Acetylated Groundnut Husk and Sugarcane Bagasse Use on Oil Sorption: Equilibrium and Fourier Transform Infrared Spectroscopy in Focus

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Abstract

In this study, Fourier Transform Infrared Spectroscopy (FTIR) was used to investigate the acetylation of groundnut husk and sugarcane bagasse. Equilibrium isotherm data were analyzed using the Langmuir and Freundlich isotherms. The regression coefficient (R^2) values for acetylated groundnut husk (0.997),raw groundnut husk(0.991),acetylated sugarcane bagasse (0.986),and raw sugarcane bagasse (0.985) for Freundlich model was higher than that obtained for Langmuir model which shows that freundlich model is suitable for explaining the sorption equilibrium of crude oil on the adsorbents. Acetylated groundnut husk and sugarcane bagasse are therefore recommended for further development for oil spill cleanup.

Keywords: Adsorbents, Acetylation, Fourier transformed infrared spectroscopy, Langmuir isotherm, Freundlich isotherm.

Introduction

Oil is often regarded as one of the most vital energies and source of raw material for producing synthetic polymers and chemical globally (Annuciado, et al 2005). Oil spills may be caused due to the discharge of crude oil into the environment as a result of human action. Oil spillage has become a global concern that has been happening since the onset of the industrial revolution which led to the invention of crude oil. According to www.science.irank.org, the total spillage of petroleum into the oceans, seas, and rivers through human activities was estimated to range 0.7 -1.7 million tons per year.

Oil spills, therefore, poses a major hazard to the environment especially in most oil-producing areas; which if not effectively managed, could lead to the total destruction of the ecosystem. Some commonly used cleanup techniques have been employed in oil spill cleanup but they are very expensive, time-consuming and not environmentally friendly.

However, the use of agricultural waste has been employed in oil spill cleanup due to their low cost, eco-friendly and availability such as rice straw, sisal and sawdust, kenaf have been investigated for oil spill cleanup applications (Choi and Cloud 1992).

The acetylation reaction is one of the most common techniques used for the hydrophobic treatment of lignocellulosic materials (e.g. wood) by a substitution reaction of a hydroxyl group (hydrophilic) with an acetyl group (hydrophobic). This reaction is usually carried out by heating lignocellulosic material in the presence of acetic anhydride with or without catalyst (Nwadiogbu et al, 2015). In this study, the acetylation of groundnut husk and sugarcane bagasse was determined and Equilibrium parameters were also determined in order to understand the mechanism of the sorption process.

Material and Methods.

2.1 Materials

Crude oil was obtained from Warri refinery, Delta state. Groundnut husk and Sugarcane bagasse were gotten from New Market in Enugu metropolis, Nigeria.

2.2 Methods

2.2.1 Characterization of Adsorbents

The following proximate analysis was carried out on the Raw and Acetylated groundnut husk and Sugarcane baggage. The ash content, volatile matter, moisture content and porosity of the adsorbents was determined using the methods reported by (Dara 1991), (Aloko & Adebayo, 2007), (ASTM, 1994) and (Behnood et al, 2013) respectively. The density, specific gravity, viscosity, and API gravity of the crude oil sample were determined using methods proposed by (Hassan et al., 2003) and (Wikipedia, 2009). The Fourier transform infrared (FTIR) spectra were recorded on Shimadzu FTIR 8400s.

2.3 Preparation of the adsorbents.

Groundnut husk and Sugarcane bagasse were thoroughly washed with clean water to remove dust and fungus. They were dried in sunlight for about 12 hours and then left to dry at 65^0C in an oven. They were ground using a manual grinding machine, size reduced and sieved through 25 British standard sieves (BSS Sieves).

Soxhlet Extraction.

This is done to reduce the influence of the fiber extract on acetylation, 10g of the sieved materials were extracted with a mixture of acetone and n-hexane (4:1, v/v) for 5hrs. The extracted samples were dried in a laboratory oven for 16hrs. The extracted content was calculated as the percentage of the oven-dried test samples.

Acetylation of the Adsorbents.

The acetylation of the groundnut husk and sugarcane bagasse under mild conditions in the presence of iodine using acetic anhydride was carried out using the method reported by Nwabueze et al (2005) which involved acetylation in a solvent-free system. The amount of substrate and reactant were combined in a ratio of 1:20(gram dried groundnut husk and sugarcane bagasse/mL acetic anhydride). The reaction temperature, time and amount of catalyst were 100^0C, 1hr, and 1%, respectively. The mixture of raw groundnut husk and sugarcane bagasse, acetic anhydride and catalyst were placed in a round-bottom flask fitted to a condenser. The flask was placed in an oil bath on top of a thermostatic heating device. Then, the flask was removed from the bath, and the hot reagent was decanted. The groundnut husk and sugarcane bagasse were thoroughly washed with ethanol and acetone to remove unreacted acetic anhydride and the acetic acid by-products. The new products were dried in an oven at 60^0C for 16h prior to analysis.

Oil sorption studies

The sorption studies were determined using the method reported by Hussien et al (2008).

Determination of the Oil Sorption Capacity

The sorbent was subjected to pressing to desorb the sorbed oil. During the pressing stage, petroleum ether was added to aid extract the oil in the fiber. Centrifuge tubes were used to collect the extracted liquid and were put in a water bath at the temperature of 55-65^{o}C for 30 minutes to break any emulsion present and then centrifuged at 2500Rpm for 30 minutes. The amount of water sorbed was (M_w) was weighed and recorded.

Oil sorption determination:

$$M_o = M_t - M_s - M_w \quad (1)$$

Where, M_o is the amount of oil sorbed(g); M_t is the total mass of sorbent, oil, water, and sieve (g); M_s is the mass of sorbent(g) and M_w is the mass of water sorbed(g). The oil sorption capacity was calculated by taking into account the weight of the sorbents and oil and the weight of the sieve/ net using the formula below:

$$\text{Oil sorption capacity (g/g)} = \frac{M_o}{M_s} \quad (2)$$

Results and discussions

Characterization of sample

Table 1: Characteristic properties of the adsorbents and crude oil

Property	RGH	AGH	RSB	ASB	Crude oil
Moisture Content(%)	7.2	6.1	7.7	6.0	-
Volatile	71.91	66.6	70.2	64.4	-

Matter(%)					
Ash (%)	1.02	0.25	1.27	1.04	-
Bulk Density(g/cm^3)	0.252	0.159	0.143	0.063	-
Tapped Density(g/cm^3)	0.306	0.201	0.190	0.087	-
Particle density(g/cm^3)	0.984	0.855	0.946	0.782	-
Porosity (%)	74.4	81.4	84.9	91.9	-
Fixed Carbon (%)	27.07	33.15	28.53	34.56	-
Viscosity @ 27^{0}C (mPa-s)	-	-	-	-	63.4
Specific gravity 60/60f	-	-	-	-	0.879
Density (g/dm^3)	-	-	-	-	0.791
API gravity(^{0})	-	-	-	-	28.89

Where ***RGH*** *represents Raw groundnut husk*
AGH *represents Acetylated groundnut husk*
RSB *represents Raw sugarcane bagasse*
ASB *represents Acetylated sugarcane bagasse*

The results of the characterization of the adsorbents and crude oil are presented in Table 1 above. The moisture content, volatile matter, Ash content, Bulk density, tapped density and particle density of the raw adsorbents reduced after acetylation. The porous nature of the material, which is one of the requirements for a good sorbent, was confirmed by the porosity result for RGH (74.4%), AGH (81.4%) and RSB (84.9%), ASB (91.9%), These values showed that acetylation increased the adsorption capacity of the adsorbents.
For the crude oil sample, API gravity value of 28.89 was recorded. The higher API gravity value (>10) indicates that the oil is less dense and float on water.

Fourier Transform Infrared Spectroscopic Studies for Raw and Acetylated Groundnut Husk

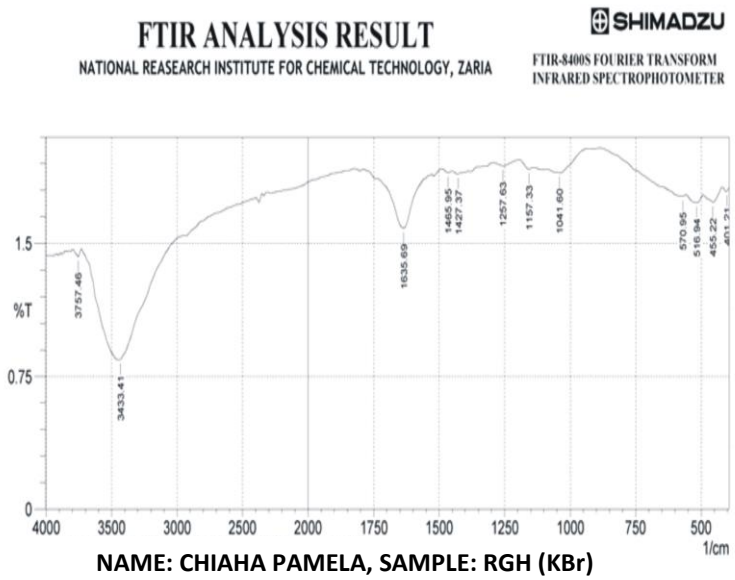


Figure 1: FTIR spectrum of Raw Groundnut Husk

An infra-red spectrum for raw and acetylated groundnut husk was presented in Fig 1&2.
The proposed assignments of the observed signals, as suggested elsewhere (Nwadiogbu et al., 2014) are presented in Table 2. The major changes before and after acetylation are enhanced carbonyl absorption peak at 1643cm^{-1} (C=0 ester) and appearance of absorption peaks in the acetylated groundnut shell at 2931cm^{-1}(-CH stretch), 2376cm^{-1}(CH3 group) and 1388cm^{-1}(CH deformation).

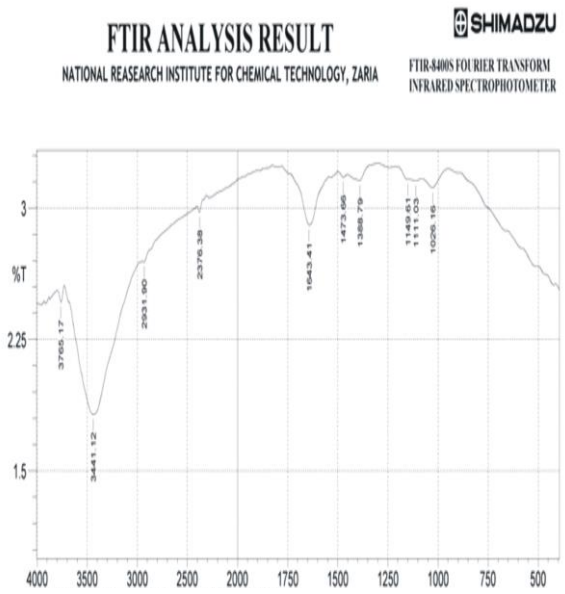


Figure 2: FTIR spectrum of Acetylated Groundnut Husk

Infrared Spectroscopic Result For Raw and Acetylated Sugarcane Bagasse
The proposed assignments of the observed signals (Nwadiogbu et al.,2014) are presented in Table 3.Vibrational signals within 3000-3600cm^{-1} are for –OH stretching vibrations (Nwadiogbu et al., 2014; Nnaji et al.,2016). Signals in the range of 1600-1745cm^{-1} are due to C=O stretching vibrations (Nnaji et al., 2016). Vibrations seen within 1100-1300cm^{-1} are characteristic of C-O stretching signals of carbonylic esters and esters (Nwankwere et al., 2010) broad absorption due to O-H signal within centre 3410 for RSB shifted to 3433 for ASB suggesting that poly hydroxyl functional groups of RSB were involved in the acetylation process.

Table 3: Assignment of IR spectra bands of functional groups of raw and acetylated sugarcane bagasse

Raw sugarcane bagasse (cm^{-1})	Acetylated sugarcane bagasse (cm^{-1})	Band assignment
3873,3757	3757,3453	-OH stretching, hydroxyl group
2931	2931	-CH stretching CH3-O group cellulose
2376	2376	CH3 group, stretching vibration in alphatic CH3 group
1643	1643	C=O esters (ascribed to hemicelluloses)
1465	1465	C=C of alkenes
1388	1404	CH deformations in O(-C=O)-CH_3 group
1234	1242	C=O stretch acetyl group (lignin)
1149	1103	C-O-O anti symmetric bridge stretching of

		hemicelluloses and cellulose
1026	1026	C-O stretching vibrations in cellulose, hemicelluloses, and primary alcohols
439	470	si-o-si band, silica

Similar results for-OH signals in the regions were proposed for –OH vibrations (Nnaji et al., 2016). In addition, it shows a remarkable change in intensity (lowering of intensity) strongly supporting evidence of acetylation of RSB. The implication is that some acetyl functional groups (from acetic anhydride) effectively attached to RSB by replacing the hydroxyl groups deformational signals of CH seen around 1388cm^{-1} for RSB shifted to 1404cm^{-1} after acetylation.

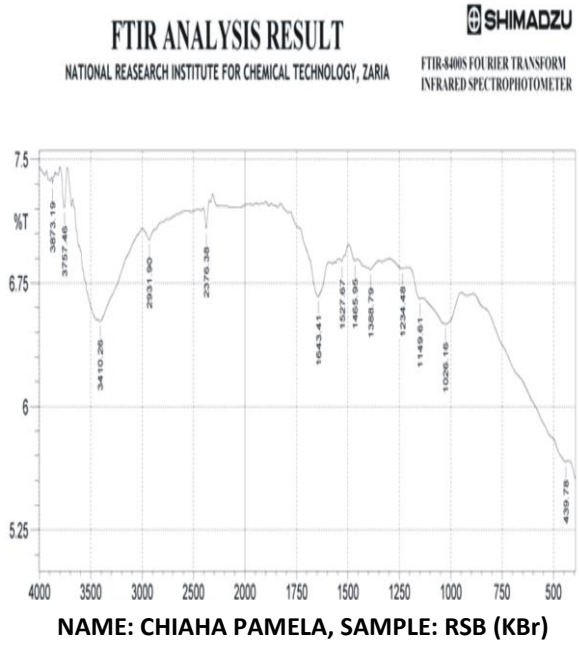
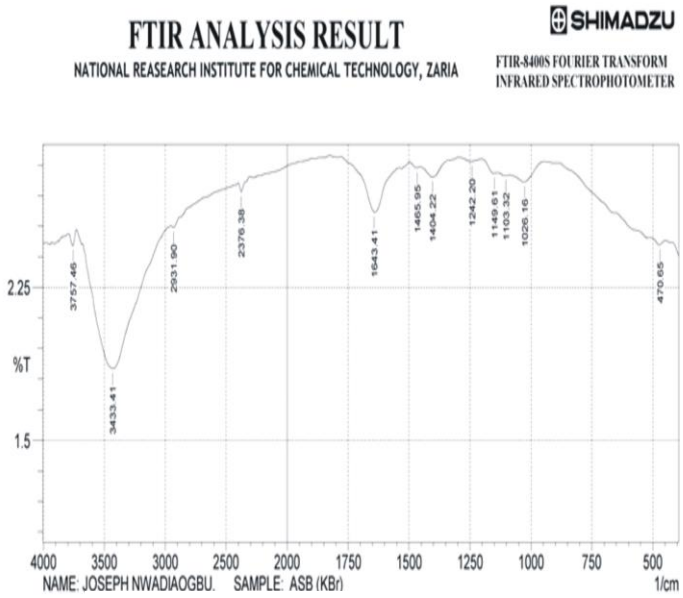


Figure.3: FTIR spectrum of Raw Sugarcane Bagasse

The absence of peaks at around 1700cm^{-1} and 1840-1760cm^{-1} in the treated samples indicated that acetylated products were free of acid by-products and unreacted acetic anhydride. The changes confirm the formation of the ester band (Nwadiogbu et al., 2014; Nwankwere, 2010). Board absorption due to 0H signal with centre at 3433cm^{-1} for the raw sample shifted to 3411cm^{-1} for the acetylated sample, suggesting that poly hydroxyl functional groups of the raw sample were involved in the acetylation process (Nnaji et al .,2016). The increase in the intensity of the absorption peak at 1149cm^{-1} in the acetylated sample suggests the formation of new ester groups. The absence of peaks at around 1700cm^{-1} and 1840-1760cm^{-1} in the treated sample indicate that the acetylated products were free of acetic acid by-products and unreacted acetic anhydride.



NAME: CHIAHA PAMELA, SAMPLE: ASB (KBr)

Figure 4: FTIR spectrum of Acetylated Sugarcane Bagasse

Equilibrium Sorption studies for the adsorbents.

The amount of crude oil adsorbed (qe) in milligrams per gram were determined using the following mass balance equation:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (3)$$

$$C_o = \frac{weight\ of\ oil\ use\ d(mg)}{volume\ of\ water\ used(l)} \quad (4)$$

$$C_e = weight\ of\ oil\ used - weight\ of\ oil\ sorbed \quad (5)$$

Where Co is the initial oil concentration in mg/L, Ce is the equilibrium oil concentration in mg/L, V is the volume of the solution in litres, and m is the mass of the adsorbent in gram. Langmuir and Freundlich isotherms were used to analyze the experimental data. The sorption isotherm represents the relationship between the amount of adsorbate removed from the liquid phase and the unit mass of the adsorbent at a constant temperature. Langmuir isotherm was used to describe the adsorption phenomena and is based on the assumption that adsorption occurs uniformly on the active sites of the sorbent. In addition, once an adsorbate occupies a site, no further sorption can occur at that site. The linear form of the Langmuir model can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \quad (6)$$

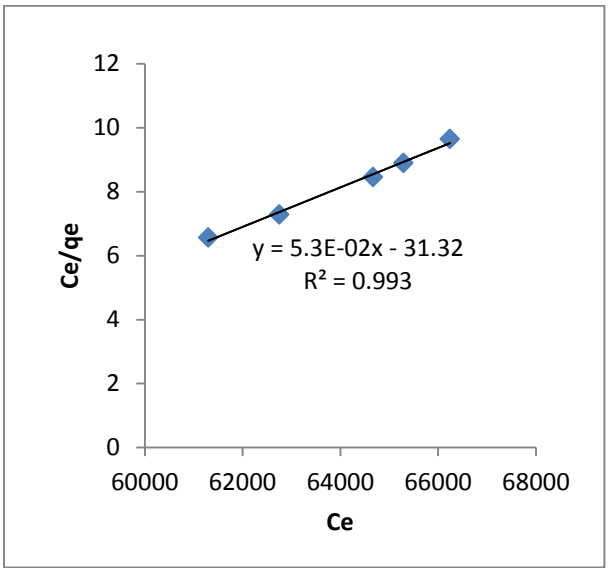


Figure 5: Graph of Langmuir Isotherm for AGH

Where q_o is the equilibrium monolayer adsorption capacity of the adsorbent (mg/g), b is the Langmuir adsorption constant (L/mg) related to the energy of adsorption, which quantitatively reflects the affinity between the adsorbent and the adsorbate, and q_o is the maximum monolayer adsorption capacity of the adsorbent (mg/g). The q_o and b constants can be determined from a linear plot of C_e/q_e as a function of C_e.

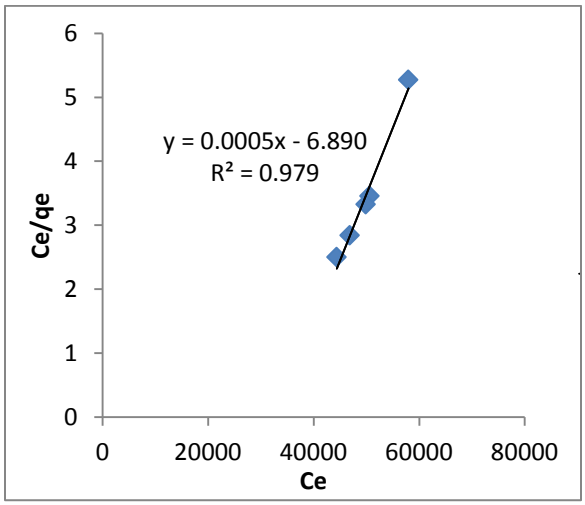


Figure 6: Graph of Langmuir Isotherm for ASB

The important feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant (ie separation factor (R_L), which is explained by the following relationship (Nwadiogbu et al 2015):

$$R_l = \frac{1}{1+bC_o} \qquad (7)$$

Where $C_o$is the initial concentration of crude oil in mg/L. The separation factor provides information regarding the nature of the adsorption process. The adsorption can be considered irreversible (R_L =0), favourable (0< R_L <1), linear (R_L =1) or unfavourable (R_L>1)

The Freundlich isotherm model has been applied to non-ideal sorption on heterogeneous surfaces, and the linear form of this equation can be expressed as (Dawodu and Akpomie 2014):

$$\ln q_e = \ln k_f + \left(\frac{1}{n}\right) \ln C_e \qquad (8)$$

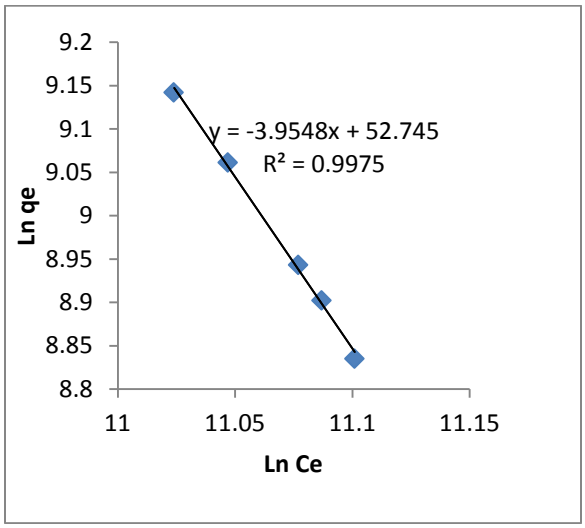


Figure 7: Graph of Freundlich Isotherm for AGH

Where k_f (mg/g) $(mg/L)^{1/n}$ and 1/n are the Freundlich adsorption capacity and the intensity of the adsorbents, respectively.

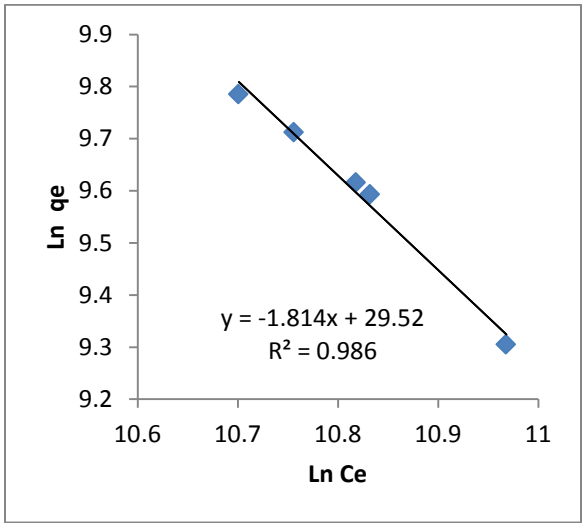


Figure 8: Graph of Freundlich Isotherm for ASB

The constants were determined from the intercept and slope of the linear plot of ln q_e as a function of ln C_e.

Table 4: Comparison of isotherm constants for crude oil sorption onto groundnut husk and sugarcane bagasse.

Isotherm models	AGH	RGH	ASB	RSB
Langmuir				
q_o	1886.7	500	200	3125
B	$1.69x10^{-5}$	$1.37x10^{-5}$	$7.25x10^{-4}$	$2.34x10^{-5}$
R_L	-2.84	-10.42	-55.01	-1.15
R^2	0.993	0.975	0.979	0.976
Freundlich				
K_f	$8.029x10^{21}$	$2.94x10^{45}$	$6.61x10^{12}$	$1.56x10^{16}$
N	1.253	1.112	1.486	1.392
R^2	0.997	0.991	0.986	0.985

As shown in Table 4, the regression coefficient (R^2) for the AGH (0.997), RGH (0.991), ASB (0.986) and RSB (0.985) for the Freundlich model was higher than that obtained for the Langmuir model. Therefore, this result indicates that the Freundlich model is suitable for relating the sorption equilibrium of crude oil on groundnut husk and sugarcane bagasse, which is in accord with earlier results (Sidik et al 2002).

Conclusion

The equilibrium sorption of oil spill cleanup using acetylated groundnut husk and sugarcane bagasse was investigated. The characterization of the adsorbents was determined and the porosity results for RGH (74.4%), AGH (81.4%) and RSB (84.9%), ASB (91.9%) shows that the sorbents are good for oil sorption. Meanwhile, acetylation increased the adsorption capacity of the adsorbents. The result of the Fourier Transform Infrared Spectroscopy shows that the absence of a peak at around $1700cm^{-1}$ and $1840cm^{-1}$-$1760cm^{-1}$ in the treated adsorbents indicated that the acetylated products were free of acid by-products and unreacted acetic anhydride and also evidence of successful acetylation. Freundlich isotherm provided the best fit to the experimental data based on the regression coefficients (R^2) which indicates that there was a heterogeneous coverage of adsorption of oil on the surface of the adsorbents

References

[1]. A.B.Hassan, M.S.Abolarin, and U.Ratchel (2003).Investigation on the use of palm oil as lubricating oil. Leonardo Electronic Journal of practices and Techniques, 8:1-8.

[2]. American Standards for Testing and Materials (ASTM) (1994). D4442-84: Standard Test Method for Direct Moisture Content of Wood and Wood-Based Materials. ASTM, 04- 09:514-518.

[3]. D.F. Aloko and G.A.Adebayo (2007). Production and Characterization of Activated carbon from Agricultural waste (Rice husk and Corn cob).Journal of Engineering and Applied Sciences 2(2)440-444

[4]. E.T.Nwankwere, C.E.; Gimba, J.A.Kagbu, and B.K.Nale (2010). Sorption studies of crude oil on acetylated rice husks. Adv. Appl. Res. (2)142-145.

[5]. F.A Dawodu. and K.G Akpomie. (2014). Simultaneous adsorption of Ni(II)and Mn(II) ions from aqueous solution unto a Nigeria Kaolinite clay, Journal of Mater.Res.Technol.3(2) 129-141.

[6]. H. Choi and .R.M Cloud. (1992) Natural Sorbent in Oil Spill Cleanup Environmental Sci. Tech 4, 772-776.

[7]. H.O. Nwabueze, P.K. Igbokwe. , E.U.Amalu. and S.E.Okoro (2015). A Study on the equilibrium and Kinetics of Oil Spill Cleanup using Acetylated Corncobs.Int.Journ.of Environmental Sciences,5 (6) 1106-1114.

[8]. J.O.Nwadiogbu, V.I.E Ajiwe, and P.A.C Okoye (2015).Removal of crude oil from the aqueous medium by sorption on hydrophobic corncobs: Equilibrium and kinetics. Journal of Taibah Univ. for Sci.28. 1525-1528.

[9]. M.Hussien, A.A.Amer, and I.I.Sawsan (2008) Oil Spill Sorption Using Carbonized Pitch Bagasse: Trial for Practical Application. International Journal of Environmental Science and Technology, 5: 233-242.

[10]. Nwabueze et al, (2015). A Study on the equilibrium and Kinetics of Oil Spill Cleanup using Acetylated Corncobs.Int.Journ.of Environmental Sciences,5(6) 1106-1114.

[11]. R.Bennod, B.Anvaripour, N.Jaafarzad Haghighi Fard and M.Farasati (2003).Petroleum Hydrocarbons Adsorption from Aqueous Solution by Raw Sugarcane Bagasse. Int. Journ. of Emerging ScienceandEngineering,1(6):96-99.

[12].S.S. Dara (1991).Experiments and Calculations in Engineering Chemistry, S.Chand, and Co.Ltd, New Delhi, 185-191.
[13].T.R. Annunciado, T.H.D. Sydenstricker and S.C.Amico.(2005) Experimental Investigation of various Vegetable Fibres as Sorbent Materials for Oil Spills, Mar. Pollu. Bull., 50(11) 1340-1346.