Application of Langmuir Isotherm on Adsorption to Monitor the Uptake of oil using Abura Sawdust in Seawater medium

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ABSTRACT

This research was conducted to examine the significance of the application of Langmuir isotherm on the rate of adsorption to monitor, predict and simulate the uptake of soil using Abura wood sawdust in sea water medium. The Langmuir isotherm concepts were adopted to determine the amount of the crude oil absorbed and the influence of the absorbent. The result obtained revealed that increase in reduction in crude oil was observed with increase in reduction in crude oil was observed with increase in dosage of the Abura wood sawdust and the possible elements identified in terms of character are Ca, K, S, Si, Sn, Cr, Zn, Pb, Mo, Nb, etc. As well as the morphology of the Abura wood sawdust species well described in this paper. The effect of time on the concentration of
the Langmuir parameter were evaluated as the result obtained also revealed decrease with increase in weight of adsorbent used and increase with increase in time. Finally, the research work demonstrates the significance of the Langmuir isotherm concept of monitoring, predicting and simulating the rate of crude oil adsorption using Abura wood sawdust in seawater medium.

Key words Application, Langmuir isotherm, adsorption, monitor, crude oil, abura sawdust, seawater medium

1. INTRODUCTION

It is of great importance to explore the capability of natural adsorbent (sawdust) for the adsorption process in clean-up operations of oil spilled environment. A better understanding of the mechanism of adsorption of crude oil on this adsorbent (sawdust materials) will require investigation into the particle size of the adsorbent and the critical factors that affect its rate of adsorption in terms of adsorbent characteristics (adsorption capacity) will be valuable in ascertaining the suitability or otherwise of these materials for oil spill cleanup. It will also involve the determination of the physical and chemical properties of the sawdust. These will entail carrying out experimental works to determine the rate of adsorption.

This work shall explore different kinds of locally available adsorbents and examine the challenges associated with their use for this process. The study will include examining their characteristics, evaluating their effectiveness and feasibility for application as remediation materials. Suggestions will be made based on findings from experimental results and appropriate adsorption models will be developed.

Crude oil is made up of hydrocarbons and other compounds. The physical and chemical properties of petroleum oil change progressively, which means these physico-chemical changes facilitate oil disintegration in aquatic environment [1, 15]. This disintegraion process is referred to as weathering, which includes spreading, vaporization, dissolution, oxidation, biodegradation, sedimentation, dispersion, agglomeration, adsorption into suspended materials, etc. To some extent the speed with which weathering showcases depends on the location where petroleum was released, that is, water surface or subsurface [2]. Spilled oil has an unpleasant taste and smell, and results in environmental nuisance, generally destroys birds and life in the sea [3]. Consequently, diverse processes have been created to take away oil from contaminated areas by use of man-made device/materials such as: booms, dispersers and skimmers, oil water separator or the use of assorted kinds of sorbent material [4]. Although the main constraint of the use of these techniques is their expense and not achieving complete uptake of contaminant via adsorption [5]. Oil sorbent materials can be separated into three major classes: organic synthetic products (polyethylene, polypropylene etc), inorganic mineral products (sand, clay, volcanic ash etc) and natural organic vegetable products (sawdust, hay, peat etc) [6]. A certain number of studies indicate that sawdust sorbents have ability for high oil sorption capacity and low water uptake when compared to materials which can be used for this purpose. And as a result sawdust sorbents could be a considerable material for oil recovery on water surface. Previous studies have shown that mechanical recovery is the transfer of oil from the spilled area to some storage materials in form of oil sorbents or skimmers in a short while [7]. Recent evaluations by several studies show that porous and natural adsorbent material have been used to conduct investigation into crude oil spill cleanup using different natural, synthetic and mineral sorbents [8, 16]. Some of these materials, which may be oleophilic, hydrophobic and floatable on water can showcase selective absorption of hydrocarbons [9]. Frequently used sorbents are sawdust sorbents made of woody materials [10]. They exhibit good oleophilic, hydrophobic and biodegradability features [11]. A biodegradable material with exceptional adsorption attributes would be beneficial in this aspect. A number of investigations have been made on natural sorbents for use in oil-spill cleanup, for example, cotton [12], these material could be splendid oil sorbent due to their hydrophobic and oleophilic character. Baltrenas & Vaisis, [13] also explored the thermal alteration influence on sorption qualities of bio-sorbents. Cellulosic sorbent that has been chemically treated such as Sugarcane bagasse was esterified with acetic anhydride using N-bromosuccinimide as a catalyst under placid conditions [14].

2. MATERIALS AND METHODS

Experiment on salt water

Firstly, 100ml of the salt water sample was measured into a beaker then 5ml of the crude oil was measured and poured into the beaker with the salt water to contaminate it. Thereafter, the wood sawdust sample was introduced into the mixture to effect remediation.

The initial concentration \( C_0 (\text{mg/l}) \) of the contaminated water was taken with a UV Spectrophotometer before applying the adsorbent (sawdust).
Thereafter, this was repeated for each sample of the four wood sawdust samples selected using the already weighed wood sawdust samples 10g, 20g, 30g, 40g, 50g of each at time interval of 1hr, 2hrs and 3hrs respectively. This was done for each of the wood sample. After the batch adsorption processes the oil/water filtered sample was sent to a spectrophotometer to determine the final oil concentration $C_e$ (mg/l) of the contaminated oil/saltwater mixture.

**Computational Procedure**

The amount of the crude oil adsorbed and percentage of removal of crude oil by the adsorbent were calculated by applying the two equation below:

$$q = \frac{C_o - C_e}{m} \times V$$

$$\%\text{ removal} = \left(\frac{C_o - C_e}{C_o}\right) \times 100$$

Where $q$ is the amount of crude oil adsorbed by the sorbent (mg/g) $C_o$ is the initial crude oil concentration put in contact with the adsorbent (mg/l) $C_e$ is the final concentration (mg/l) after the batch adsorption procedure, V is the volume of aqueous solution (L) that the sum of volume of crude oil and water in the plastic container (L) put in content with the adsorbent and $M$ is the mass (g) of the adsorbent.

**Application of Langmuir Adsorption Isotherm Equation**

Langmuir Adsorption Isotherm Equation was employed to evaluate the adsorption process;

$$q_e = \frac{(C_o - C_e)V}{M}$$

Where $q_e$= Oil Adsorption Capacity in mg/g

$C_o$ = Initial concentration In mg/L (69.25mg/L)

$C_e$ = Final Concentration In mg/L

V= Volume of crude oil solution in L (100ml)

M= mass of Adsorbent in gram

![Figure 1 Experimental Set Up for the Batch Adsorption Process](image)
3. RESULTS AND DISCUSSION

Adsorption test was also carried out on seawater to monitor the uptake of oil using sawdust; the Langmuir isotherm was also applied to evaluate the level of adsorption.

The plot of $\frac{C_e}{q_e}$ versus $C_e$ are presented thus:

$$y = 8.7252x - 146.34$$
$$R^2 = 0.9994$$
(b) 20g ABURA

\[
y = 17x - 258.72 \\
R^2 = 0.8824
\]

(c) 30g ABURA

\[
y = 50.05x - 953.48 \\
R^2 = 0.7527
\]

(d) 40g ABURA

\[
y = 11.112x - 0.0137 \\
R^2 = 1
\]
Figure 4(a), (b), (c), (d), (e): A plot of Langmuir Isotherm $\frac{C_e}{q_e}$ versus for Abura

Figure 4(a), (b), (c), (d) and (e) illustrates the relationship between the Langmuir isotherm functional parameter of $\frac{C_e}{q_e}$ and the $C_e$ value of the various wood sawdust sample species. The equation of line for 10g of Abura is given as $y = 8.7252 - 146.34$ with the square root of the best fit given as $R^2 = 0.9994$ for Figure 4(a). Considering Figure 4 (b), it is shown that the equation of the line is given as $y = 1.7x - 2.58.72$ with the square root of the best fit as $R^2 = 0.8824$ (20g of Abura used for the analysis). For 30g of Abura we have the equation of the line as $y = 50.5x - 953.48$ with the square of the best fit $R^2 = 0.7527$. For 40g of Abura specie we have the equation of the line as $y = 11.112x - 0.0137$ with the square root of the best fit $R^2 = 1$, whereas for 50g of Abura it is seen that the equation of the line is given as $y = 325x - 8E-11$ with the square root of the best fit given as $R^2 = 1$. The variation in the Langmuir isotherm functional parameter of $\frac{C_e}{q_e}$ can be attributed to the variation in the concentration of $C_e$. The results obtained revealed that the rate of adsorption is more effective with increase in concentration of the wood sawdust dosage.

Based on the evaluation made using Langmuir adsorption isotherm and the adsorption of crude oil using selected wood sawdust the $R^2$ value was significant which depicts that mahogany has high sorption capacity. Mahogany sample could be recommended for remediation process.

Table 1 Abura Adsorption Experiment with seawater

<table>
<thead>
<tr>
<th>LANGMUIR PAREMETERS</th>
<th>Weight of Adsorbent Used(M) (grams)</th>
<th>Conc.(mg/l)/Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>1Hr</td>
</tr>
<tr>
<td>$q_e$</td>
<td>10</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.16</td>
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<tr>
<td></td>
<td>40</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.11</td>
</tr>
<tr>
<td>$C_e$</td>
<td>10</td>
<td>32.2</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td>30</td>
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<td></td>
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<td>19.4</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>18.9</td>
</tr>
<tr>
<td>$\frac{C_e}{q_e}$</td>
<td>10</td>
<td>82.56</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>99.17</td>
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<td></td>
<td>30</td>
<td>146.25</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>149.23</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>171.82</td>
</tr>
</tbody>
</table>
Characterization of Abura Sample using XRF and EDXRF

For the Abura sample, the quantity of the elements present in terms of intensity and energy content is low but present in traces. The same elements found in the other samples are also seen in Abura sample. Majorly, Ca, K, S, P, Si, Sn, Cr, Zn, Pb, etc are seen in small quantities and traces too. The rest of the elements are having zero intensity versus energy content values. Quantitatively, the EDXRF test profile described the presence of the elements, Mo, Nb, Ca, K, Z, which were prevalent than Si, S, Rb, Pb, Zn, Cu, and P whereas the rest had zero content. Figure 4.19 presents the intensity versus the energy in XRF and EDXRF analyzer and the following elements were identified.

![Image of XRF and EDXRF analyzer profile]

**Figure 5** Plot of Intensity (c/s) against Energy (°) for Abura before Contamination

![Image of SEM pictures]

**Figure 6(a)** SEM pictures – Morphology of the raw wood sawdust before contamination with Crude oil

**Figure 6(b)** SEM pictures – Morphology of the raw wood sawdust contaminated with Crude oil

4. CONCLUSION

The following conclusion was drawn from the research work, such as:
1. The Abura wood sawdust is a good adsorbent, which can be used in bioadsorption processes.
2. It is observed that the presence of the microorganism made it possible for increase in the rate of degradation of crude oil as well as increases the rate of adsorption in the process.
3. The Langmuir isotherm concept is a mechanism adapted to monitory, predict and simulate the rate of adsorption of the Abura wood sawdust in terms of its functional parameters of $g_e, C_a$ and $C_a/g_e$ ration of the process.
4. The relationship of the intensity and the energy in XF and EDXRF was considered to identify the possible elements process.
5. The morphology of the raw Abura wood sawdust and the mixture of crude oil and the Abura wood sawdust were shown in this research wood and shape nature well defined.

REFERENCE