A study on the equilibrium and kinetics of oil spill cleanup using acetylated corn cobs

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ABSTRACT

The present study investigates the potential of acetylated corn cobs as an adsorbent for oil spills cleanup. The equilibrium, isotherm and kinetics of the acetylated corn cobs were all carried out at room temperature, different reaction times as well as oil concentration. The sorption model and crude oil absorptive behavior of the ACC were studied using the Langmuir and Freundlich isotherm models. The experimental methods adopted for the determination and estimation of the sorption coefficients are also described. The correlation values obtained showed that the model better fitted the Freundlich isotherm than the Langmuir isotherm. That is, the adsorption of oil on the adsorbent consists of heterogeneous adsorption sites that are similar to each other in respect of adsorption phenomenon. The kinetic data were best fitted to pseudo second-order kinetic model. ACC are therefore recommended for oil spills clean up, as well as for further development.

Keywords: Adsorbent, Langmuir model, Freundlich model, kinetic models, acetylated corn cobs.

1. Introduction

An oil spill must have resulted from a number of causes. Due to the adverse effects of oil spillage, the environment is growing increasingly uninhabitable. Oil spills may be due to the release of crude oil from offshore platforms, drilling rigs, oil wells, or spills of refined petroleum products such as gasoline and diesel, or spills from heavier fuels used by large ships such as bunker fuels.

The release of oil in coastal waters is becoming a global concern. With the attendant effect of these spills, both on man, the environment, as well as aquatic animals, effort are geared towards cleanup and recovery of spilled oil. There exist a number of techniques used in oil spill cleanup. Most of these techniques are time consuming, expensive and most times causes more harm than the ones they are intended to remedy (for example, uncontrolled Insitu-Burning), There is therefore the need to develop a more efficient, cost effective and cleaner method of oil spill cleanup.

Low cost of adsorbent could be generated from agricultural waste because of their low-cost and widespread availability. Some examples of agro waste that have been used for the
removal of oil are barley straw (Ibrahim, et al., 2009), walnut (Srinivasan and Viaraghvan, 2008) wool fibers (Rajakovic, et al., 2007), olive waste (El-Hamouz, et al., 2007). The use of sorbents to clean-up oil spill presents nearly many advantages due to simplicity of approach and the inexpensive nature of the materials (Chung and Vennosa, 2008). In addition, plant derived organic sorbents are biodegradable thus leaves no permanent residue. Poile (1990) discussed the collection and cleaning methods available in oil spill. He found that natural and biodegradable sorbents have particular advantages over synthetic sorbents. Choi and Cloud (1992) conducted further studies on milkweed and cotton fibers. The results showed that milkweed and cotton sorb oil more efficiently. This present study measures the equilibrium and kinetics of the effectiveness of crude oil spill cleanup using cheap and readily available agricultural waste (corn cobs),

2. Material and methods

2.1 Materials

Corn cobs (CC) were obtained from Inyi Achi in Oji River Local Government area, Enugu state. The crude oil sample was collected from Port Harcourt Refinery Rivers State.

2.2 Methods

2.2.1 Sample characterization

The moisture content, bulk density, ash content and volatile content of the raw and acetylated corn cobs were determined using methods proposed by (ASTM, 1994), (European Committee for Standardization, CEN/TS 15103, 2005), (Dara, 1991) and (Aloko and Adebayo, 2007), respectively. The specific gravity, viscosity, density and API gravity of the crude oil sample were also determined using methods proposed by (Hassan et al., 2003) and (Wikipedia, 2009).

2.3 Sample preparation

Corn cobs sample preparation: The corn cobs were thoroughly washed with water to remove dust, fungus, foreign materials and water soluble components. The washed cobs were dried properly in sunlight for twelve hours and then left to dry at 65°C in the oven.

Soxhlet extraction: Soxhlet extraction was carried out using hexane as solvent. The extraction of corn cobs was carried out for four hours to wash and to remove extractible components from the corn cobs. The extracted samples were dried in a laboratory oven for 16 hours at a temperature of 60°C.

Sieving: After drying, the cobs were sieved with laboratory sieves to obtain homogenous particle sizes. The corn cobs (CC) were sieved using the BS410/1986 laboratory test sieves of aperture sizes, 0.43, 0.85, 1.18, 1.4mm. A mechanical shaker was used to separate the corn cobs into the desired particle sizes.

2.4 Acetylation of corn cobs

The acetylation of the corn cobs under mild conditions, in the presence of iodine, using acetic anhydride was carried out using the sun et al., (2004) method of acetylation in a solvent free system. Weight Percent Gain (WPG) of the corn cobs due to acetylation was calculated thus:
2.5 Oil sorption studies

The sorption studies were carried out using a scaled down modification of the method presented by Choi and Cloud (1992).

The mass of oil sorbed was calculated thus:

\[ M_{\text{oil}} = M_{\text{final}} - M_{\text{w/glass}} - M_{\text{sorbent}} \]  

(2)

Where \( M_{\text{oil}} \) is the mass of oil sorbed, \( M_{\text{final}} \) is the mass of sorbent + mass of oil + mass of watch-glass after oven drying, \( M_{\text{w/glass}} \) is the mass of the watch-glass and \( M_{\text{sorbent}} \) is the mass of the sorbent.

The oil sorption capacity (OSC) was then obtained thus:

\[ \text{OSC} = \frac{\text{Weight of oil sorbed}}{\text{weight of sorbent}} \times 100 = \frac{M_{\text{oil}}}{M_{\text{sorbent}}} \times 100 \]  

(3)

The oil sorption capacity (OSC) was recorded as gram per gram of sorbent. The procedure was carried out in duplicates and the mean of the results reported.

3. Result and conclusion

3.1 Characterization of sorbents

Table 1 below shows the results of the proximate analysis and physical properties of the raw and acetylated corn cobs with particle size distribution of 1.4mm. The proximate analyses on the sorbents were carried out to determine the weight fractions of volatile matter, fixed carbon and ash contents of the sorbents. The result showed similarity in the ash content implying that acetylation did not affect the ash content. The ash content of RCC and ACC were both 1.6% and corresponds with the findings of T. Vaughan et al, 2001; that the ash content of corn cobs is 1.6%. There was an increase in volatile content after acetylation. This increase was probably due to a relative percentage decrease of more liable corn cobs components such as hemicellulose and lignin during acetylation. Acetylation also improved the physical properties of RCC. The high moisture content of RCC which was as a result of the hydrophilic nature of the material was reduced from 14% to 4%. The ACC had the least porosity indicating that the water retaining ability of RCC was reduced by acetylation making it a promising sorbent for oil spill application. The changes in the physical properties of RCC after acetylation are evidences of successful acetylation, and an improvement in the physical properties of the RCC.

<table>
<thead>
<tr>
<th>Characterizing Properties</th>
<th>RCC</th>
<th>ACC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (%)</td>
<td>14.2</td>
<td>4</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>1.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Characterizing property</th>
<th>NNPC Crude Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity @ 25°C (Mpa.s)</td>
<td>63.6</td>
</tr>
<tr>
<td>Specific Gravity 60/60°F</td>
<td>0.88</td>
</tr>
<tr>
<td>Density (g/dm³)</td>
<td>0.7934</td>
</tr>
</tbody>
</table>

RCC represents raw corn cobs, ACC represents acetylated corn cobs

3.2 Characterization of oil types

The characterizing properties of the oil samples carried out were viscosity, specific gravity, and density and API gravity. The characterized properties of the four oil types are shown in Table 2.

3.3 Equilibrium sorption studies of acetylated corn cobs

To facilitate the estimation of the sorption capacities of the ACC, the isotherm data were analyzed using adsorption type isotherm models. Since the adsorption isotherms are important to describe how adsorbates will interact with adsorbents and are critical for design purposes, the correlation of equilibrium data using an equation is essential for practical sorption operations (Hashem et al., 2007). The two isotherm equations adopted in this study to describe the sorption equilibrium are the linearized Langmuir and Freundlich isotherm models. The Langmuir model was chosen for the estimation of maximum sorption capacity to biomass surface saturation. The Freundlich model was chosen to estimate the adsorption intensity of the crude oil towards the ACC.

The Langmuir and Freundlich isotherms are the most commonly used solid to liquid phase isotherms. These isotherms relate the amount of oil sorbed at equilibrium per unit weight of sorbent, \( Q_e (\text{mg/g}) \) to the sorbate concentration at equilibrium, \( C_e (\text{mg/L}) \). According to the Langmuir’s model, adsorption occurs uniformly on the active sites of the sorbent, and once an adsorbate occupies a site, no further sorption can take place at that site. The Langmuir model (Langmuir, 1916) is defined by the equation:

\[
Q_e = \frac{abC_e}{1 + bC_e}
\]

(4)

the linearized form is expressed as

\[
\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{1}{aC_e}
\]

(5)

Where, \( b \) is a Langmuir coefficient related to the affinity between the sorbent and sorbate and \( a \) is the maximum OSC to form a complete monolayer on the surface bound at high \( C_e (\text{g/100ml}) \). In the Langmuir’s model, the mass of the solute sorbed per unit mass of sorbent \( (Q_e) \), increases linearly by increasing the solute concentration at low surface coverages,
approaching to an asymptotic value \( a \) when adsorption sites approaches saturation (Site, 2004). The plot of \( C_e/Q_e \) against \( C_e \) is illustrated in Figure 1. The isotherm constants and their coefficients of determination, \( R^2 \), are listed in Table 3.

The Freundlich model equation describes non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. The isotherm model can be defined as:

\[
Q_e = KC_e^{1/n}
\]

(6)

where, \( k \) and \( n \) are Freundlich constants. \( k \) is the relative indication of adsorption capacity (L/mg) and \( n \) indicates the intensity of adsorption. The linearized Freundlich model equation applied is expressed as

\[
\log Q_e = \log K + (1/n)\log C_e
\]

(7)

Figure 2 shows the Freundlich model for the acetylated corn cobs sample. By taking the logarithm of Equation 3.3, if \( \log Q_e \) against \( \log C_e \) is plotted, the constants may be evaluated from the slope \( n \) and the intercept \( \log K \). Plot of \( \log Q_e \) against \( \log C_e \) is given in Figure 2. The isotherm constants and their coefficients of determination, \( R^2 \), are listed in Table 3 below.
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Figure 2: Freundlich model of adsorption

Table 3: The Langmuir and Freundlich isotherm model constants

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$  $B$  $R^2$</td>
<td>$K$  $N$  $R^2$</td>
</tr>
<tr>
<td>ACC</td>
<td>62.6  1.3  0.881</td>
<td>19.95  2.632  0.894</td>
</tr>
</tbody>
</table>

The magnitude of the exponent, $1/n$, gives an indication of the favorability of adsorption. Values of $n > 1$ represent favorable adsorption condition (Ho and Mckay, 1998). The plot of log $q_e$ versus log $C_e$ in Figure 2 shows a straight line with a coefficient of determination of 0.894. The constant $K$ and $1/n$ value was determined from the plot. The value calculated was listed in Table 3. The value of $n$ determined from Freundlich isotherm was 2.63.

As seen from Table 3, a higher coefficient of determination was shown by Freundlich model. This indicates that the Freundlich model was suitable for describing the sorption equilibrium of oil by ACC. Similar results were reported for oil adsorption on powder and flakes chitosan (Ahmad et al., 2005) and sorption equilibrium and kinetics of oil from aqueous solution using banana pseudo stem fibers (Nurul Izza Husin et al., 2011). Conclusively, adsorption of oil on the adsorbent consist of heterogeneous adsorption sites that are similar to each other in respect of adsorption phenomenon.

4. Kinetic studies

Two kinetic models were applied to the experimental data in order to analyze the sorption kinetics of oil on the acetylated corn cobs. First, the kinetic adsorption was analyzed by the Lagergren pseudo first order equation thus:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

(8)
Where $q_e$ and $q_t$ are the amount of oil adsorbed on the adsorbent at equilibrium and time $t$, respectively (mg/g) and $k_1$ is the rate constant of first order adsorption (min$^{-1}$). The value of $k_1$ at ambient temperature was calculated from plots of $\log(q_e - q_t)$ vs $t$ (figure not shown).

The parameters of pseudo-1st-order model were summarized in Table 3. The $R^2$ value obtained was poor and the experimental $q_e$ value did not agree with the calculated value obtained from the linear plot. This suggests that the adsorption of oil onto the acetylated corn cobs is not a first-order reaction.

The experimental data were further analyzed in terms of the pseudo-second order kinetic rate model proposed by Ho et al. (1995). The pseudo-second order equation is usually expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

Where $K_2$ is the pseudo second order rate constant of adsorption (g/mg/min). Since the pseudo–second order is applicable, the plot of $t/q_t$ against $t$ gave a linear plot from which $q_e$ and $K_2$ were determined. The model is represented in Figure 3 and equation for the model obtained was

$$y = 0.011x + 0.15$$

The slope ($1/q_e$) obtained was 0.011 and the intercept ($1/K_2 q_e^2$) was 0.15. The $q_e$ and $K_2$ values were calculated from the slope and the intercept respectively. $k_2$ is the pseudo-second-order rate constant of adsorption (g mg$^{-1}$min$^{-1}$). The straight linear line in plot $t/qt$ vs. $t$ (Fig.3) proves a better agreement of experimental data with the kinetic model.

<table>
<thead>
<tr>
<th>Pseudo first – order kinetic model</th>
<th>Pseudo second – order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_e$ (exp)</td>
<td>$K_2$</td>
</tr>
<tr>
<td>69.5</td>
<td>0.06</td>
</tr>
</tbody>
</table>

**Figure 3:** Pseudo second–order kinetic model

**Table 4:** The pseudo first and second–order kinetic model constants
Table 4 also lists the computed results obtained for the second-order kinetic model. The coefficient of determination ($R^2$) for the second-order kinetic model is 0.988. Furthermore the calculated $q_e$ values obtained agree very well with the experimental $q_e$ value. This indicates that this model was applicable to describe the adsorption process of oil onto ACC, based on the assumption that the rate-limiting step maybe chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate, provide the best correlation of data (Ho and Mckay, 1999). Similar results were reported for the adsorption of oil by powder and flake chitosan (Ahmad et al., 2005).

5. Conclusions

The equilibrium and kinetics of the effectiveness of oil spill cleanup using acetylated corn cobs was investigated. The oil sorption capacity of the sorbent was characterized in this case by oil sorption in simulated conditions. The results showed the maximum values of oil sorption capacity of the acetylated corn cobs was gotten as 68.8g/g ACC at a temperature of 20°C, sorption time of 10mins, sorbent weight of 1.5g and 1.4mm particle size. A high WPG of 17.6% is also an evidence of successful acetylation. Equilibrium data fitted well with Freundlich model, which suggests a heterogeneous coverage of oil molecules on the surface of ACC. The kinetic data were best fitted to pseudo second-order kinetic model.

6. References


