Further Study of Adsorption of Crude Oils onto Acetylated Corn Silk and its Kinetics and Equilibrium Isotherm

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ABSTRACT

Oil spills from tanker or oil well have detrimental effects on environment and economy. One of the most economical and efficient methods for oil spill clean-up is mechanical extraction by sorbents which are not only the safest methods but also the least expensive of spill control. The potential use of agricultural by-products such as corn silk for adsorbent of crude oil from water systems was published in our previous work [1]. In the current research, the percentage of acetylation and hydrophobicity of the treated corn silk were measured. The reflux time for the acetylation process was one of the primary parameters that enhanced the acetylation process. The characteristics of the enhanced corn silk was determined at different reflux times by FT-IR spectroscopy. The experimental data followed the pseudo second order kinetic model. The study suggested the Freundlich model show good correlation coefficients for the adsorption of crude oil on acetylated corn silk.


1. INTRODUCTION

Oil contamination from the petroleum industry has attracted the attention of many environmental researchers [1]. The exploration, transportation, and storage of petroleum pose a very serious threat of pollution of seawater. Spilled oil may also cause a serious concern on aquatic life; it may effect on the growth of green algae that disrupts the oxygen supply of aquatic living system [2]. The properties of oil are changed after spills through the processes of evaporation, dispersion, dissolution, photo-oxidation and microbial degradation [3-5]. These processes are only viable for long-term recovery. Thus, oil spill clean-up is an important step in environmental protection. Mechanical methods, such as the use of booms, skimming, in situ ignition, chemical degradation, and use of sorbents have been applied for the removal of oil from the contaminated area [6].

However, the non-biodegradability of the materials make them an inappropriate choice for environmental purposes. Inorganic sorbents, such as vermiculite, organoclay, zeolite and perlite, have inherent disadvantages such as high density, poor reusability, and poor oil sorption capacity [8]. Sorbents of agricultural origin have been attracting the attention of researchers because they are readily available locally at low cost. Most of them are waste products of the major agricultural activity in the country. Sawdust, kenaf, sugarcane bagasse, wool, rice husk, oil palm empty fruit bunch fibers, tree bark, cattail fiber, corn starch and kapok are now gaining popularity as alternatives to synthetic sorbents [9-12].

The main components of wood and other agricultural materials are lignocellulose consisting of cellulose, hemicelluloses, and lignin. Cellulose, hemicelluloses are hydrophilic because of their hygroscopic nature. Thus they are more prone to absorb water as compared to lignin [13]. Their structure shows that the hydroxyl (-OH)
OH) groups, which have very strong bonds, are mainly responsible for the hygroscopic nature of cellulose and hemicellulosic material. These shortcomings can be overcome by changing the functional groups of these molecules by replacing the hydroxyl (−OH) groups with the ester (C=O) and acetyl (C-O) groups [14]. These treatments enhance the ester bond and reduce the hydroxyl (−OH) group.

Corn silk is available in large quantities as a by-product from the harvest of corn grain. Nearly 82 million tons of dry corn stover were produced from corn residues in the United States [15]. The bulk of which is not being utilized for any further downstream operations. It would be beneficial to the environment to recycle the waste to produce eco-material. Conversion of these agro-wastes into valuable sorbent to remove inorganic pollutants can resolve both environmental problems viz. reducing or recycling the wastes and remediating the environment. The disadvantage of agro-waste materials is their hydrophobicity which allows them to absorb water as well as oil. Modification of these materials will significantly change the surface functional groups to overcome their deficiencies [16]. Our previous research showed that corn silk has a high sorption capacity compared to raw corn silk. Modification of corn silk by fatty acids and acetic anhydride increases its sorption capacity for oil [16,13].

This work investigates the physical characteristics of the corn silk, namely the surface area and pore diameter, were analyzed using N₂ (g) adsorption. The kinetic models pseudo-first and second-order and Langmuir and Freundlich isotherm models were tested to identify a suitable description of the adsorption process.

2. MATERIALS AND METHODS

2.1. Physical Description of Corn Silk and Experimental Oil
The corn silk in this study was acquired from a local market (Seri Iskandar, Malaysia). The dust and impurities were first removed manually from the corn silk followed by washing and drying in an oven. Analysis of the treated corn silk was carried out using Fourier transform infrared (FTIR) spectrum ranging from 400 cm⁻¹ to 4000 cm⁻¹. The results were used to compare the presence of functional groups and their intensity in the raw and treated corn silk at various reflux times. The pore diameter and surface area of the sorbent were analyzed via N₂ (g) adsorption using ASAP 2020 analyzer (Micromeritics, USA) and the Brunauer–Emmett–Teller (BET) method. Two types of crude oils, namely, Tapis and Arabian crude oils, were used in this study. They were acquired from Petronas Melaka Refinery. Tapis crude oil represents low viscosity oil, such as light crude oil, whereas Arabian crude oil represents medium viscosity oil. Physical properties of experimental oils namely viscosity, density, and API gravity at 25 °C are presented in Table 1.

| TABLE 1. Physical properties of oils used for the study at 25 °C |
|-----------------|-----------------|-------------|-------------|
| Experimental oil | Density (g/cm³) | Viscosity (c.p) | API° |
| Tapis crude oil  | 0.80            | 2.32        | 44.9       |
| Arabian crude oil| 0.89            | 44.9        | 31.8       |

2.2. Percentage of Acetylation
The method of corn silk acetylation was described in our previous study [16]. The process involved acetylation by acetic anhydride using N-bromosuccinimide (NBS) as a catalyst. Various parameters viz. reaction time (1-9h), temperature (90 and 120±5 °C) and percentage of catalyst (1-3%) were used in the experiment. The result showed that the highest oil sorption of acetylated corn silk was achieved at 3% catalyst concentration in acetic anhydride and temperature of 120 °C for 6 h reflux time. The percentage of acetylation was determined by back titration method [17]. In a volumetric flask, a mixture of 1 g of treated corn silk and 50 mL of ethyl alcohol (75 % by volume) was heated on a hot plate at 50 °C for 30 min. After cooling to room temperature, 40 mL of 0.5 M KOH was added to the mixture. The remaining KOH was determined by back titration against 0.5 M HCl with phenolphthalein indicator. To complete the back titration, 2 h additional time was given to allow complete reaction to take place. The same method was repeated for the raw sorbent as a blank reading (BR). Percent acetylation was calculated using the following formula (Equation (1)).

\[
\% \text{Acetylation} = \frac{(B_R - S_R) \times \text{molarity} \times HCL + 0.043 \times 100}{\text{Acetylated sample weight}} (1)
\]

where BR and SR are the titration volumes in mL for the raw and modified samples, respectively, and the sample weight is the dry weight of sample in g.

The degree of acetylation was used to determine the degree of substitution (DS) as reported in literature [18], as shown in (Equation (2)).

\[
DS = \frac{162 \times \text{Acetylation} \%}{4300 - (42 \times \text{Acetylation} \%)} \times 100 (2)
\]

2.3. Degree of Hydrophobicity (DH)
The degree of hydrophobicity (DH) of sorbent showed the percentage of hydrogen from hydroxyl groups, -OH, replaced with C=O and C-O groups, which made them hydrophobic. The method for determining DH was suggested by Sidik et al. [20]. In this method, the acetylated corn silk was soaked in distilled water for 20 min then mixed with equal volume of hexane and stirred for 3 min. Two immiscible layers developed after the mixture was allowed to settle for 5 min. The corn silk was recovered from the hexane by decantation. This represents the hydrophobic portion of the fiber. The residual fiber that represents the hydrophilic portion was filtered and dried in an oven at 80 °C for 6 h and then was
2. 4. Batch Experiments and Oil Sorption Study

Batch adsorption isotherms and kinetic experiments were carried out using an oil/water mixture at room temperature (25 °C). Artificial seawater with a concentration of 3.5 % NaCl was prepared. For the isotherm study, 400 mL of artificial seawater and 5-50 g of oil were mixed in a beaker using a magnetic stirrer. One g of the corn silk was weighed and added to the beaker. Various contact times (5 to 50 min) were applied for the study of kinetics. The mixture was filtered to recover the corn silk. Weighing of the sorbent was carried out after draining the material for 1 min. The oil sorption capacity (OSC) of the corn silk was determined using Equation (4):

\[ \text{OSC (g/g)} = \frac{w_s - (w_w + w_c)}{w_c} \]  

where \( w_s \) is the weight of the corn silk after the test; \( w_c \) is the initial weight of the corn silk (in gram) and \( w_w \) is the weight of water. The amount of water adsorbed by the corn silk was determined according to ASTM D1533 using Karl Fischer technique.

3. RESULTS AND DISCUSSION

3. 1. Results from FTIR Analysis

FTIR spectra of raw corn silk and acetylated corn silk at different reflux times are shown in Figure 1. A comparison of the spectral bands of the four different reflux times indicates noticeable increases and decreases in the intensities of various peaks. After 2 h of reflux, a new band at 1740 cm\(^{-1}\), attributed to the carbonyl (C=O) stretching of esters was created. The band showed a sharp increase in adsorption as the time of reflux was increased to 4 and 6 h. The intensities of the band vibration of the acetyl groups at 1374 cm\(^{-1}\) and the C-O vibration at 1245 cm\(^{-1}\) were also enhanced with increasing reflux time. A drop in the intensity of the peak at 3570 cm\(^{-1}\), related to the hydroxyl (-OH) group, was observed as the reflux time was increased from 2 to 6 h. These results indicated the replacement of the hydroxyl groups by acetyl groups. Thus, an increase in reflux time from 2 to 6 h resulted in a decrease in the intensity of the hydroxyl (-OH) bond at 3570 cm\(^{-1}\) and an increase in the intensities of the three ester bands at 1740, 1376 and 1245 cm\(^{-1}\). This represents the increase of acetylation, which is in agreement with the WPG data discussed before [19]. An increase in carbonyl groups in acetylated corn silk resulted in the creation of a non-polar layer on the surface of the fiber and reduced the hygroscopic nature of the cell wall of corn silk.

3. 2. Surface Area Measurement

The surface area and pore diameter of the raw and acetylated corn silk (with highest WPG) were analyzed by N\(_2\) gas adsorption. The results show that the raw and acetylated corn silk have a surface area of 0.1992 and 0.2964 m\(^2\)/g, respectively (Table 1). The morphology of corn silk, elucidated by Field Emission Scanning Electron Microscope (FESEM), shows a hollow structure and porous interior with holes and voids [16] as shown in Figure 2. The porosity of the interior fiber is the contributing factor for the high sorption capacity. The high sorption capacity of corn silk (16.68 and 14.02 g/g for Arabian and Tapis, respectively) is not in agreement with its low surface area (Table 2). It has been reported that some agricultural biomass with porous interior showed an incorrect apparent value of the surface area [19]. This finding is observed because the intermolecular structure consisting of hollow tubes collapsed in the BET test as a result of dehydration. Prior to the N\(_2\) adsorption test, the sample was prepared by vacuum drying to remove the water molecules. This resulted in the collapse of the cellulose chains. Concurrently, the intermolecular structure of the fiber was clogged. Therefore, the measurement came from only the external surface of fiber.

Results reported for and kapok fibers also indicated a similar pattern of high sorption capacities despite its low surface areas [20,19]. Thus, probably a similar phenomenon occurred during the measurement of the surface area of corn silk in this study. The pore diameter of acetylated corn silk was slightly increased after acetylation (Table 2). Thus, the acetylation treatment did not have a significant effect on the average pore diameter.

3. 3. Degree of Hydrophobicity and Acetylation

The degree of hydrophobicity of corn silk was measured subsequently weighed [16]. The hydrophobicity of the acetylated corn silk was determined by the ratio of corn silk present in the organic phase (g) and the initial mass (g), as shown in Equation (3):

\[ \text{DH (°)} = \frac{\text{Weight of sorbent in hexane}}{\text{Initial weight of acetylated corn silk}} \times 100 \] (3)
TABLE 2. Average pore diameter and BET surface area of raw and acetylated corn silk

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET Surface Area (m²/g)</th>
<th>Average Pore Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw corn silk</td>
<td>0.1992</td>
<td>83.2009</td>
</tr>
<tr>
<td>Acetylated corn silk</td>
<td>0.2964</td>
<td>97.4366</td>
</tr>
</tbody>
</table>

before and after modification, and the results are shown in Table 3. The hydrophobic properties of organic materials are contributed by the hydroxyl groups (-OH) in cellulose, hemicellulose, and lignin. After treatment with acetic anhydride, the hydrogen from hydroxyl groups was partially replaced by C=O and C-O groups, resulting in increased hydrophobicity. The alkyl chain of acetic anhydride creates a non-polar layer on the surface of the sorbent. This leads to a drastic increase in hydrophobicity and reduction of the water sorption capacity. The degrees of acetylation and substitution (DS) are other terms to describe the surface functional group modification. These values are determined by the extent of replacement of hydroxyl groups by acetyl groups, resulting in an increase in weight of the modified sample. Table 3 shows the degree of acetylation and degree of substitution (DS) of acetylated corn silk under optimal conditions (with highest WPG).

### 3. 4. Kinetic Study of Sorption of Oil onto Acetylated Corn Silk

The kinetics of sorption of oil onto acetylated corn silk were examined from experimental data. Both kinetic models representing pseudo first and second-order adsorption were examined. The linear forms of the two models are represented by Equations (5) and (6), respectively.

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \\
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \(q_e\) and \(q_t\) are the quantity of oil adsorbed onto the sorbent at equilibrium and at time \(t\) in mg/g, respectively. \(k_1\) and \(k_2\) are the rate constants of the first-order and second-order models, in 1/min, respectively.

first-order was calculated from the plot of \(\log (q_e - q_t)\) vs. \(t\) (Figure 3), while \(k_2\) of the second order was calculated from the plot of \(t/q_t\) vs. \(t\) (Figure 4). The intercept and slope of the line were determined and the values of \(q_e\) and \(k\) were calculated. The correlation coefficients, \(R^2\) for the two models are shown in Table 4, which also indicates that the kinetics of oil uptake by acetylated corn silk are best represented by the pseudo-second order model with \(R^2 > 0.98\). The pseudo-second order model was selected as the suitable representative model based on the \(R^2\) and predicted \(q_e\) values. Although the value of \(R^2\) for pseudo first-order also shows a good correlation coefficient \(R^2 > 0.9\), the deviation of the calculated \(q_e\) values from the experimental \(q_e\) values is larger.

TABLE 3. Degree of acetylation of acetylated corn silk and degree of hydrophobicity of raw and acetylated corn silk

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Degree of hydrophobicity (%)</th>
<th>Degree of acetylation (%)</th>
<th>Degree of substitution (DS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw corn silk</td>
<td>50.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acetylated Corn</td>
<td>88.3</td>
<td>10.05</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Figure 2. FE-SEM of the cross section of corn silk

Figure 3. Pseudo- first order adsorption kinetics of Tapis and Arabian crude oil sorbed onto acetylated corn silk

Figure 4. Pseudo- second order adsorption kinetics of Tapis and Arabian crude oil sorbed onto acetylated corn silk
3.5 Isotherm Study of Sorption of Oil onto Acetylated Corn Silk

The data collected from the adsorption isotherm experiments were subjected to non-linear estimation using the two adsorption isotherms commonly adopted in the field of environmental engineering (Langmuir and Freundlich). The basic assumption of the Freundlich isotherm is a non-uniform distribution of sorbate onto the heterogeneous surface of the sorbent, while the Langmuir model hypothesizes that the sorption happens on a homogeneous surface of the sorbent (the adsorbed layer is one molecule in thickness and once the site is occupied by a molecule [21]. The Langmuir isotherm can be expressed in the linear form as Equation (7):

\[
\frac{C_e}{q_e} = \frac{1}{q_0} + \frac{1}{q_0C_e} \tag{7}
\]

where \( q_e \) is the quantity of oil adsorbed at equilibrium (mg/g), \( C_e \) is the concentration of oil at equilibrium (mg/L), and \( q_0 \) and \( b \) are the constants for the adsorption capacity and adsorption rate in Langmuir model. The plot of \( C_e/q_e \) vs. \( C_e \) is a straight line where the slope and intercept were used to calculate the values of \( q_0 \) and \( b \). The affinity between the sorbate and sorbent can be predicted by a dimensionless constant separation factor, \( R_L \), which is a critical feature of the Langmuir model, as expressed in Equation (8). The characteristics of a sorbent can be described according to \( R_L \), as shown in Table 5.

\[
R_L = \frac{1}{1 + bC_0} \tag{8}
\]

where \( b \) is the constant for the adsorption capacity which was calculated by Equation (7) and \( C_0 \) is the initial adsorbate concentration. The linear mathematical expression of the Freundlich adsorption isotherm model can be described as Equation (9):

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{9}
\]

where \( C_e \) is the concentration of the oil (mg/L), \( q_e \) is the quantity of the oil adsorbed at equilibrium, (mg/g), and \( K_f \) and \( n \) are constants, \( K_f \) is also known as Freundlich constant and indicates the adsorption capacity of the adsorbent while \( n \) indicates the intensity of adsorption.

A value of \( 1/n \) between 0 and 1 indicates that the adsorption is favorable. As the value approaches zero, the sorbent is more heterogeneous. The plot base on Equation (9) was used to determine the value of \( K_f \) and n. Figures 5 and 6 show the linear plots of Langmuir and Freundlich isotherms for adsorption of crude oil onto acetylated corn silk.

The Freundlich model was found to have a better fit for sorption of Tapis crude oil by acetylated corn silk as exhibited by the higher \( R^2 \) value. The \( R_L \) values were between 0 and 1, showing the adsorption to be favourable. However, the Langmuir model seemed to be more suitable for Arabian crude oil, as indicated by its higher \( R^2 \) value (Table 6), but, in spite of the slightly lower \( R^2 \) in the Freundlich model in the Arabian crude oil (\( R^2=0.982 \)), this model is most likely more suitable than Langmuir model.

### Table 4. Kinetics of Tapis and Arabian crude oil sorption onto acetylated corn silk

<table>
<thead>
<tr>
<th>Oil type</th>
<th>( q_e ) (mg/g) (experimental)</th>
<th>Pseudo first-order kinetic</th>
<th>Pseudo second-order kinetic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tapis</td>
<td>14020</td>
<td>8396.5</td>
<td>0.9454</td>
</tr>
<tr>
<td>Arabian</td>
<td>16680</td>
<td>14628.5</td>
<td>0.9602</td>
</tr>
</tbody>
</table>

### Table 5. Characteristics of adsorption according to the separation factor \( R_L \)

<table>
<thead>
<tr>
<th>Separation factor, ( R_L )</th>
<th>Characteristics of adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_L &gt; 1 )</td>
<td>Unfavorable</td>
</tr>
<tr>
<td>( R_L = 1 )</td>
<td>Linear</td>
</tr>
<tr>
<td>( 0 &lt; R_L &lt; 1 )</td>
<td>Favorable</td>
</tr>
<tr>
<td>( R_L = 0 )</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

![Figure 5. Linear form of Langmuir adsorption model for Tapis and Arabian crude oil onto acetylated corn silk](image-url)
Thus, the adsorption of Tapis and Arabian crude oil by corn silk is interpreted as a non-uniformly distributed multilayer adsorption over a heterogeneous surface. The results of different sorbents showed that both isotherm models, Langmuir and Freundlich, were fitted well [22,23,20,24].

4. CONCLUSION

The potential of agricultural waste as a sorbent to remove two different crude oils (Tapis and Arabian crude oil) from water was considered via a series of batch studies. Acetylation of corn silk represents an effective and suitable method for the preparation of oil sorbents with enhanced hydrophobic characteristics. The hydrophobicity of corn silk was increased from 50 % to 88.3 % after acetylation. The degrees of acetylation and substitution were 10.05 % and 0.41, respectively. The FTIR spectra at different reaction times (2 to 6 h) also indicated the enhancement in the intensity of the three ester peaks and a decrease in the OH stretching band. The adsorption of crude oil onto acetylated corn silk was better described by pseudo-second-order kinetic model and Freundlich isotherm showed a good fit with the experimental adsorption equilibrium data for crude oil onto the acetylated corn silk. Having high oil sorption capacity and being inexpensive and easily available locally are the further advantages of acetylated corn silk. More importantly, it was found that the oil sorption capacities of the acetylated corn silk were much greater than those of synthetic sorbents such as polypropylene fiber (10 g/g).

However, due to the unacceptable of $q_0$ due to the far from to the $q_e$ experimental, the Freundlich model was therefore considered as the better model for the sorption of oils by corn silk. For all experimental data of adsorption of crude oil onto the corn silk which are agreed with Freundlich isotherm implied that stronger binding sites are engaged for sorption firstly and with the increase in degree of site occupation, the binding force decrease. Freundlich model incorporates the heterogeneity of the surface sustaining sites of extensive affinities. This model is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface.

<table>
<thead>
<tr>
<th>Type of oils</th>
<th>Langmuir Isotherm</th>
<th>Freundlich Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$ (mg/g)</td>
<td>$q_0$ (mg/g)</td>
</tr>
<tr>
<td>Tapis</td>
<td>14020</td>
<td>25000</td>
</tr>
<tr>
<td>Arabian</td>
<td>16680</td>
<td>25000</td>
</tr>
</tbody>
</table>

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