Adsorption of Crude Oil using Meshed Corncobs

B. A. Olufemi¹*, L. A. Jimoda², N. F. Agbodike³

¹Senior Lecturer, Chemical Engineering Department, University of Lagos, Akoka, Yaba, Lagos, NIGERIA
²Senior Lecturer, Chemical Engineering Department, Ladoke Akintola University of Technology, Ogbomosho, NIGERIA
³M. Sc. Graduate, Chemical Engineering Department, University of Lagos, Akoka, Yaba, Lagos, NIGERIA

ARTICLE INFO

Received: Jan 24, 2014
Accepted: Feb 28, 2014
Published: Mar 31, 2014

ABSTRACT

The potential of using corncobs a typical agro-based waste as an adsorbent for removal of oil contaminated water was investigated in this work. Gradually, the awareness of the impact of spilled crude oil and products from it on human health and environment is on the increase. Corncobs wastes generated in local maize flour processing plants, road-side corn vendors and individuals, were converted into an adsorbent. The corncobs were treated and meshed to adsorb crude oil from water at various experimental conditions. Investigations carried out include the effects of parametric variations of different adsorbate and adsorbent masses, time, temperature, particle size and mixing speed on the adsorption of crude oil. Meshed corncobs, especially the 80 micrometer particle size exhibited high affinity for crude oil adsorption. The maximum adsorption was observed at 15 °C for the temperature range considered. The results demonstrated that a crude oil adsorption with this readily available and biodegradable waste material is feasible. Due to its high affinity for oil and low water pick up, meshed corncobs adsorbent is convincingly oleophilic or hydrophobic.

Keywords: Corncobs, adsorbent, adsorbate, crude oil, isotherm

INTRODUCTION

Investigation into the adsorption capability of various materials as good adsorbents is an interesting and continuously expanding field of study. The use of adsorbents seems to have been identified as an effective control measure in many oil spill scenarios.
Uzoije et al. (2011) have studied crude oil sorption onto activated groundnut shell carbon (AGSC) with the conclusion that AGSC is a good mop-up and low-cost alternative medium for oil spilled surfaces. Adsorption of crude oil by ordinary and modified bentonites recorded about 410 % particle volume increase after adsorption (Gitipour et al., 2010). As a further advancement in this field, Jadhav et al. (2011) had reported that separation of oil from water by human hair as an adsorbing medium is found to be very efficient at laboratory scale, in addition, compared to existing methods, they claimed that their oil recovery process was low cost, effective, and user friendly. Also, the adsorption of crude oil from aqueous solution by hydrogel of chitosan based polyacrylamide prepared by radiation induced graft polymerization was carried out by Sokker et al. (2011).

Freundlich and Langmuir models fitted their experimental data properly, while the adsorption of oil onto the hydrogel behaves as a pseudo-second-order kinetic models rather than the pseudo-first-order kinetic model according to them. Adsorption of crude oil using meshed groundnut husk was also investigated by Nwokoma and Anene (2010), and they pointed out that the optimum adsorption temperature was between 25 – 45 °C. Over the years, adsorption of crude oil on the arctic terrain had been investigated by Moore and Phillips (1975), where the arctic terrain was divided into three layers, moss, detritus and clay, and each layer was contacted with Norman wells crude oil. The outcome of their study showed that the chromatographic analysis of the crude oil extracts of the terrain layers signified that the adsorption capacity of the terrain increased with increasing organic content. Sorption studies of crude oil on acetylated rice husks had been reported, with the conclusion that the adsorption was monolayer (Thompson et al., 2010). The equilibrium isotherm of Langmuir, Freundlich, Tempkin and the three parameter Redlich-Peterson isotherms had been correlated for the equilibrium sorption of crude oil by expanded perlite using different adsorption isotherms at 298.15 K (Alihosseini et al., 2010). Their results showed that the Redlich-Peterson model better represented the equilibrium isotherm data for the crude oil on the expanded perlite.

To further portray the developed interest of researchers in this field of study, adsorption of crude oil on surfaces using quartz crystal microbalance with dissipation (QCM-D) under flow conditions revealed that the size of adsorbed aggregates decreased with $n$-alkane carbon number (Abudu and Goual, 2010). It is interesting to know further, that adsorption of spilled oil from seawater by waste plastic had been subjected to investigation by Aboul-Gheit et al., (2006) and they stated that polyethylene powder and sheets as well as polypropylene powder absorb more strongly heavier crude oils than lighter ones; however, polypropylene sheets adsorb more light oil than heavier oil.

Adsorbents from the pyrolysis of rice husk had been shown to have very good buoyancy characteristics, high oil sorption capacity and high hydrophobicity (Angelova et al., 2011). The Langmuir model was found to better describe the adsorption process over the concentration range considered in the kinetics of methylene blue adsorption KOH-activated carbon using corn cobs (Diya'uddeen et al., 2011). Modified oil palm leaves adsorbent with enhanced hydrophobicity for crude oil removal had been investigated. The authors observed that the isotherms studied revealed that the experimental data agreed with the Freundlich isotherm model (Sidik et al., 2012). It had been reported that temperature variation study showed that malachite green adsorption was endothermic and spontaneous with increased randomness at the solid solution interface for activated carbon prepared from Borassus bark, a low-cost source, by sulphuric acid activation, for its ability to remove malachite green in aqueous solution (Arivoli et al., 2009). Two sets of adsorbents were prepared from locally available raw materials, characterized and tested, with the observation that the activated carbonaceous materials developed porous
structures which form defective graphitic sheet ensembles that serve as additional adsorption sites (Sueyoshi et al., 2012).

Activated carbon prepared using solid waste called *Terminalia Catappa Linn* shell was investigated to explore the adsorption copper ion from aqueous solution had been studied, with the outcome that the adsorbent was found to be effective and economically viable (Arivoli et al., 2009). Conversion of some waste products into adsorbents had been found to remove various organic pollutants ranging from 80 to 99.9% (Ali et al., 2012). Adsorption of organic gases / vapors: carbon tetrachloride, methane, and ammonia, on the surface of activated charcoal has been studied manometrically, with the conclusion that ammonia is a better adsorbate on the surface of activated charcoal as compared to carbon tetrachloride and methane (Khan et al., 2003).

On another exploratory platform of investigation in similar fields of adsorption studies, this work is set forth to investigate the possibility of using meshed corncobs to adsorb crude oil as well as report on various relevant process parameters as they influence the adsorption process with regard for some theoretical background knowledge of the subject. The outcome of the research is expected to propose corncobs as a possible useful material for environmental control of crude oil spillage.

**MATERIALS AND METHODS**

**APPARATUS AND REAGENTS**

The following materials and apparatus were utilised for the experimental work: Meshing Machine (Magimix Cuisine System 5000), Mesh Sieve (B.S. 410/43), Orbital Shaker (HY-2 model, NYC), Thermometer, Graduated Bottles and Beakers (Pyrex, England), Weighing Balance (AL Mettler Toledo GmbH 2004) and Boat, Whatman Filter Paper, Oven (Gallenkamp, England), Corncobs, Jenway 6405 Model Ultraviolet (UV) Spectrophotometer, Crude Oil Bonny Export Blend sample from Okoro Well, Akwa Ibom Waters by Afren Energy Facility, De-ionized Water, Analytical Grade Potassium Carbonate.

**EXPERIMENTAL PROCEDURE**

A small oil spill of 0.025 g/l initial concentration (Co) was simulated by pouring 25 g of crude oil into 1000 ml of water in a beaker. A 200 ml of the simulated spill oil of concentration of 0.025 g/l was measured into a 500 ml beaker. Batch adsorption equilibrium constant were performed for different parameters; adsorbent loading, adsorbate loading, temperature, time, rotational speed, particle size. A constant room temperature of 25 °C was used throughout the experiments. The absorbance for various concentrations of oil was determined through a blank run before the experimental runs. About 2.0 g Corncobs (CC) was introduced into the beaker oil / water solution. The contents of the beaker were agitated for 1 hour which is necessary for equilibrium to be attained in the adsorption system. The corncob (CC) was filtered out of the solution using a Whatman No. 1 filter paper to drain them completely. The equilibrium concentration of crude oil in water for each measured sample was determined using UV spectrophotometer at a wavelength of 380 nm. The weight (M) of the corncob (CC), volume (V) of simulated oil spill and the corresponding equilibrium concentration (Ce) were recorded.

For each batch run, the quantity of crude oil adsorbed per unit weight of Corncob (CC) denoted as qe was determined as expressed by Uzoije et al. (2011) as:

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

(1)
The Langmuir isotherm was given as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$  \hspace{1cm} (2)$$

while the linear form was expressed as:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m}$$  \hspace{1cm} (3)$$

The Freundlich isotherm was also given as:

$$q_e = K_f \times C_e^{1/n}$$  \hspace{1cm} (4)$$

with the linear form given as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$  \hspace{1cm} (5)$$

The variation of ln $q_e$ with ln $C_e$ expected to be a linear plot according to the Freundlich isotherm was done from where the Freundlich constants ($K_f$, $n$) were determined. Variation of $1/q_e$ with $1/C_e$ was plotted also which was expected to give linear plots according to the Langmuir isotherm from where the constants ($K_L$, $q_m$) were obtained.

Batch adsorption experiments were carried out with 0.025 g/l initial concentration (Co) of oil. Water and oil do not mix but form emulsion. Water was added to determine the affinity of the adsorbent for oil and water. A mass of 2.0 g of 80 μm Corncob adsorbent was added to this mixture. The 500 ml beaker was placed on an orbital shaker, and then shaken at 200 rpm at a constant room temperature of 25 °C for 1 hour. The wetted adsorbent was then removed from the beaker; oil and water were filtered through a Whatman No 1 filter paper. The amount of oil remaining was measured using an UV spectrophotometer. From the data obtained, the equilibrium concentration ($C_e$) was obtained. Experimental procedures of various process parameters investigated are:

**Different adsorbent loading:** About 0.025 g/l initial concentration oil sample was added to mixtures of 1.0 g, 2.0 g, 3.0 g, 4.0 g and 5.0 g of 80 μm corncobs adsorbent respectively in a 500ml beaker. The beaker was placed on an orbital stirrer, and then stirred at 200 rpm at room temperature for an hour each. The absorbance values were recorded carefully during the experiments.

**Different contact time:** A 0.025 g/l initial concentration oil sample was added to a mixture of 2.0 g of 80 μm corncobs adsorbent in a 500 ml beaker. The beaker was placed on an orbital stirrer, and then stirred at 200 rpm at a constant room temperature of 25 °C for a specified period of contact time: 15, 30, 45, 60, and 75 min. After stirring, the samples were withdrawn at the specified time intervals, filtered through a Whatman No 1 filter paper and the filtrate measured using a UV machine. The absorbance values were then recorded carefully.

**Different Temperature:** Batch adsorption experiments were carried out at different temperatures of 15, 25, 35, 45, 55 and 60 °C. About 2.0 g of meshed adsorbent was shaken with 0.025 g/l initial concentration oil sample in a 500 ml beaker at 200 rev/min for 60 minutes to permit adequate equilibrium adsorption at various temperatures. The wetted adsorbent was then removed from the beaker, while the oil and water were filtered
through a Whatman No 1 filter paper and the filtrate measured using a UV machine. The absorbance values were obtained and recorded carefully.

**Different mesh sizes:** The adsorbent was meshed and sieved into different particle sizes of 80, 150, 300, 425 and 600 μm. Batch adsorption experiments were carried out for the various particle sizes of the adsorbent by shaking 2.0 g of the meshed adsorbent with 0.025 g/l initial concentration oil sample in a 500 ml beaker at 200 rev/min using room temperature for 60 min. The wetted adsorbent was then removed from the beaker, while the oil and water were filtered through a Whatman No 1 filter paper and the filtrate measured using a UV machine. The absorbance values were then recorded appropriately.

**Different rotational speeds:** The adsorption dynamics in terms of contact time was studied experimentally by adding 0.025 g/l initial concentration oil sample to a 2.0 g 80 μm corncobs adsorbent in a 500 ml beaker. The beaker was placed on an orbital stirrer, and then stirred at room temperature for a specified revolution per minute for 60 min. Various rotational speeds of 100, 200, 300, 400 and 500 rev/min were used. After stirring, the samples were withdrawn at the specified time intervals, filtered through a Whatman No. 1 filter paper and the filtrate measured using a UV machine. The absorbance values were then recorded as required.

**Different adsorbate loading:** Batch adsorption experiments were carried out at different adsorbate loading, whereby 2.0 g of meshed adsorbent was shaken with 2, 4, 6, 8, and 10 g crude oil sample per 200 ml water mix in a 500 ml beaker to give varying oil concentrations at 200 rev / min for 60 min using constant ambient temperature. The wetted adsorbent was then removed from the beaker, while the oil and water were filtered through a Whatman No. 1 filter paper and the filtrate measured using a UV machine. The absorbance values were then taken correctly.

**RESULTS AND DISCUSSIONS**

The results and adsorption isotherm study of the experiments carried out under varying temperature, time, adsorbent dosage, adsorbate dosage, particle sizes and rotational speed are presented below:

<table>
<thead>
<tr>
<th>Table I: Crude oil adsorption by corncobs with varying adsorbate concentration at 25 °C and 200 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Conc. (g/l)</td>
</tr>
<tr>
<td>C_0 (g/l)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table II: Corncobs adsorption of 0.025 g/l oil at varying mass of adsorbent at 25 °C and 200 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (g)</td>
</tr>
<tr>
<td>C_0 (g/l)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table III: Corncobs adsorption of 0.025 g/l crude oil with varying time at 25 °C and 200 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
</tr>
<tr>
<td>C_0 (g/l)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table IV: Corncobs adsorption of 0.025 g/l crude oil with varying temperature and 200 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
</tr>
<tr>
<td>C_0 (g/l)</td>
</tr>
</tbody>
</table>
Several experimental runs to determine the adsorption isotherm and to study the kinetics of oil adsorption onto meshed corncobs were conducted. The result of adsorption of crude oil onto different adsorbate masses as shown in Table I revealed that the adsorption of crude oil reduced with higher adsorbate doses. As the crude oil dose increased from 0.01 g/l to 0.05 g/l with a constant weight of 2 g of corncob, the amount of crude oil adsorbed reduced. This is because the same adsorption sites are available for the varying concentration of sorbate (crude oil). In other words adsorbed oil-water ratio reduces with increase in oil added having less adsorption sites at higher adsorbate doses.

In Table II, the result of adsorption of crude oil onto different adsorbent masses showed that the adsorption of crude oil increased with adsorbent doses. As the adsorbent dose increased from 1 g to 5 g the amount of crude oil adsorbed increased. This is because more adsorption sites are available for the same concentration of adsorbate medium (crude oil). In other words, adsorbed oil-water ratio decreased with increase in initial adsorbent mass. Thus, for a given adsorbate value, at any time, adsorption capacity of sorbent and adsorbed oil-water ratio decreases with increase in initial adsorbent mass, having more adsorption sites at higher adsorbent dose.

The result of the adsorption of crude oil at different contact time showed that the adsorption of crude oil onto the adsorbents and the oil removal increased with time as presented in Table III. For a temperature of 25 °C, as the time increased from 15 to 75 min, the adsorption capacity and removal of crude oil from water increased. The result showed that the rate of adsorption and oil removal was very high initially, especially between 15 and 45 min, subsequently; quasi-stationary states were witnessed within 60 and 75 min. As depicted in Table IV, the result of batch adsorption experiments carried out for different temperatures of adsorbent showed that adsorption capacity was higher at lower temperatures. Adsorption was more pronounced at 15 °C for the temperature range considered. The results further showed that the percentage removal of the crude oil decreased with increase in temperature, indicating the dependence of adsorption on temperature.

The result of the adsorption of crude oil at different mixing speed in Table V showed that the adsorption of crude oil onto the adsorbents and the oil removal increased with speed. Lin and Liu (2000) reported that the mass transfer rate increases with the increase in stirring speed. The increase in stirring speed resulted in a reduction in surface film resistance, thereby allowing residual oil to reach the particle surface more easily. Surface film resistance slowed down the rate of adsorption. The rate of oil adsorption increased with an increase in mixing speed. For a temperature of 25 °C, as the mixing speed increased from 100 to 500 rev / min, the adsorption capacity and removal of crude oil from water increased. The result showed that the rate of adsorption and oil removal gradually increased with speed and the most remarkable adsorption occurred at about 500 rev/min (Table V).

The result of batch adsorption experiments carried out for different particle sizes showed that smaller particles have relatively higher adsorption capacity, higher oil removal and
adsorbed oil-water ratio. It has been shown that the particle size distribution affects the rate of adsorption and the sorption efficiency according to (Hjelmeland, et al., 1986). The rate of adsorption increased with increase in surface area of the adsorbent, while sorption efficiency increases with holding capacity as depicted in Tables III and VI. This is because smaller particle possess, not only larger surface areas and interstitial packing, but also the tendency of faster rate of adsorption as shown in Table VI.

The calibration plot for determining the absorbance of various oil concentrations is presented in Fig 1. In Figures 2 to 13, the Langmuir and Freundlich isotherms for the adsorption of crude oil using corn cob (CC) at varying parameters of different adsorbate concentration, adsorbent loading, time, temperature, particle size and mixing speed are presented. The Langmuir equation assumes that there is no interaction between the sorbate molecules and that the sorption is localized in a monolayer. It is then assumed that once a crude oil molecule occupies a site, no further adsorption operation can take place at that site. Theoretically, therefore, a saturation value is reached; beyond which no further adsorption can take place. Compared to the Langmuir isotherm, the Freundlich model was generally found to be better suited for characterizing multi-layer adsorption process.

The Langmuir parameters, q_m and K_L were computed from the slopes and intercepts of the straight lines of plot of (1/ q_e) vs.1/ C_e (Figures 2, 4, 6, 8, 10 and 12), while the values of Freundlich constants, K_f and n were calculated from the plots of ln C_e against ln q_e (Figures 3, 5, 7, 9, 11 and 13) for varying parameters of different adsorbate and adsorbent masses, time, temperature, particle size and mixing speed respectively. Constants q_m and K_L are Langmuir constants related to adsorption capacity and energy of adsorption, respectively, while K_f indicates the adsorption capacity and 1/n is indicative of the intensity of adsorption. The experimental results were expressed in linear form on which regression analyses were carried out representing Langmuir and Freundlich models. The plots as shown in Figures 2 to 13 were somewhat found to fit Freundlich isotherm better than the Langmuir isotherm model based on the correlation coefficients (R^2 values) that were found to be better which is in line with the literature. Therefore the claim that Freundlich model is a better model for adsorption from such liquids was justified from this work. The data obtained from the isotherm constants for various adsorbates, adsorbents, different parameters of temperature, time, mass, particle size and mixing speed are given in Table VII.

![Fig. 1: Calibration plot of absorbance at varying concentration](image-url)
Fig. 2: Langmuir plot for oil adsorption using CC at varying mass of adsorbate at 25 °C and 200 rpm

Fig. 3: Freundlich plot for oil adsorption using CC at varying mass of adsorbate at 25 °C and 200 rpm

Fig. 4: Langmuir plot for adsorption of 0.025 g/l oil at varying mass of CC adsorbent using 25 °C and 200 rpm
Fig. 5: Freundlich plot for adsorption of 0.025 g/l oil at varying mass of CC adsorbent using 25 °C and 200 rpm

Fig. 6: Langmuir plot for adsorption of 0.025 g/l oil with CC at varying time using 25 °C and 200 rpm

Fig. 7: Freundlich plot for adsorption of 0.025 g/l oil with CC at varying time using 25 °C and 200 rpm
Fig. 8: Langmuir plot for adsorption of 0.025 g/l crude oil using CC at varying temperature stirring at 200 rpm

Fig. 9: Freundlich plot for adsorption of 0.025 g/l crude oil using CC at varying temperature stirring at 200 rpm

Fig. 10: Langmuir plot for the adsorption of 0.025 g/l crude oil with CC at varying speed and 25 °C
Fig. 11: Freundlich plot for the adsorption of 0.025 g/l crude oil with CC at varying speed and 25 °C

Fig. 12: Langmuir plot for the adsorption of 0.025 g/l oil using CC with varying meshed CC sizes at 25 °C and 200 rpm

Fig. 13: Freundlich plot for the adsorption of 0.025 g/l oil using CC with varying meshed CC sizes at 25 °C and 200 rpm

Table VII: Various adsorption isotherm constants for Corncobs (CC) using different parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Freundlich constants</th>
<th>Langmuir constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kf (l/g)1/n</td>
<td>N</td>
</tr>
<tr>
<td>Time (min)</td>
<td>2.5 × 10³</td>
<td>3.716</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>1.9 × 10³</td>
<td>4.474</td>
</tr>
<tr>
<td>Size (µm)</td>
<td>5.739</td>
<td>2.154</td>
</tr>
<tr>
<td>Adsorbent mass (g)</td>
<td>1.11 × 10²</td>
<td>2.863</td>
</tr>
<tr>
<td>Adsorbate mass (g)</td>
<td>2.56 × 10²</td>
<td>5.984</td>
</tr>
<tr>
<td>Speed (rev / min)</td>
<td>2.677 × 10³</td>
<td>3.22</td>
</tr>
</tbody>
</table>
CONCLUSION

The ability of corncob (an agro waste material) as a natural adsorbent to remove crude oil from effluent water had been investigated in this work. The results demonstrated that crude oil removal by adsorption onto biodegradable corncobs with good availability at almost no cost, being a waste material is feasible. The adsorption and percentage removal of crude oil from effluent water was found to be dependent on adsorbent dose, adsorbate dose, contact time, temperature and particle size and also speed of agitation. The adsorbed oil-water ratio of the corncob adsorbent was more than unity in all cases investigated, which indicates higher adsorption selectivity for crude oil over water by the adsorbent. The test adsorbents were evaluated for their initial and final capacities, with respect to oil pickup and potential as observed.

Meshed corncobs (CC), especially 80μm, exhibit high affinity for oil adsorption, with time. The adsorption is due to larger surface areas. The considered adsorption temperature range lies between 15 - 60 ºC, with the maximum adsorption observed at 15 ºC. The correlation coefficient indicated that the sorption process was dominated by the adsorption process. Based on the high affinity for oil with low water pick up, meshed corncobs used as an adsorbent could be expressly regarded as an oleophilic or hydrophobic substance. The equilibrium adsorption isotherm analysis using Langmuir and Freundlich, was carried out as presented. Langmuir and Freundlich isotherm models fitted the equilibrium data reasonably well. In conclusion, the results from the Freundlich isotherm model seems to be most significant than that of Langmuir as shown. This is similar to the findings of Sidik et al., (2012), when modified oil palm leaves adsorbent with enhanced hydrophobicity for crude oil removal was studied, where the authors observed that the isotherms studied revealed that the experimental data agreed more with the Freundlich isotherm model.

REFERENCES


