



ASSESSMENT OF REMOVAL OF CRUDE OIL AND ITS LOWER FRACTIONS FROM LAND AND AQUEOUS MEDIUM USING ACTIVATED CORNCOB CARBON



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Abstract: Activated corncob carbon was prepared and tested for removal of crude oil, diesel, kerosine and petrol from land and aqueous medium by comparing its oil uptake, recovery of sorbed oil and retain ability of sorbed oil with a standard; conventional synthetic sorbent used in oil spill removal. The experiment was conducted under the same experimental condition by batch adsorption method. The result of the study shows that the standard sorbed 11.50 g/g of crude oil, 10.38 g/g of diesel, 8.20 g/g of kerosine and 6.30 g/g of petrol while activated corn cob carbon sorbed 4.15 g/g of crude oil, 3.27 g/g of diesel, and 2.66 g/g of kerosine and 2.40 g/g of petrol. The standard performed better in terms of oil uptake and recovery, while activated corncob carbon retained more of the sorbed. Activated corncob carbon is suitable where oil recovery is not required. Textural properties and functional group studies shows that the standard has larger surface area (1633 m² g) than activated corncob carbon (784 m² g), it is mesoporous and predominantly hydrocarbon, while, activated corncob carbon is microporous and has surface acidic groups. The difference in porosity, surface chemistry and functional group present in the sorbents contributed to higher uptake by the standard. The volume of water sorbed together with each sorbate onto activated corncob carbon and the standard was 3 ml (0.70 g) and 6 ml (1.2 g), respectively. These volumes are minimal for each of the sorbent, indicating that activated corncob carbon can be employed in oil spill mop in aqueous environment. Langmuir isotherm model can describe the adsorption process of crude oil and its lower onto activated corncob carbon and standard. Kinetic models employed suggest that the sorption process of the sorbates onto activated corncob carbon and the standard occurs via a surface reaction and intraparticle diffusion mechanism. The result of the study indicates that activated corncob carbon is a viable oil spill sorbent.

Keywords: Activated carbon, kinetic model, corncob, crude oil, textural properties

Introduction

Oil spill have detrimental effects on the environment, for this reason, steps are taken to clean up oil once it spills. There are several methods involved in oil spill clean-up, these, include; oil containment, recovery of oil and oil removal. Oil is contained through the application of booms and ancillary equipment, while, it is recovered using skimmers, sorbents and manual recovery. In-situ burning, chemical agents and biological agents are used for oil removal (Fingas, 2013). Sorbents are insoluble materials or mixture of materials used to recover liquids through the mechanism of absorption, or adsorption, or both (Thomas, 2010). Sorbents are categorized into natural and synthetic sorbents: Synthetic sorbents include; polyurethane, polystyrene, polyester and urea formaldehyde. Natural sorbents can be organic or inorganic: natural inorganic sorbents include; perlite, talc and vermiculite. Natural organic sorbents are straw, bark, peat et cetera (Okonkwo and Eboatu, 1999).

Synthetic materials are the most commonly used commercial sorbents due to their oleophilic and hydrophobic properties (Teas *et al.*, 2001). However, these materials are not biodegradable, which is a major disadvantage (Nwadiogbu *et al.*, 2016). To abate these problems various studies have been conducted on the viability of natural materials as oil spill sorbent because of their low cost and biodegradability. The main draw-backs of plant-derived sorbents are their relatively low oil sorption capacity, low hydrophobicity and poor buoyancy compared to synthetic sorbents (Annunciado *et al.*, 2005; Bayat *et al.*, 2005). Once plant-derived sorbents are applied to saturated environments, preferential water sorption is favoured over the sorption of oil because the sorbents are typically hydrophilic in nature, due to their associated hydroxyl functionalities (Nwadiogbu *et al.*, 2014). This group (hydroxyl) are abundantly available in all three major chemical components of plant-based materials.

To be useful in combating oil spill, sorbents need to be both oleophilic and hydrophobic (Thomas, 2010). The

effectiveness of plant-derived sorbents in saturated environments would be enhanced when the density of the hydroxyl functionalities is decreased (Bodirlauet *et al.*, 2009). This may be achieved through conversion of a plant material to activated carbon; also conversion of plant material to activated carbon may increase sorption capacity because of increased porosity and surface area (Yahya *et al.*, 2015).

Corn cob a biodegradable, available and abundant agricultural waste is obtained from maize. Maize is grown widely throughout the world with the United States, China and Brazil being the top three maize-producing in the world (Ranumet *et al.*, 2014). Maize can be processed into a variety of food and industrial products, including starch, sweeteners, oil, beverages, glue, industrial alcohol and fuel ethanol (Ranumet *et al.*, 2014). Maize is the world's most widely grown cereal, and more maize is produced annually than any other grain (Olaniyi, 2015). It is the most important staple food in sub-Saharan Africa and Latin America (Olaniyi, 2015). The largest African producer of Maize is Nigeria with nearly 8 million tons (Olaniyi, 2015). Corncob is generated in large quantities in Nigeria and is hardly managed as Nigeria faces the problem of solid waste management. Corncob is composed of cellulose, hemicelluloses and lignin; these three major chemical components of corncob are rich in hydroxyl group, which makes it hydrophilic in nature (Budaiet *et al.*, 2014; Nwadiogbu *et al.*, 2014). Apart from the three major chemical components of corncob that are rich in hydroxyl group, corncob contains high quantity of Si, K, Fe, Al and P. These minerals contribute to the hydrophilic nature of the material (Ribeiro *et al.*, 2000). Mineral composition of materials can be reduced when activated (Al-Qodah and Shawabkah, 2009). Conversion of materials to activated carbon yields product that is carbonaceous with large surface area and high porosity. During the activation process the precursor is converted into a hydrophobic carbonaceous material which has surface functional groups that are hydrophilic (Viswanathan *et al.*, 2009).

The performance of sorbing materials often needs to be compared. By performance of the sorbent is usually meant its uptake (q) of a sorbate (Volesky, 2004). The sorbents can be compared by their respective equilibrium adsorption capacity obtained from experiment or maximum equilibrium adsorption capacity q_m values which are calculated from Langmuir isotherm. A good sorbent would feature a high sorption uptake capacity q_m . Also desirable is a high affinity between the sorbent and sorbate (Volesky, 2004). This helps in efficient application of sorbents. Efficient application of sorbents requires knowledge of data on the sorbent sorption capacity and a good understanding on the basic mechanism behind the sorption capabilities (Singh *et al.*, 2013). In order for the comparison of two or more sorbents to be fair, it must be done under the same experimental conditions

The aim of this study is to assess the performance of activated carbon prepared from corncob, in crude oil, diesel, kerosene and petrol removal and also to determine the possibility of managing solid waste generated from corncob through recycling as an oil spill sorbent.

Materials and Methods

Sample collection

The crude oil used in this study was obtained from Shell Petroleum Development Company, Warri, Delta state, Nigeria. Diesel, kerosene and petrol were obtained from Total filling station, Asaba, Delta State, Nigeria. Corncob was obtained as waste material from corn sellers located in Asaba, Delta state, Nigeria. Conventional synthetic sorbent mat used as standard in this study was obtained from Shell Petroleum Development Company, Port Harcourt, Rivers State, Nigeria.

Preparation of sample

Corncobs were washed with water and soap to remove dirt, rinsed severally with water and dried under the sun for two weeks. The production of activated carbon by chemical activation method as described by Gamalet *al.* (2014) was used for the preparation of activated carbon from corncob. Corncobs were cut into small pieces, grained and sieved to an average particle size (0.05 mm). The raw material was subjected to chemical treatment followed by pyrolysis. The activation was carried out by impregnation of the corncob samples with phosphoric acid in a ratio of 1:2 (w/w) for 24 h, and then washed with distilled water several times until pH reached 4. After that, the samples were dried at 100°C then pyrolysed in a muffle furnace in absence of air at 400°C for 2 h. After pyrolysis, the resulting samples were washed with distilled water until the pH of the washing solution reached 7.00. The activated carbon samples were dried at 100°C and kept dry till use

Proximate analysis of activated corncob carbon

Ash content determination

Ash content of activated corncob carbon was determined according to the ASTM D2866-94, (1999) test method for determination of total ash content of activated carbon. The % ash content (dry basis) was calculated from the equation:

$$\text{Ash (\%)} = \frac{\text{Ash weight (g)}}{\text{Dry weight of activated carbon (g)}} \times 100$$

Moisture content determination

Moisture content of activated corncob carbon was determined according to ASTM 2867-99, (1999) standard test method for moisture in activated carbon. The moisture content in percentage was calculated from the equation:

$$\text{Moisture content (\%)} = \frac{\text{Loss in weight on drying (g)}}{\text{Initial weight of sample (g)}} \times 100$$

Volatile content determination

Volatile matter content was determined according to ASTM 5832-98, (1999) standard test method for volatile matter

content of activated carbon. The percentage volatile matter content was determined from the equation:

$$\text{Volatile content (\%)} = \frac{\text{Loss in weight on drying (g)}}{\text{Initial weight of sample (g)}} \times 100$$

Fixed carbon determination

Fixed carbon content was determined by subtracting the sum of percentage compositions of volatile matter content, moisture content and ash content from 100 (Obiora *et al.*, 2014; Nwabunne and Igbokwe, 2012).

Fixed carbon (%) = 100 – (ash content + moisture content + volatile content)

Determination of textural properties of activated corncob carbon and conventional synthetic sorbent

Apparent density determination

Apparent density of activated corncob carbon and conventional synthetic sorbent were determined according to ASTM D 2854-96, (2000) standard test method for apparent density of activated carbon. The weight (g) of the adsorbent divided by the volume (ml) gives the apparent density (g/ml) of the adsorbent.

Bulk density determination

This was determined by the method described by Bhatia, (2006). The bulk density of the test sorbents was obtained from the express:

$$\text{Bulk density (g/cm}^3\text{)} = \frac{\text{Mass of sample (g)}}{\text{Volume of water displaced (ml)}}$$

Porosity of the adsorbents was computed using the following relationship (Akinyemi and Taiwo, 2004)

$$\% \text{ Porosity} = \frac{\text{Apparent density} - \text{bulk density}}{\text{Apparent density}} \times 100$$

Estimation of specific surface area

Specific surface area and pore size distribution of activated corncob carbon and synthetic sorbent were determined by N_2 adsorption on the surface of the sorbents at 77K using Autosorb-1-C Quantachrome, USA. The automated equipment which utilizes Quantochromeautosorb software, automatically measured the adsorption and desorption isotherms at 77K and from the data, it calculated the specific surface area of the sorbents by applying Brunauer, Emmett and Teller (BET) equation for surface area. Pore size distribution was also calculated. Prior to analysis, the samples were out-gassed overnight at 200°C under vacuum.

Boehm's titration

The presence of surface functional groups in the activated carbon was determined by Boehm, (1995) and Boehm, (2002) titration method. The phenolic group content on the carbon surface was determined as the amount of 0.1MNaHCO₃ consumed by the sample. Lactonic group content was calculated as the difference between the amounts of 0.1MNa₂CO₃ and 0.1MNaHCO₃ consumed by the activated carbon sample. Carboxylic group determined by subtracting the amount of 0.1MNa₂CO₃ consumed by the activated carbon from the amount of 0.1 M NaOH consumed. This method was used to calculate the concentration of acid groups on activated carbon surface under the following assumptions; NaOH neutralizes carboxylic, phenolic and lactonic groups. Sodium carbonate (Na₂CO₃) neutralizes only carboxylic and phenolic groups. Sodium bicarbonate (NaHCO₃) only neutralizes carboxylic groups. The basicity of the surface-oxygen groups was determined by neutralization with 0.1MHCl.

FTIR spectroscopic analysis of conventional synthetic sorbent mat

The functional groups present in the synthetic sorbent were determined by FTIR spectroscopy. The FTIR analysis was carried out using SHIMADZU FTIR-8400S spectrophotometer with a NaCl cell. The sample was ground into fine powder and spread uniformly in between two

NaCl based cells. The cells were fixed into the machine and an incident ray of light passed through it. The FTIR spectrophotometer was operated under the following conditions; interferometer: Michelson type with 30° incident angle, dynamic alignment, sealed desiccated, optical system: single beam optics, beam splitter: germanium-coated HBr plate, light source: high brightness ceramic, detector: temperature controlled high sensitivity detector (DLATGS detector), S/N ratio: greater than 20,000: 1 (KRS-5 window), 4cm⁻¹, 1 minute, 2200 cm⁻¹, P-P, wave number: 7,800 – 350 cm⁻¹, resolution: 0.85, 1, 2, 4, 8, 16 cm⁻¹, mirror speed: 3 steps; 2.8, 5, 9 mm/sec, data sampling: He-Ne laser, sample compartment: W200 x D230 x H170 mm, temperature: 15-30°, relative humidity: less than 70%.

Determination of equilibrium adsorption capacity, oil recovery and oil retention capacities.

Crude oil, diesel, kerosine and petrol (1 dm³ each) whose weight had been predetermined were put in a pre-cleaned 2 dm³ beaker. The beaker containing petrol was covered during the experiment. The weight of each sorbate was used as the initial concentration of each sorbate. Five (5) g of activated corncob carbon/synthetic sorbent was weighed and added into the beaker and left for a required contact time at 28°C. The contact times used in this study ranged from 10 to 100 min at 10 min interval. At the end of each contact time, the content in the beaker was passed through a sieve of 350µm into another pre-cleaned and pre-weighed 2 dm³ beaker and allowed to drain. The weight of the 2 dm³ beaker containing unadsorbed sorbate was weighed, after which, the weight of the 2 dm³ beaker subtracted from it to obtain the weight of unadsorbed sorbate. The weight of the unadsorbed sorbate was used as final concentration of each sorbate.

The amount of sorbate sorbed onto a unit mass of activated corncob carbon/synthetic sorbent was calculated from:

$$q = \frac{C_i - C_f}{M}$$

Where q = Amount of sorbate adsorbed onto a unit mass of activated corncob carbon /synthetic sorbent.

C_i = Initial concentration of sorbate in grams (g).

C_f = Final concentration of sorbate in grams (g).

M = Mass of sorbent in grams (g).

Or

$$q = \frac{\text{Initial weight of sorbate} - \text{Final weight of sorbate}}{M}$$

The amount of each sorbate recovered from each sorbent was determined by removing the sorbent from the sieve, weighing it and afterwards subjecting it to pressing using a carver hydraulic press, Model M, serial No. 12000 – 137, operated at a pressure of 25 tonnes, for five minutes, at 28°C. After pressing, the sorbent was re-weighed; the weight of sorbate recovered was determined by weight difference.

The amount of sorbate recovered per unit mass of sorbent was determined from the expression:

$$q = \frac{\text{Initial weight} - \text{Final weight}}{M}$$

The amount of sorbate retained per unit mass of sorbent was obtained from the expression:

q = Quantity of sorbate adsorbed per unit mass of sorbent – Quantity of sorbate recovered per unit mass of sorbent.

Each experiment was performed in triplicate, the average and standard deviation was calculated and used.

Verification of adsorption process of crude oil, diesel, kerosine and petrol onto activated corncob carbon /synthetic sorbent using adsorption isotherm

The verification of adsorption process of the sorbates onto activated corncob carbon/synthetic sorbent was done using Langmuir, Freundlich, Elovich, Temkin and Dubinin – Radushkevich adsorption models. Five different initial

concentrations (measured in volume and weight) of each sorbate; 0.5, 0.75, 1.00, 1.25 and 1.5 dm³ were used for the experiment. The sorbate – sorbent system was left to contact for 80 min. Triplicate determination was conducted and the average used.

The favourable nature of adsorption and affinity between the sorbates and sorbents was determined by application of dimensionless separation factor equilibrium parameter of Hall *et al.* (1966)

Kinetic studies

The Mechanism and rate of sorption of crude oil and its lower fractions onto activated corncob carbon and synthetic sorbent were investigated using Lagergren’s pseudo-first-order, pseudo-second-order, liquid film diffusion and intraparticle diffusion models. The expressions are:

Pseudo-first-order kinetic model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \text{ (Dawodu, 2014)}$$

Pseudo – second order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \text{ (Ho, 1998)}$$

intraparticle diffusion model:

$$q_t = k_d \cdot t^{1/2} + I \text{ (Weber et al., 1963)}$$

Liquid film diffusion kinetic model:

$$\ln(1 - F) = -k_f d \cdot t \ln(1 - F) = -k_f d \cdot t \text{ (Taffarelet et al., 2009)}$$

Determination of mopping ability of crude oil and its lower fractions displaced on water onto activated corncob carbon/synthetic sorbent

1 dm³ of water was poured into a 2 dm³ beaker, 0.2 dm³ of sorbate was added to the water. Five grams of activated corncob carbon/synthetic sorbent was weighed and added into the sorbate displaced on water and left for 80 min. It was observed during the experiment that activated corncob carbon/synthetic sorbent remained in the organic layer (sorbate). At the end of contact time, the sorbent was carefully separated from the sorbate displaced on water by passing it through filter paper fitted onto a glass funnel inserted into another 2 dm³ beaker. Small amounts of sorbate which formed the boundary layer between water and the sorbate were not separated from water during the filtration, because oil will be lost. The sorbate was carefully removed using syringe and added to the filtrate (sorbate) in the beaker. The volume and weight of separated water from sorbate was determined.

Results and Discussion

Characterization of sorbents

Result of the proximate analysis of activated corncob carbon is presented in Table 1. The table shows that activated corncob carbon has low ash content (15.10 %). Low ash content of activated corncob carbon makes it suitable for use in removal of oil from an aqueous medium, as ash content can lead to increase hydrophilicity.

Table 1 shows the result of the surface chemistry of activated corncob carbon having 0.62% total acidity (0.25% carboxyl, 0.15% lactonic, 0.22% phenol), which indicates that the surface of activated corncob carbon is mainly acidic. This result is consistent with previous results of Ketchaet *al.* (2012) and confirms the report of Sheikha (2010) who reported that chemically activated carbons are characterized by domination of surface acidic groups.

The result of porosity (%) and surface area of activated corncob carbon (0.93%) and synthetic sorbent (0.97 %) are presented in Table 2. The result shows that both sorbents have high porosity. However, the surface area of standard (1633 m² g) is larger than that of activated corncob carbon (784 m² g).

Table 1: Proximate analysis (%), surface acidity and surface basicity (Meq/g) of activated corncob carbon

Ash content	Moisture content	Volatile content	Fixed carbon	Carboxyl	Lactonic	Phenolic	Total acidic	Total basicity
15.10	11.05	28.36	45.49	0.25	0.15	0.22	0.62	0.10

Table 2: % Porosity and surface area of activated corncob carbon and synthetic sorbent

Sample	Apparent density (g/cm ³)	Bulk density (g/cm ³)	Porosity (%)	S _{BET} (m ² /g)
Activated corncob carbon	2.94	0.18	0.93	784
Synthetic sorbent	3.95	0.11	0.97	1633

Equilibrium adsorption capacity (q_e) of crude oil, diesel, kerosine and petrol by activated corncob carbon and synthetic sorbent are presented in tables 3 - 10. The results show that the q_e of crude oil, diesel, kerosine and petrol by activated corncob are 4.15 g/g at 80 min (36% of crude oil sorbed by standard), 3.26 g/g at 100 min (31 % of diesel sorbed by standard), 2.66 g/g at 80 min (32 % of kerosinesorbed by standard) and 2.40 g/g at 60 min (38 % of petrol sorbed by standard), respectively; while, the q_e of these oils onto the synthetic sorbent are 11.50 g/g at 40 min (crude oil), 10.38 g/g at 40 min (diesel), 8.20 g/g at 40 min (kerosine) and 6.30 g/g at 40 min (petrol). These results revealed that activated corncob carbon has lesser oil sorption capacity than the synthetic sorbent. Many factors may have contributed to the lesser oil sorption capacity of activated corncob carbon compared with that of the synthetic sorbent. Such factors include percentage fixed carbon, surface chemistry and surface area. These results are presented in Tables 1 and 2. The equilibrium adsorption capacity (q_e) of activated corncob carbon seems to be directly related with the percentage fixed carbon; the oils are predominantly hydrocarbons, therefore, they would be more attracted to the non-polar active carbon site than to the polar surface functional groups of activated corncob carbon which are polar in nature.

FTIR spectrum of synthetic sorbent is shown on Fig. 1, the prominent peaks are 829.42 cm⁻¹ (s) C-H of alkene, 983.73 cm⁻¹ (s) C-H of alkene, 1159.26 cm⁻¹ (s) C-C of alkane, 1369.50cm⁻¹ (s) C-H of alkane , 1453.41 cm⁻¹(s) C-H of alkane, 2925.15 cm⁻¹(s) C-H of alkane. This suggests that the synthetic sorbent mat is a polyhydrocarbon; therefore, the oils would be attracted to it. Nitrogen adsorption isotherm of activated corncob carbon at 77K is shown in Fig. 2, based on IUPAC classification the shape of this isotherm indicates type I isotherm.

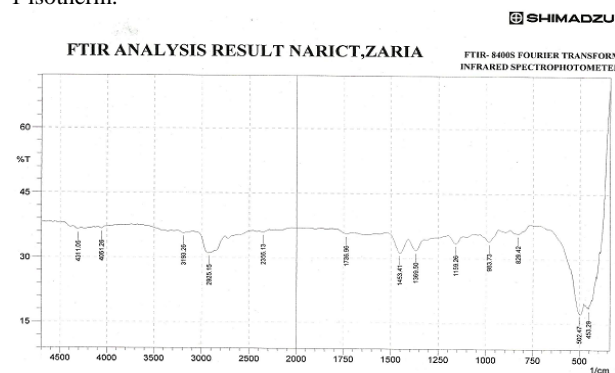


Fig. 1: FTIR spectrum of synthetic sorbent

Type 1 isotherm is produced by microporous materials. This indicates that activated corncob carbon is microporous. The nitrogen adsorption isotherm of synthetic sorbent at 77K is shown in Fig. 3, based on IUPAC classification, the shape of the isotherm and presence of hysteresis indicate a type IV isotherm ascribed to the existence of a large fraction of mesoporosity. This indicates that the synthetic sorbent is

mesoporous. Mesoporous structures have higher pore volumes and diameters. The mesoporous nature of the synthetic sorbent contributed to its higher oil uptake. Furthermore, the standard has higher surface area (1633 m² g) than activated corncob carbon (784 m² g), the specific surface area will provide a larger oil contacting area leading to more oil sorption by the standard.

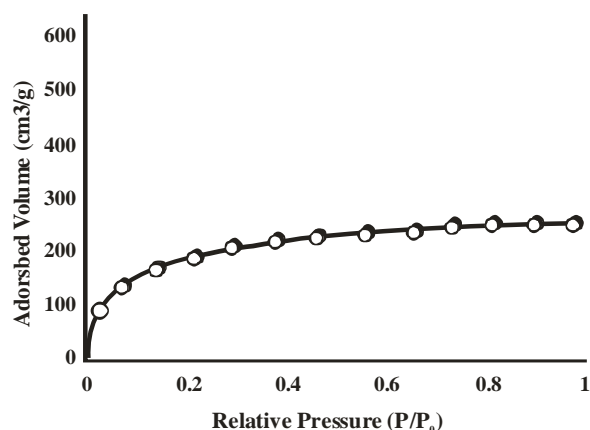


Fig. 2: Nitrogen adsorption isotherm of activated corncob carbon at 77K

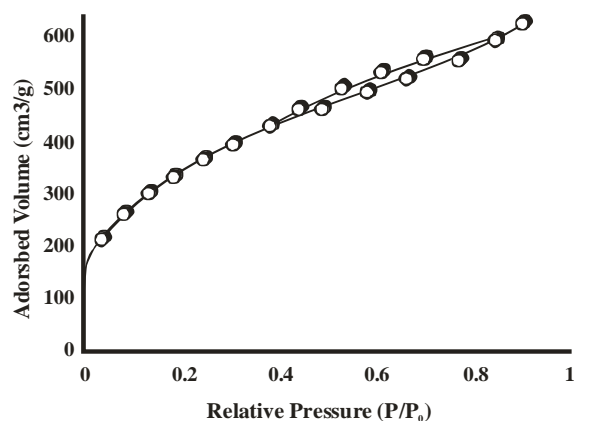


Fig. 3: Nitrogen adsorption isotherm of synthetic sorbent at 77K

Tables 3 – 10 shows that as sorption time increased, sorption capacity also increased until equilibrium was attained in activated corncob carbon, while this was not the case for the standard. This can be attributed to the microporous nature of activated corncob carbon and mesoporous nature of the standard. Microporous materials have small pore volumes and diameters hence can absorb and store small molecules, this makes sorption gradual (Lim *et al*, 2015). The presence of the mesopores allows a fast sorption and in a very short time equilibrium is reached.

Table 3: Amount of crude oil sorbed onto activated corncob carbon, recovered from activated corncob carbon and retained by activated corncob carbon

Amount of crude oil sorbed per unit mass (q) (g/g)	Amount of crude oil recovered per unit mass (g/g)	Amount of crude oil retained per unit mass (g/g)	Contact time (Min)
3.75±0.23	1.90 ±1. 01	1.85	10
3.80 ±0.59	2.00 ±0.97	1.80	20
3.83 ±1.21	2.01±0.92	1.82	30
3.96 ±0.45	2.05 ±1.80	1.91	40
4.02 ±0.67	2.06 ±1.05	1.96	50
4.14 ±0.91	2.07 ±0.78	2.07	60
4.13 ± 0.65	2.07 ±0.98	2.06	70
4.15±0.61	2.07±0.90	2.08	80
4.12±0.91	2.06±0.76	2.06	90
4.12±0.97	2.06±0.52	2.06	100

Table 4: Amount of diesel sorbed onto activated corncob carbon, recovered from activated corncob carbon and retained by activated corncob carbon

Amount of diesel sorbed per unit mass (g) (g/g)	Amount of diesel recovered per unit mass (g/g)	Amount of diesel retained per unit mass (g/g)	Contact time (Min)
2.83 ± 0.78	1.22 ±0. 01	1.61	10
2.90 ± 0.66	1.25 ±0.82	1.65	20
3.01 ± 0.34	1.27±0.54	1.74	30
3.07 ± 0.32	1.31 ±1.21	1.76	40
3.20 ± 0.90	1.34 ±0.95	1.86	50
3.21 ± 0.78	1.34 ±0.81	1.87	60
3.27 ± 0.74	1.36 ±0.60	1.91	70
3.27± 0.65	1.36±0.53	1.91	80
3.25 ± 0. 92	1.35±0.42	1.90	90
3.26 ± 1.06	1.36±0.63	1.90	100

Table 5: Amount of kerosinesorbed onto activated corncob carbon, recovered from activated corncob carbon and retained by activated corncob carbon

Amount of kerosinesorbed per unit mass (g) (g/g)	Amount of kerosine recovered per unit mass (g/g)	Amount of kerosine retained per unit mass(g/g)	Contact time (Min)
2.41 ±1.21	1.20 ±0.98	1.21	10
2.53 ±0.87	1.25 ±0.54	1.28	20
2.55 ±0.68	1.25±1.10	1.30	30
2.61 ±1.80	1.27 ±0.43	1.34	40
2.65 ±0.81	1.27 ±0.72	1.38	50
2.66 ±0.91	1.28 ±1.11	1.38	60
2.65 ± 1.21	1.27 ±0.93	1.38	70
2.66±0.72	1.28±1.30	1.38	80
2.64 ±0. 85	1.27±0.78	1.37	90
2.64±0.90	1.27±0.63	1.37	100

Table 6: Amount of petrol sorbed onto activated corncob carbon, recovered from activated corncob carbon and retained by activated corncob carbon

Amount of petrol sorbed per unit mass (g) (g/g)	Amount of petrol recovered per unit mass (g/g)	Amount of petrol retained per unit mass(g/g)	Contact time (Min)
2.30 ± 0.21	1.00 ±0.09	1.30	10
2.34± 0.11	1.02 ±0.64	1.32	20
2.37 ± 0.72	1.06±0.51	1.31	30
2.40 ± 1.80	1.08 ±0.52	1.32	40
2.40 ± 1.09	1.07 ±0.97	1.33	50
2.40 ± 1.00	1.08 ±0.31	1.32	60
2.39 ± 0.21	1.07 ±0.33	1.32	70
2.40± 0.41	1.08±0.70	1.32	80
2.38 ± 0. 53	1.07±0.61	1.31	90
2.40 ± 0.18	1.08±0.87	1.32	100

Table 7: Amount of crude oil sorbed onto synthetic sorbent, recovered from synthetic sorbent and retained by synthetic sorbent

Amount of crude oil sorbed per unit mass (g) (g/g)	Amount of crude oil recovered per unit mass (g/g)	Amount of crude oil retained per unit mass (g/g)	Contact time (Min)
11.40 ±0.50	9.50 ±0. 69	1.90	10
11.50 ±0.65	9.60 ±0.55	1.90	20
11.50 ±0.61	9.65±0.98	1.85	30
11.50 ±0.23	9.68 ±0.46	1.82	40
11.52 ±0.11	9.72±0.33	1.80	50
11.50 ±0.27	9.70 ±0.39	1.80	60
11.50 ±0.78	9.70 ±1.04	1.80	70
11.51 ±0.30	9.70±0.72	1.81	80
11.45 ±0.42	9.60±0.94	1.85	90
11.44 ±0.30	9.60±0.87	1.84	100

Table 8: Amount of diesel sorbed onto synthetic sorbent, recovered from synthetic sorbent and retained by synthetic sorbent

Amount of diesel sorbed per unit mass (g) (g/g)	Amount of diesel recovered per unit mass (g/g)	Amount of diesel retained per unit mass(g/g)	Contact time (Min)
10.35 ±1.00	8.72 ±0. 57	1.63	10
10.38 ±0.43	8.60 ±0.48	1.78	20
10.37 ±0.90	8.47±0.83	1.90	30
10.38 ±0.71	8.48 ±0.74	1.90	40
10.38 ±0.56	8.44 ±0.85	1.94	50
10.38 ±0.87	8.43 ±0.71	1.95	60
10.37 ±0.94	8.43 ±0.92	1.94	70
10.36 ±0.66	8.40±0.81	1.96	80
10.38 ±0.69	8.44±0.60	1.94	90
10.35 ±0.87	8.40±0.74	1.95	100

Table 9: Amount of kerosinesorbed onto synthetic sorbent, recovered from synthetic sorbent and retained by synthetic sorbent

Amount of kerosine adsorbed per unit mass (g) (g/g)	Amount of kerosine recovered per unit mass (g/g)	Amount of kerosine retained per unit mass(g/g)	Contact time (Min)
8.18 ±0.83	6.28 ±0. 11	1.90	10
8.20 ±1.12	6.40 ±0.75	1.80	20
8.20 ±0.67	6.50±0.47	1.70	30
8.20 ±0.98	6.50 ±0.33	1.70	40
8.20 ±0.99	6.50 ±1.03	1.70	50
8.20 ±1.00	6.50 ±0.92	1.70	60
8.20 ±0.65	6.60 ±0.12	1.60	70
8.22 ±0.78	6.50±0.10	1.72	80
8.20 ±0.94	6.60±0.51	1.60	90
8.20 ±0.34	6.50±0.46	1.70	100

Oil recovery and retention characteristics

The quantity of oils recovered from and retained by activated corncob carbon and synthetic sorbent are presented in Tables 3-10. 2.07 g/g of crude oil, 1.36 g/g of diesel, 1.28 g/g of kerosine and 1.08 g/g of petrol were recovered from activated corncob carbon, while, 9.68 g/g of crude oil, 8.48 g/g of diesel, 6.50 g/g of kerosine and 4.56 g/g of petrol were recovered from the standard. 2.08 g/g of crude oil (50 % of absorbed crude oil), 1.90 g/g of diesel (58 % of absorbed diesel), 1.38 g/g of kerosine (52 % of absorbed kerosine) and 1.32 g/g of petrol (55 % of absorbed petrol) were retained by activated corncob carbon, while, the standard retained 1.80 g/g of crude oil (16 % of absorbed crude oil), 1.96 g/g of diesel (19 % of absorbed diesel), 1.60 g/g of kerosine (20 % of absorbed kerosine) and 1.74 g/g (28 % of absorbed petrol). The high volume of oil recovery and lesser oil retention by the standard can be attributed to its mesoporous nature which enables more sorbates diffuse into the pores and effuse easily.

The high retention of the sorbates by activated corncob carbon proves that it is suitable for removal of the sorbates; since one of the features of a good sorbent is high degree of oil retention (Hoskin, 2006). Activated corncob carbon is more suitable when oil recovery is not required. Tables 3-10 shows that q_e of both sorbents increase with increase in chain length and viscosity of sorbates.

Table 10: Amount of petrol sorbed onto synthetic sorbent, recovered from synthetic sorbent and retained by synthetic sorbent

Amount of petrol sorbed per unit mass (q) (g/g)	Amount of petrol recovered per unit mass (g/g)	Amount of petrol retained per unit mass (g/g)	Contact time (Min)
6.28 ± 0.23	4.57 ± 0.30	1.71	10
6.30 ± 0.81	4.56 ± 0.62	1.74	20
6.30 ± 0.44	4.56 ± 0.67	1.74	30
6.31 ± 0.42	4.56 ± 0.98	1.75	40
6.30 ± 0.89	4.56 ± 0.40	1.74	50
6.30 ± 0.80	4.56 ± 0.41	1.74	60
6.30 ± 0.41	4.56 ± 0.32	1.74	70
6.30 ± 0.90	4.56 ± 0.64	1.74	80
6.28 ± 0.77	4.54 ± 0.21	1.74	90
6.30 ± 0.79	4.56 ± 0.44	1.74	100

Table 11: Parameters of Langmuir isotherm for the adsorption of crude oil, diesel, kerosine and petrol onto activated corncob carbon

Isotherm	Crude oil	Diesel	Kerosine	Petrol
Langmuir (C_e/q_e versus C_e)				
$b(L g^{-1})$	1.00	1.00	1.00	1.00
$q_m (g g^{-1})$	4.35	3.33	2.70	2.50
r^2	0.999	0.999	0.999	0.999
APE (%)	-3.70	-0.90	0.14	-2.60
K_R	0.0011	0.0012	0.0012	0.0014

Table 12: Parameters of Langmuir isotherm for the adsorption of crude oil, diesel, kerosine and petrol onto synthetic sorbent

Isotherm	Crude oil	Diesel	Kerosine	Petrol
Langmuir (C_e/q_e versus C_e)				
$b(L g^{-1})$	1.00	1.00	1.00	1.00
$q_m (g g^{-1})$	11.62	10.52	8.40	6.36
r^2	0.999	0.999	0.999	0.999
APE (%)	-0.92	-1.18	-1.54	-0.09
K_R	0.0011	0.0012	0.0012	0.0015

Adsorption isotherm studies

Amongst the adsorption isotherm models used to verify the adsorption process of crude oil and its lower fractions onto activated corncob carbon and synthetic sorbent, Langmuir adsorption isotherm produced the best fit isotherm with coefficient of determination r^2 value of 0.999. This indicates monolayer adsorption of the sorbates onto the sorbents and no interaction between adsorbed molecules.

In order to check the validity of the Langmuir model the adsorbed amounts were recalculated using the equilibrium concentration values and Langmuir parameter q_m . To obtain the average percentage errors (APE) according to the equation:

$$APE (\%) = \frac{\sum_{i=1}^N |q_{e,exp} - q_{e,cal}|}{q_{e,exp}} \times 100$$

The low value of average percentage errors (APE) obtained for activated corncob carbon and synthetic sorbent (Tables 11 and 12) shows that the Langmuir model can describe the equilibrium data.

The dimensionless separation factors calculated for activated corncob carbon and synthetic sorbent are presented in Tables 11 and 12. The K_R values were less than 1 and greater than zero indicating favourable adsorption.

The calculated maximum adsorption capacity value (q_m) is; crude oil 4.35 g/g, diesel 3.33 g/g, kerosine 2.70 g/g and petrol 2.50 g/g for activated corncob carbon and that of synthetic sorbent is crude oil 11.62 g/g, diesel 10.52, kerosine 8.40 and petrol 6.36 g/g (Tables 11, 12). These values are slightly higher than the experimental equilibrium adsorption capacity value of the sorbates by activated corncob carbon and synthetic sorbent (Table 13). This further shows that Langmuir isotherm provides better fit to the experimental data.

Kinetic studies

Tables 13 and 14 show the correlation coefficients (R^2) values and the calculated equilibrium adsorption capacities ($q_{e,calc}$) of the sorption of the oils onto activate corncob carbon and synthetic sorbent. R^2 values of most of the oils were low while few were high up to 1. Although some of the R^2 values were found to be high in some cases, the calculated equilibrium adsorption capacities were by far lower than the experimental values which indicate that the sorption of crude oil and its lower fractions onto activated corncob carbon and the synthetic sorbent is not a first order reaction. Moreover, the plot of $\ln(q_e - q_t)$ versus t produced a straight line from the origin just for a limited range of contact time, this also implies that the sorption of crude oil and its lower fractions onto activated corncob carbon and the synthetic sorbent is not a first order reaction.

Table 13: Pseudo – first order kinetic model (Lagergren equation) for the sorption of crude oil and its lower fractions onto activated corncob carbon

Oil type	$q_{e,exp}$ (mg/g)	$q_{e,Calc}$ (mg/g)	$K_1(S^{-1})$	R^2
Crude oil	4150	2980.95	-0.0014	0.800
Diesel	3270	812.40	-0.0007	0.928
Kerosine	2660	403.42	-0.0008	0.894
Petrol	2400	244.69	-0.001	0.992

Table 14: Pseudo – first order kinetic model (Lagergren equation) for the sorption of crude oil and its lower fractions onto synthetic sorbent

Oil type	$q_{e,exp}$ (mg/g)	$q_{e,Calc}$ (mg/g)	$K_1(S^{-1})$	R^2
Crude oil	11500	121.51	-0.0066	0.930
Diesel	10360	735.09	-0.0009	0.865
Kerosine	8200	365.03	-0.001	1.00
Petrol	6300	221.40	-0.001	1.00

Tables 15 and 16 presents the correlation coefficients (R^2) and the calculated equilibrium adsorption capacities ($q_{e,calc}$) values of the sorption of each oil onto ACCC and synthetic sorbent, the R^2 values are 0.999 which shows the fitness of the sorption of the oils onto the sorbents into pseudo-second order kinetics. $q_{e,calc}$ of each oil is higher than the experimental values, this further indicates that the sorption process is a pseudo-second order reaction. This implies that chemisorption was involved in the adsorption process.

Table 15: Pseudo – second order kinetic model (Lagergren equation) for the sorption of crude oil and its lower fractions onto ACCC

Oil type	$q_{e,exp}$ (mg/g)	$q_{e,Calc}$ (mg/g)	$K_2(S^{-1})$	R^2
Crude oil	4150	4545.45	4.8×10^{-6}	0.999
Diesel	3270	3448.27	9.0×10^{-6}	0.999
Kerosine	2660	2720	1.4×10^{-6}	0.999
Petrol	2400	2500	1.6×10^{-6}	0.999

Table 16: Pseudo – second order kinetic model (Lagergren equation) for the sorption of crude oil and its lower fractions onto synthetic sorbent

Oil type	$q_{e, exp}$ (mg/g)	$q_{e, Calc}$ (mg/g)	$K_2(S^{-1})$	R^2
Crude oil	11500	12500	7.5×10^{-8}	0.999
Diesel	10360	10880	8.1×10^{-8}	0.999
Kerosine	8200	8333.33	1.4×10^{-7}	0.999
Petrol	6300	6666.66	2.2×10^{-7}	0.999

The intercept I and the slope k_d of intraparticle diffusion rate constant in $mg/g s^{1/2}$ were calculated from the plot of q_t as a function of $t^{1/2}$. When the intercept is large, surface sorption contributes more to the rate-determining step (Nwadiogbu, 2016). The values of the intercepts are presented in Tables 17 and 18; the values are low indicating that surface sorption is not the only rate determining step. When the plot is linear and passes through the origin intraparticle diffusion is the rate-determining step (Dawodu, 2014). Regression coefficient (R^2) of the plot is high (Tables 17 and 18) but the values of the intercepts are less than zero (non zero intercept), implying that both intraparticle diffusion mechanism and external mass transfer were parts of the rate controlling steps of the adsorption process.

Table 17: Intraparticle diffusion and liquid film diffusion for the sorption of crude oil and its lower fractions onto ACCC

Oil type	Intraparticle diffusion		Liquid film diffusion	
	K_d (meq $g^{-1}S^{1/2}$)	R^2	I	R^2
Crude oil	9.76	0.934	-3800	0.874
Diesel	14.01	0.968	-2850	0.939
Kerosine	7.40	0.965	-2450	0.793
Petrol	3.70	1.00	-2360	0.996

Table 18: Intraparticle diffusion and liquid film diffusion for the sorption of crude oil and its lower fractions onto synthetic sorbent

Oil type	Intraparticle diffusion		Liquid film diffusion	
	K_d (meq $g^{-1}S^{1/2}$)	R^2	I	R^2
Crude oil	58.82	0.898	-1143	#N/A
Diesel	9.06	0.888	-10100	0.752
Kerosine	9.85	1.00	-8100	1.00
Petrol	3.94	1.00	-6250	#N/A

Liquid film diffusion kinetic model applied to determine the sorption mechanism of the sorbates onto the sorbents is presented in Tables 17 and 18. Low regression coefficients (R^2) were obtained. Intraparticle diffusion model for both sorbents produced a better R^2 than the liquid film diffusion model, indicating that intraparticle diffusion (penetration into the pores of the sorbent) contributed more than external mass transfer (surface sorption).

The amount of water sorbed together with each sorbate onto activated corncob carbon and synthetic sorbent are 3 ml (0.70 g) for ACCC and 6 ml (1.2 g) for the standard. These amounts are minimal for each of the sorbent, indicating that activated corncob carbon can be employed in oil spill mop in an aquatic environment.

Conclusion

Activated carbon prepared from corncob performed less than the conventional synthetic sorbent in terms of oil removal; activated carbon from corncob has lesser oil sorption capacity than the conventional synthetic sorbent. The difference in performance can be attributed to difference in surface area, surface chemistry of both sorbent and functional group present in each sorbent. The quantity of oil sorbed on the

sorbents depends on contact time, hydrocarbon chain length and viscosity of sorbates. Activated carbon from corncob has high oil retention which is a feature of a good sorbent. The standard (conventional synthetic sorbent) has high oil recoverability which makes the standard better in terms of oil recovery. Though the standard has higher oil sorption capacity than activated carbon from corncob, activated carbon from corncob has good oil sorption capacity and high oil retention which makes it viable for use in oil spill cleanup exercise. Activated carbon from corncob can be applied in oil spill cleanup on land and aquatic environment. The adsorption process of crude oil and its lower fractions onto activated carbon from corncob and the standard follows the Langmuir model, sorption of the oils; crude oil, diesel, kerosine and petrol onto activated carbon from corncob and the standard occur by surface reactions and intraparticle diffusion mechanism.

Conflict of Interest

Authors declare that there is no conflict of interest.

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