surface.

The activation energy can be determined from the change of the absorption rate constant, k with temperature, T (K) using the Arrhenius equation [7, 18]:

$$\ln k = \ln A - \frac{E_a}{RT}$$

Where A is the pre-exponential factor and R is the gas constant (8.314 J/mol K). By plotting $\ln[k_2]$ against $1/T$, E_a and $\ln A$ can be calculated respectively, from the slope and intercept. The pseudo-second-order constant was used in the activation energy manipulation because the kinetic equation that best fitted the kinetic models is the second-order.

In this studies, the best kinetic model of each sorbent was used at different temperatures of 303, 313, 323 and 333 K. The natural logarithms of the absorption rate constants, k_1 was plotted against the $1/T$. In a nut shell, the sorbents that were best fitted with say, Pseudofirst- order, the rate constant k, was determine at four different temperatures. However, such rates were plotted against the corresponding $1/T$.

Plots of $\ln k$ versus $1/T$ are presented in (Figure 6), the activation energy value is presented in Table 7.

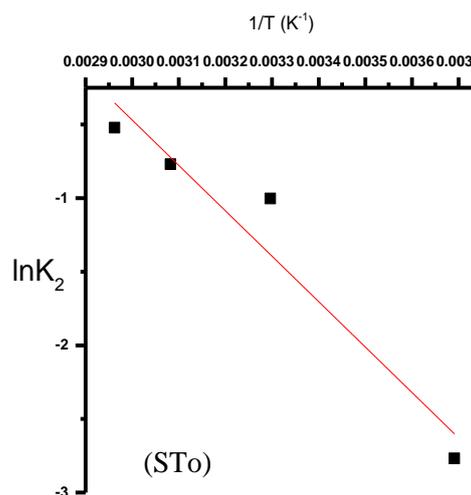


Figure 7: Plot of $\ln k_2$ against $\frac{1}{T}$ for crude oil adsorption of optimized kenaf shive sorbent for activation energy parameters

Generally speaking, the developed sorbent has lower activation energy because is between 5-50kJ/mol [7, 17-20]. Pseudo-second-order model has higher than those of the pseudo first-order model. This is because the corresponding models used for the absorption process controlled by chemisorption, which involves higher forces than in physisorption. Moreover, the physisorption phenomenon that was observed by the sorbents/mixture interface is an isosteric heat behavior of its enthalpy (ΔH) [13].

Recovery of Crude Oil from Aqueous Medium by Optimised Styrene/Kenaf Shive Graft-Based Sorbent Via Regeneration Method: Study of the Equilibrium, Kinetics and Activation Energy

IV. CONCLUSION

The imparting hydrophobic property on to kenaf shive was achieved and effective via regeneration (grafting) method. The merit of using this cellulosic material (kenaf shive) is due to its low economic importance and high abundance moreover, withstand different climatic changes. Combating this menace using the kenaf shive added value as it is the 60-70% of the plant. The variables (particle sizes, initiator and monomer concentration) which have important role in the modification of this facile sorbent were studied. Comparing the developed eco-friendly sorbent with natural based sorbent shows a remarkable sorption capability of $8.0 \pm 0.02 \text{ g/g}$. The basis for this facility is supported by structural analysis. FTIR support the achievement for the modification. BET, DT-TGA and XRD elucidate in the surface structure of the optimized sorbent consequently, increase the crude oil uptake from water/oil mixture. The kinetic model exhibited by the regenerated kenaf shive developed is pseudo-second-order model. The sorption is controlled by film-diffusion via internal diffusion transport mechanism. Comparing the Freundlich sorption isotherm, the Langmuir equation best fitted the sorption process of crude oil onto optimized regenerated kenaf shive sorbent. The experimental data obtained from thermodynamic parameters in this study validate the spontaneity and exothermic phenomenon of the crude oil sorption. The low activation energy indicates physisorption phenomenon.

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