Insight into the Sorption and Activation Energy Phenomenon of Kenaf Shive Sorbents in Crude Oil/Water Mixture

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Authors’ contributions

This work was carried out in collaboration among all authors. Authors MS, BHD and MKY designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors SUI and MAS and YLG managed the analyses of the study. Author SPU managed the literature searches. All authors read and approved the final manuscript.

ABSTRACT

The secondary effect discovery of synthetic sorbents opened another research direction for many field of studies. However, the sorption parameters of lignocellulosic sorbents are rarely reported most importantly, kenaf shive. This paper centered at the sorption behavior of optimized kenaf shive sorbents using Response Surface Methodology (RSM) via surface deposit technique. Five-level Central Composite Design (CCD) experimental matrix was used to analyze the effect of particle sizes (125-1000 µm), stirring time (5-30min) and methyltrimethoxysilane (MTMS) concentration (5-20% v/v) as individual and combined variables process in the developed sorbents. The unmodified shive was compared with the modified, and it reveals a positive shift in the sorption capability. Instrumental analysis such as FTIR (Fourier Transform Infra-Red), DT-TGA (Differential Thermal-Thermogravimetric analysis) and BET (Brunauer-Emmett-Teller) were carried out on the optimized sorbent and the results were in conformity with the sorption results. The sorption behavior deployed fits the pseudo-first-order and Langmuir isotherm with regression coefficient...
85% and lignin [15,30,31].

This research paper critically studied the sorption behavior of this novel, ultralight, robust and facile sorbent in dense crude oil/seawater system with reference to temperature, oil concentration and sorption time.

2. METHODOLOGY

2.1 Materials

The used chemicals are analytical grades, without further purification and dried Kenaf stalks were obtained from National Research Institute for Chemical Technology (NARICT), Zaria. The crude oil and seawater samples used for the sorption test were obtained from Petroleum Research Laboratory, Warri, Delta state, Nigeria. The raw crude oil was kept at room temperature and sea water was stored below 0°C in refrigerator.

2.2 Fabrication and Hydrophobia Coating of Kenaf Shive Sorbent

The sorbents were fabricated as reported by Salisu et al. [13]. For brevity, a pulverized Kenaf shive was dispersed in (2 wt%) sodium hydroxide/urea solution (1.9 wt%/10 wt%) and stirred for 6mins using mechanical stirrer to achieve homogeneity in the dispersion. Aftermath, the sample was gelated by placing in a refrigerator for more than 24hrs. Then, the mixture was thawed at room temperature after...
frozen, followed by immersion into ethanol (99 vol %) for coagulation. The beaker in which the preparation takes place was used as mold to control the specimen thickness. It is imperative to know that no cross linker was used which makes the particles a bit loose. Coagulation was directly carried out by immersing the gel in DI water for 2 days. Freeze-drying was carried out on the sample for 2 days at approximately −60°C after pre-freezing the sample at −18°C for 12 hr.

The afore-fabricated aerogel of kenaf shive was coated using chemical vapor deposition (CVD) technique for silation, i.e. methyltrimethoxysilane (MTMS). Then the resulted sample was capped and heated in an oven at 70°C for 2 hrs for a completed silation reaction. Thereafter, the coated sample was placed in a vacuum oven to remove the excess coating reagent at approximately small pressure.

2.3 Characterisations

Infrared spectra of the sorbent in KBr pellets was analysed and scanned from 4000 – 400 cm⁻¹ using Shimadzu FTIR-8400S. The test was carried out on the raw (unmodified) and modified optimized unextracted sorbent that bears the highest oil sorption to confirm the modifications by taking the advantage of the unique vibration/stretching property for each functional group. The sorbent structure was determine using Shimadzu XRD 6000 (Tokyo, Japan) with CuKα radiation (λ= 1.542 Å) operated at 30 kV and 30 mA whereby the ground sorbent was scanned at rate of 0.05°/min at angle range of 3° ≥ 2θ ≤ 90°. The generated raw data were used to replot the diffractogram aided by Origin Pro 9.0 16 Bit, Fig. 3. Surface area was determined using Brunauer, Emmette 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.

2.4 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 [15,31,32]:

\[ S_w = \frac{S_{wa}-S_o}{S_o} \]  

Where; \( S_w \) is the sorption rate (g (liquid)/g (sorbent)), \( S_o \) is the quality of the shive fibre before sorption, and \( S_{wt} \) is the quality of the kenaf shive fiber after sorption. 1 g of raw and modified shive fibres was immersed into a beaker, and measurements was recorded after every 5 min. According to ASTMF-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.

2.5 Batch Experiments

Equal mixture of 15 mL petroleum ether and 1 mL of 1+1 sulfuric acid were shaken in a reparator funnel for 15mins. The lower aqueous organic layer was released after settling for about 10min. The organic layer was poured into a beaker containing 1.2 g of drying agent (anhydrous sodium sulfate), then the mixture was drain into glass funnel. Consequently, the solution was filtered into the colorimeter coupled with 25 mL 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 1 g 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 1-90 min.

Isotherm studies was carried out at room temperature (298K) by varying the initial concentrations 5-30 g/L at interval of 5 g/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 323 K).

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

\[ Q = \frac{(C_o-C_e)V}{S} \]  

Where, \( C_o \) and \( C_e \) 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 [15,31]:

\[
\frac{dQ_t}{dt} = K_1(Q_e - Q_t)
\]  \(3\)

When boundary conditions are reached, \(t = 0, Q = 0\) and \(t = t, Q = Q_t\), the equation can change to:

\[
\ln(Q_e - Q_t) = \ln Q_e - K_1 t
\]  \(4\)

dressed as:

\[
Q_t = Q_e(1 - e^{-K_1t})
\]  \(5\)

Where, \(k_1\) is the pseudo first-order rate constant; \(Qe\) and \(Qt\) 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 [15,33,34]:

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

The linearized-integrated form of the equation is:

\[
Q_t = \frac{k_2Q_e^2t}{1+k_2Q_et}
\]  \(7\)

where \(k_2\) 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 [34,35]:

\[
Q_t = k_p t^{0.5} + C
\]  \(8\)

where \(k_0\) is the intraparticle diffusion rate constant; and \(C\) is a constant related to the bounding layer thickness.

2.7 Adsorption Isotherm

2.7.1 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 [15,31,35]:

\[
Q_e = \frac{k_1Q_0C_e}{1+k_1C_e}
\]  \(9\)

where \(Qo\) 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:

\[
Q_e = k_2C_e^{1/n}
\]  \(10\)

where \(K2\) (mg/g) (L/mg) \(1/n\) is the Freundlich constant; and \(n\) is the adsorption intensity.

2.8 Adsorption Thermodynamics

The adsorption thermodynamics of the crude oil adsorption process need to be further investigated. Various thermodynamic parameters such as enthalpy (∆H), entropy (∆S), and Gibbs free energy (∆G) can be obtained by isothermal adsorption studies [31,36]. ∆G of adsorption can be represented by the classical Van't Hoff equation:

\[
\Delta G = RT \ln K_0
\]  \(11\)

where \(K_0\) can be calculated by the following equation:

\[
K_0 = Qe /Ce
\]

The apparent enthalpy (∆H) of adsorption and the entropy (∆S) are calculated as follows:

\[
\ln \left( \frac{Qe}{Ce} \right) = \frac{\Delta S}{T} - \frac{\Delta H}{RT}
\]  \(12\)

where ∆G is in (kJ/mol); ∆H is in (kJ/mol); ∆S is in (kJ/(molK)); R is the universal gas constant (8.314 J/mol); T is the adsorption temperature (K).

2.9 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 [33]:

\[
\ln k = \ln A - \frac{E_a}{RT}
\]  

(13)

Where A is the pre-exponential factor obtained from the intercept plot of \(\ln k\) (kinetic rate constant of the best fitted model) 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.

3. RESULTS AND DISCUSSIONS

3.1 The crude Oil Sample was Characterised using Rheometer Instrument

In Table 1, the physical properties of the used crude oil are expatiated. Hence, viscosity and density played a vital role in adsorption. However, different crude oil has unique physical properties and were recorded, thus results the yardstick for differentiation. This is insight of the heavy crude oil. This has some difficulties in penetrating through the sorbent than the medium or light crudes [11,37]. The composition ratios of the synthesized sorbents and number of runs as well as considered responses were shown in Table 2.

3.2 Structural Characterisation

In Fig. 1 is the FTIR spectra indicating peaks of the raw (unmodified) and, modified (optimized sorbent) kenaf shive. The results are fully discussed in [8], for succinctness is not discussed herein. The Brunere-Emmitte-Teller (BET) result is briefly discussed here. The BET results indicates an increase in surface area from 100 to 301.1 m\(^2\)/g. This attribute to the high crude oil sorption of the optimized sorbent was observed than in the unmodified shive based on the investigated variables (see Table 3). Couple with the cementing materials effect which was vividly shown in Fig. 1. The cementing material decrease the oil sorption in the sorbent because it is less porous compare to the pulverized shives [18].

The DT-TGA spectra in Fig. 2 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 optimized sorbent’s degradation. This attribute indicates the optimized sorbent is highly organic and decomposability consequently, eco-friendly.

Differences sorption capacities of different sources of sorbents were reported in Table 4. This is portray the efficacy of the synthesized sorbent when compared with the few reported ones, hence, considered as an alternative sources of sorbent development.

3.3 Adsorption Kinetics

Adsorption kinetics curve for the modified and optimized Kenaf Shive sorbent was exemplified in Fig. 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. 0-5 min. A slow increase in adsorption was observed up to 30 min, after, the curve flattens indicating equilibrium adsorption [31,41]. 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 30 min [15].

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 0.950 with sorption capacity 12.020 g/g. The corresponding R\(^2\) and sorption capacities were shown in Table 5. Despite the high adsorption shown in pseudo-second-order yet is less assured based on the recorded R\(^2\) value [42].
Table 1. Specifications of crude oil samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>K. Viscosity (m²/s)</th>
<th>Speed (m/s²)</th>
<th>Torque (Nm)</th>
<th>Temp. (°C)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
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<tr>
<td>Crude oil</td>
<td>1.33</td>
<td>30.00</td>
<td>0.10</td>
<td>24.5</td>
<td>0.8965</td>
</tr>
<tr>
<td></td>
<td>0.67</td>
<td>60.00</td>
<td>0.00</td>
<td>24.5</td>
<td></td>
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</tbody>
</table>

Table 2. Design matrix for crude oil silane (SL) modified sorbents

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Experimental Design</th>
<th>Results</th>
<th>Predicted</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Experimental Design</td>
<td>Experimental</td>
<td>Predicted</td>
</tr>
<tr>
<td></td>
<td>Residence time (min)-A</td>
<td>Particle size (µm)-B</td>
<td>MTMS conc. (%)</td>
</tr>
<tr>
<td>1</td>
<td>5.00</td>
<td>1000.00</td>
<td>20.00</td>
</tr>
<tr>
<td>2</td>
<td>17.50</td>
<td>562.50</td>
<td>12.50</td>
</tr>
<tr>
<td>3</td>
<td>17.50</td>
<td>1000.00</td>
<td>12.50</td>
</tr>
<tr>
<td>4</td>
<td>17.50</td>
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<td>20.00</td>
</tr>
<tr>
<td>5</td>
<td>5.00</td>
<td>125.00</td>
<td>5.00</td>
</tr>
<tr>
<td>6</td>
<td>30.50</td>
<td>1000.00</td>
<td>5.00</td>
</tr>
<tr>
<td>7</td>
<td>17.50</td>
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<td>12.50</td>
</tr>
<tr>
<td>12</td>
<td>17.50</td>
<td>562.50</td>
<td>12.50</td>
</tr>
<tr>
<td>13</td>
<td>30.00</td>
<td>125.00</td>
<td>5.00</td>
</tr>
<tr>
<td>14</td>
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</tr>
<tr>
<td>20</td>
<td>30.00</td>
<td>1000.00</td>
<td>20.00</td>
</tr>
</tbody>
</table>

Fig. 1. FTIR photogram of unmodified (UM) and optimized silane (SLo) kenaf shive sorbent
Table 3. Functional group assignment of the optimized silane kenaf shive sorbent for FTIR spectra

<table>
<thead>
<tr>
<th>WAVE NUMBER (CM⁻¹)</th>
<th>VIBRATION</th>
<th>STRUCTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>786</td>
<td>sv (SiC)</td>
<td>–Si–C</td>
</tr>
<tr>
<td>2922</td>
<td>™s (CH₃)</td>
<td>–CH₃</td>
</tr>
<tr>
<td>3324</td>
<td>δs (OH)</td>
<td>–OH</td>
</tr>
<tr>
<td>2051</td>
<td>δas(CH₂)</td>
<td>–CH₂</td>
</tr>
<tr>
<td>1673</td>
<td>δas(CO)</td>
<td>–C=O</td>
</tr>
<tr>
<td>1591</td>
<td>δs(CC)</td>
<td>–CH=CH₂</td>
</tr>
<tr>
<td>1151</td>
<td>sv(CH₃)</td>
<td>–CH₃</td>
</tr>
<tr>
<td>1021</td>
<td>δs(SiOSi)</td>
<td>–Si–O–Si</td>
</tr>
</tbody>
</table>

sv: symmetrical vibration, δs: symmetrical stretching, δas: Asymmetrical stretching

Fig. 2. DT-TGA plots showing the thermal effect on the optimized modified silane sorbent

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

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Maximum Sorption Capacity (g/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crosslinked-1-Octene/styrene/DVB terpolymer</td>
<td>40</td>
<td>[38]</td>
</tr>
<tr>
<td>Carbon fibre aerogel</td>
<td>115</td>
<td>[39]</td>
</tr>
<tr>
<td>Graphene coated melamine sponge</td>
<td>165</td>
<td>[12]</td>
</tr>
<tr>
<td>Silanized melamine sponge</td>
<td>163</td>
<td>[40]</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>15</td>
<td>[33]</td>
</tr>
<tr>
<td>Banana skins</td>
<td>5-7</td>
<td>[7]</td>
</tr>
<tr>
<td>Silanized cellulose aerogel from paper waste</td>
<td>24.4</td>
<td>[11]</td>
</tr>
<tr>
<td>Acrylic acid modified kenaf shive</td>
<td>7</td>
<td>[8]</td>
</tr>
<tr>
<td>Styrene modified kenaf shive</td>
<td>8.03</td>
<td>[15]</td>
</tr>
<tr>
<td>Silanized kenaf shive sorbent</td>
<td>12.02</td>
<td>[18]</td>
</tr>
</tbody>
</table>

Fig. 3. Kinetics of crude oil sorption on silane optimized kenaf shive sorbent
Table 5. Kinetic parameters for modified/optimized kenaf shive sorption in oil/water system

<table>
<thead>
<tr>
<th>Kinetic Model</th>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>Q&lt;sub&gt;e&lt;/sub&gt;</td>
<td>12.020</td>
</tr>
<tr>
<td></td>
<td>K&lt;sub&gt;1&lt;/sub&gt;</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.950</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>Q&lt;sub&gt;e&lt;/sub&gt;</td>
<td>15.040</td>
</tr>
<tr>
<td></td>
<td>K&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.611</td>
</tr>
<tr>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.843</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>K&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.145</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>8.717</td>
</tr>
<tr>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.720</td>
</tr>
</tbody>
</table>

3.4 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 Fig. 4 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 [43]. 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 [34].

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 [34]. The equilibrium data were treated with the linearized Freundlich isotherm equations.

The mathematical model for the adsorption isotherm for modified and optimized kenaf shive sorbent in an oil/water mixture at 313 K is presented. The results are shown in Fig. 4 and Table 6. Comparison of the R<sup>2</sup> 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 (SLo).

3.5 Thermodynamic Studies

The thermodynamic parameters, values ∆G and ∆H can be calculated by plotting ln(Q<sub>e</sub>/Ce) versus 1/T (Fig. 5 and Table 7). The ∆G values of the developed sorbent ranges between approximately -1.9 to 2.8 kJ/mol at temperatures of 303, 313, 323, 333 K, indicates that in the adsorption process, crude oil molecules are relatively spontaneous for the mixture on to the surface of the optimized silane sorbent. This appeared for the sorbents having a negative ∆Gs, however, for positive ∆G appeared implied nonspontaneous sorption process. It also observed that as the temperature increases ∆G 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 [31,44]. If ∆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/seawater system due to the highly ordered crude oil molecules in the hydrophobic layer of
the sorbents at adsorption equilibrium. In other words, negative $\Delta S$ (entropy) shows an associated mechanism of the reaction and is enthalpy driven [35]. The negative enthalpy ($\Delta H$) attributed to the exothermic behavior of the sorption phenomenon [15,42].

![Graph showing isotherm of crude oil sorption on modified and optimized kenaf shive sorbent (STo)](image)

**Fig. 4. 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**

<table>
<thead>
<tr>
<th>Isotherm Model</th>
<th>Isotherm Constants</th>
<th>Temperature (313K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$Q_0$</td>
<td>12.60</td>
</tr>
<tr>
<td></td>
<td>$K_1$</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.940</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$n$</td>
<td>0.600</td>
</tr>
<tr>
<td></td>
<td>$K_2$</td>
<td>0.180</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.840</td>
</tr>
</tbody>
</table>

![Graph showing plot of $\ln(Q_e/C_e)$ against $1/T$ for crude oil adsorption of optimized kenaf shive sorbent for thermodynamics parameters](image)

**Fig. 5. Plot of $\ln (Q_e/C_e)$ against $1/T$ 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

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔG (kJ.mol⁻¹)</th>
<th>ΔH (kJ.mol⁻¹)</th>
<th>ΔS (J.mol⁻¹.K⁻¹)</th>
<th>Ea (kJ.mol⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>-1.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>-2.20</td>
<td>-7.04</td>
<td>-29.50</td>
<td>25.30</td>
<td>0.9360</td>
</tr>
<tr>
<td>323</td>
<td>-2.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>-2.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### 3.6 Activation Energy

Activation energy, $E_a$ 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 [44]:

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

Where A is the pre-exponential factor and R is the gas constant (8.314 J/mol K). By plotting $\ln[k_1]$ against $1/T$, $E_a$ and $\ln A$ can be calculated respectively, from the slope and intercept. The pseudo-first-order constant was used in the activation energy manipulation because the kinetic equation that best fitted the kinetic models is the pseudo-first-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 nutshell, the sorbents that were best fitted with say, Pseudo-first-order, the rate constant $k$, was determined at four different temperatures. However, such rates were plotted against the corresponding $1/T$.

Plots of $\ln k_1$ versus $1/T$ are presented in (Fig. 6), the activation energy value is presented in Table 7.

Generally speaking, the developed sorbent has lower activation energy because it is between 5-50kJ/mol [34,44]. Pseudo-second-order model has higher binding energy 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 physiosorption. Moreover, the physisorption phenomenon that was observed by the sorbents/mixture interface is an isosteric heat behavior of its enthalpy ($\Delta H$) [45].

![Fig. 6. Plot of $\ln k_1$ against $1/T$ for crude oil adsorption of optimized silane kenaf shive sorbent for activation energy parameters](image-url)
4. CONCLUSION

A silanized kenaf shive sorbents were feasible via surface deposit technique. Effect of some important parameters were studied and optimized using Response Surface Methodology that increase the sorption capability to >12g/g. Containment of this menace using this agro-based waste with no/and little economic value make an economic sense besides its eco-friendliness. To ascertain the feasibility of this facile and robust sorbent, analytical tests were carried out on the optimized sorbent such as: FTIR, BET and DT-TGA which show a backing informations to this great achievement. Of course, in order to complete the studies enthertor, a critical study on sorption phenomenon were undertook such as: kinetics, isotherms and thermodynamics which respectively, reveals the fitness of pseudo-first-order, Langmuir and physic-sorption of the developed sorbent with an exothermic reaction process.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES


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