

Production of Activated Carbon from Corncobs and its Utilization in Crude Oil Spillage Clean Up

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ABSTRACT

Lignocellulosic materials from agricultural by-products were used to develop high surface area activated carbons by chemical activation using KOH pellets. Surface and textural characterizations of the activated carbon were respectively investigated using micrometrics and BET technique at low temperature (77K) of nitrogen. It was observed that the optimum activation temperature for the production of activated carbon from corncobs was 700⁰C and the temperature had no appreciable effect on both the apparent and solid densities of the activated carbons. Minor crude oil spillage was simulated and the adsorptive capacity of the adsorbent on crude oil removal was investigated at ambient conditions. Purity indices of the adsorbate were investigated before and after the adsorption experiment. Maximum adsorption of 17.2 % was observed with the corncobs activated with KOH at 700⁰C against 24.6% for the commercial adsorbent.

Keywords: Activated carbon, carbonization, activation, corncob, spillage clean up, Nigeria.

1. INTRODUCTION

Nigeria is abundantly blessed with crude oil and ranked the sixth in the world in terms of production with a daily production quota of 2.4 million barrels (OPEC, 2005). Due to exploration, the volume of activity both on land and water resulting directly from the transportation and processing of this crude oil increases the potential for its spillage. It has been estimated that annual average volumetric spill is 14 million gallons of oil from more than 10,000 accidental spills (Egwaikhide, et al., 2007) out of which less than 4% of the total amount discharge into the sea is the result of tanker accidents while 22.5% is from operational discharges (Allowary and Ayres, 1993). Other minor crude oil spillage sources include leakages of pipelines and flow stations, overpressure failure, overflow of process equipment components, failures of hose and along pump discharge manifolds due to negligence by operators and act of sabotage to flow line (Wardley-Smith, 1979; Egwaikhide, et al., 2007). The environmental impacts of these spillages in the Niger Delta region, the centre of crude oil production in Nigeria, are ignored due to the country's haste to develop the oil industry (Alamu et al., 2007).

The serious adverse effects of crude oil spills on economy, health and environment are much and regulatory measures put in place by government and relevant authorities in handling of crude oil only minimize the chances of these spills but do not eliminate it. As such the Nigerian petroleum industry expends so much resource on importing crude oil spill adsorbents for combating and

cleaning of these minor spills (Odozi et al., 1986). Estimated costs of spill clean up stand at 2 billion dollars per annum (Egwaikhide, et al., 2007).

Adsorbents with large surface area and affinity to organic compounds could be developed from cost effective and readily available agricultural by-product such as rice husk, corncobs, coconut shell and oil palm shell (Tseng, 2007; Gua and Lua, 2003; Mahvi et al., 2004; Tsai et al., 2001). This paper reports on the use of corncobs in the production of adsorbents for use in crude oil spillage.

2. MATERIALS AND METHODS

2.1 Materials Sourcing, Preparation and Characterization

The corn cob samples were obtained from the Ahmadu Bello University (ABU) Farms in Shika, Zaria, Nigeria. The raw materials were washed with water to remove dirt and then sun dried for twenty-four (24) hours, after which they were crushed in a local pestle and mortar in order to be processed in laboratory mill.

The raw precursors were characterized by carrying out a thermo-gravimetric analysis (TGA) using a Perkin Elmer SDT-2960 to monitor the weight loss profile and establish the temperature range where major portion of the volatile matter would be devolatilized (Banerjee and Destidar, 2005), hence determining the appropriate carbonizing temperature. Alumina pan of the machine (SDT 2960) was selected. The sample was placed on the pan and heated under nitrogen flowing at 2.5 ml/min. A heating rate of 20⁰C/min was maintained to a final temperature of 1000⁰C from room temperature (30⁰C).

2.2 Production of Activated Carbon

Based on the TGA profile obtained, the precursors were *carbonized* in a carbonization rig (Carbolite HTR 11/75) for two (2) hours at 20⁰C/minute to a final temperature of 300⁰C and the weight loss of sample with temperature profile recorded. The carbonized samples were then physically *impregnated* with KOH pellets at ratio 1:3 precursors to activating agent (Lillo-Rodenas et al., 2003) and using distilled water, the mixture was made into a homogeneous moist sticky paste which was immediately charged into a furnace and heated slowly from room temperature to 110⁰C for twenty four (24) hours.

The dried carbonized samples were then washed with distilled water and *activated* in the carbonization rig under nitrogen flowing at 20⁰C/min to a final temperature of 600⁰C, 700⁰C, 800⁰C and 900⁰C separately for two (2) hours. Activated carbon produced was washed with distilled water and dried in an oven at 110⁰C overnight.

2.3 Characterization of Activated Carbon

Surface area and pore size distribution of the produced activated carbon were determined by the application of Brunauer, Emmett and Teller (BET) technique in an automated AUTOSORB-1C analyzer system that utilizes AS1Win software (version 1.5). Samples were out-gassed under flow of helium before the physical adsorption using nitrogen at 77.4K. Micropore volumes were determined by employing the Dubunin-Raduskhevich model. Apparent and solid densities of the

adsorbent were determined employing the procedures described in Ahmedna et al (1997). Porosity of the adsorbents was computed using the following relationship (Akinyemi and Taiwo, 2004):

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

2.4 Adsorbent Tablets

The activated carbons produced were in powdered form as such in order to make them into tablet forms; circular ring of a hydraulic press was used. The adsorbents were mixed with water (just enough to cause homogeneous mixing) and manually compacted into the ring. The adsorbent was then gently pushed out and dried in an oven at 60⁰C overnight.

2.5 Crude Oil Adsorption

A minor crude oil spill was simulated by pouring 2ml of crude oil into a 250ml beaker containing 200ml of tap water having a pH of 8.2. In order to determine the equilibrium contact time, adsorbent ACC700 which had the highest surface area was contacted with the crude oil-water system for sixty (60) minutes and amount adsorbed computed using the method described in (Cheremisinoff and Ellerbush, 1975).

The established equilibrium time was used as a basis to contact the same system with adsorbent tablet samples produced. The amount of crude oil adsorbed was determined by weight difference employing the method described in (Jimoh and Mohammed, 2005).

2.6 Characterization of Adsorbate

The physical properties of the crude oil before and after adsorption were determined, using standard analytical methods, to ascertain whether a chemical transformation had taken place during the process. The parameters analyzed were density, specific and API gravities, viscosity and refractive index.

3. RESULTS AND DISCUSSION

3.1 Precursor Characterization

Table 1 presents the proximate and elemental compositional analysis of the raw corncobs (CC) and their ashes (CCA). Carbon content of a precursor is one of the most important indices for choosing a precursor for activated carbon production (Shaw and Avery, 1993) and as can be seen from the Table1, the local variety of corncobs was found to have high potentials for activated carbon production due to its high carbohydrate (87.27%) and low ash (2.87%) content. However, the inorganic elemental analysis of the precursors showed metallic oxides (K, Na and Al) that are stable and have no tendency for changing the adsorption process from physical to chemical at room temperature.

Figure 1 shows the TGA profile of the raw corncobs between 0 - 1000⁰C temperature ranges. It can be seen from the figure that there was an initial weight loss at temperatures below 200⁰C, which could be from evaporation of the moisture originally contained in the precursor. Weight loss occurring above this temperature is considered to be due to vaporization of volatile organic compounds (as reported by Kim et al., 2001). The major portion of the volatile matter of the organic precursors was volatilized at a temperature range of 270-400⁰C. That was the basis for carbonizing at 300⁰C in order to trap more organic volatiles and subsequent KOH activation.

3.2 Adsorbent Characterization

Table 2 presents the characteristic properties of the produced activated carbons from corncobs at activating temperatures of 600⁰C to 900⁰C (ACC600, ACC700, ACC800 and ACC900). From the table, it can be observed that a moderate temperature of 700⁰C favored the development of larger surface area with the highest micropore volume as observed in corncob activated at 700⁰C (ACC700) compared to those activated at 600, 800 and 900⁰C. Adsorbent ACC700 had the highest surface area and porosity of 1084 m²/g and 97.34% respectively compared to ACC600, ACC800 and ACC900. It can therefore be inferred that increase in activation temperature above 700⁰C leads to decrease in the surface area and porosity of the corncob activated carbon. However, temperature had no definite effect on both the apparent and solid densities of the activated carbons.

Table 1. Proximate and elemental compositional analysis of the raw corncobs and its ashes

Sample ID	Proximate Analysis, %wt.					
	Carbohydrate	Protein	Crude fiber	Ash	Moisture	Lipid
CC	87.27	2.69	-	2.87	4.95	2.39
	Elemental Analysis					
	SiO ₂	K	Na	Al	LOI*	
CC	2.41	1.13	0.76	0.70	96.37	
CCA	28.76	28.17	6.23	1.57	23.98	

*LOI-Loss on Ignition

Table 2. Properties of the produced corncob activated carbons (ACC)

Sample ID	Surface Area, m ² /g	Micropore width, Å	Micropore volume, cm ³ /g	Density, g/cm ³		Porosity, %
				Apparent	Solid	
ACC600*	598.4	8.87	6.21	3.9206	0.1009	97.43
ACC700*	1084	10.61	15.69	3.9206	0.1031	97.34
ACC800*	674.1	13.46	13.46	2.9931	0.0918	96.93
ACC900*	592.4	16.74	11.54	4.1769	0.1415	96.61

*ACC600-900 means activated carbons produced from corncobs employing the activation temperatures of 600, 700, 800 and 900⁰C respectively

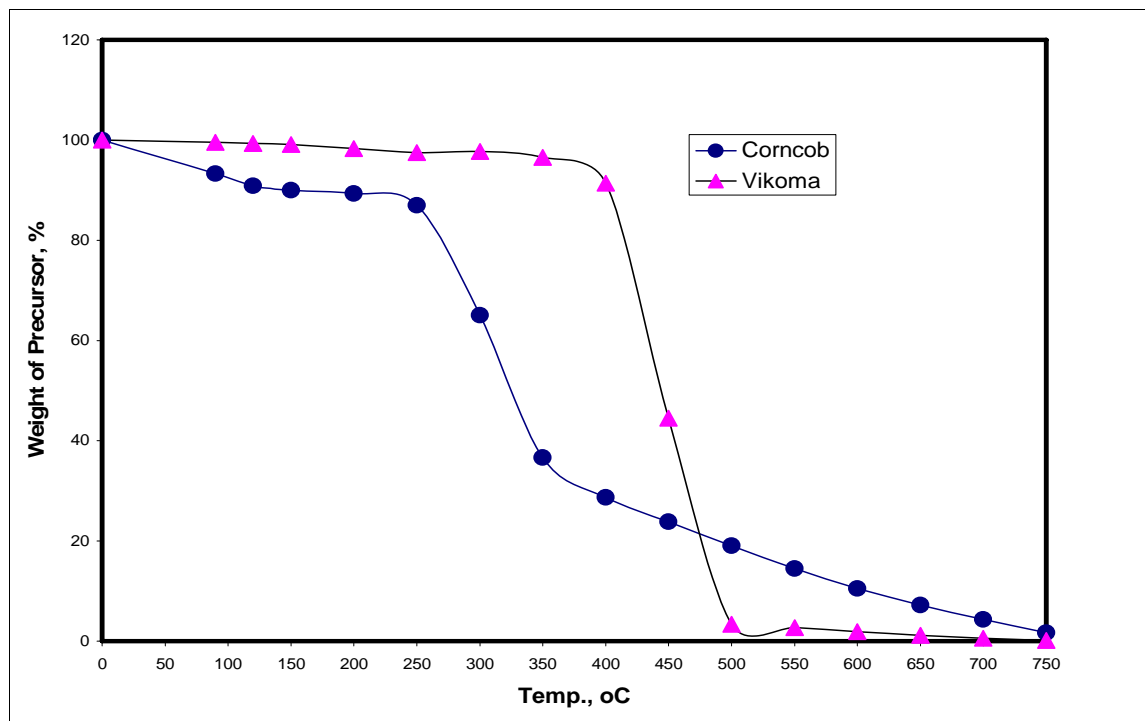


Figure 1. TGA profile of raw corncob and Vikoma

3.3 Adsorbent Tablets

Figure 2 shows a pictorial view of adsorbent tablet samples produced. Each tablet is circular in shape, having an approximate diameter and thickness of 5.0 cm and 1.5 cm respectively. It should be noted that some of the tablets formed got cracked after desorption of the adsorbed crude oil samples, hence tablets molding needs to be improved upon.



Figure 2. Pictorial view of crude oil adsorbent tablets

3.4 Crude Oil-Adsorbent Contact

Figure 3 presents the equilibrium contact time between the crude oil and the adsorbent. In order to establish the equilibrium contact time, the adsorbent ACC700 was used because of its high surface area. The crude oil adsorption was carried out within the time limit of 60 minutes. There was an initial rapid crude oil uptake between 0 – 20 minutes as can be observed in Figure 3. From 20-30minutes, there was a slight rise in the slope and after 30minutes contact only infinitesimal change was observed. It was therefore inferred that the equilibrium contact time was 30 minutes.

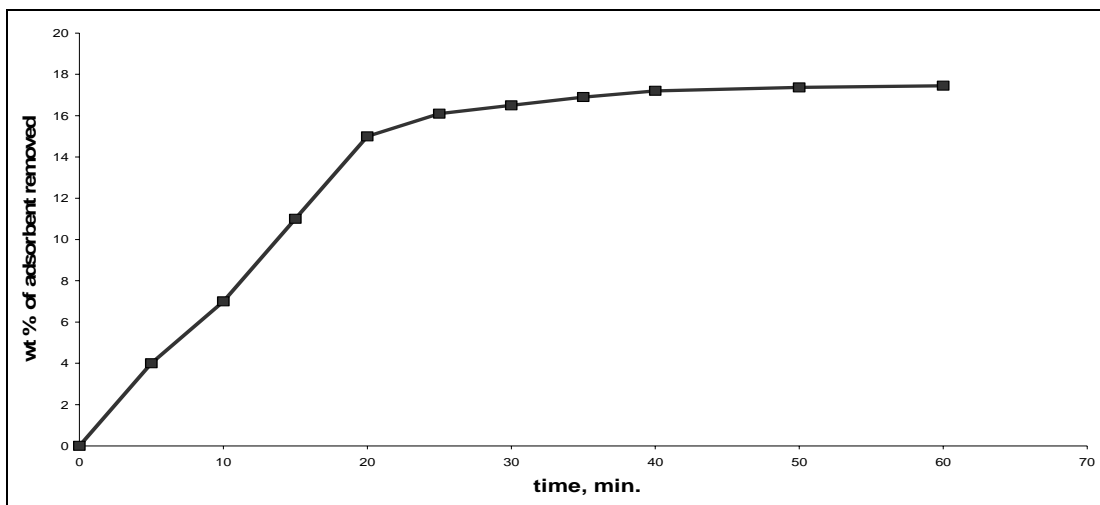


Figure 3. Determination of equilibrium adsorption time for crude oil

The absorptive capacities of the various developed adsorbents are illustrated in Table 3. From the table it can be observed that, the corncob activated at 700⁰C gave the highest adsorptive capacity by adsorbing 17.2%wt of the crude oil sample. The highest adsorptive capacity of this sample could be associated with its high surface area compared to other adsorbents (ACC600, ACC800 and ACC900). From this result it can be established that, the optimum temperature for the activation of this variety of corncobs employing KOH as the activating agent was 700⁰C. The table also presents the adsorptive capacity of a commercial crude oil spill adsorbent (VICOMA) employed by the Kaduna Refinery, Nigeria. The adsorptive capacity of this product is higher than that of produced adsorbent from agricultural by-products, corncobs. A minimum literature value of 2 nm for the smallest crude oil molecule size (Wu and Praustnitz, 1998; Storm et al., 1991; Sheu et al., 1992; Carnaham et al., 1993) is larger than the largest micropore width for all the adsorbents. Adsorption was therefore only limited to mesopores and macropores of the adsorbents. This limitation is only on a small scale as mesopores and macropore volume of the adsorbents constitute 80-94% of the total adsorbents volume as can be observed in Table 2.

3.5 Adsorbate Characterization

The physical properties of the fresh (before adsorption) and the recovered (adsorbed) crude oil samples are indicated in Table 4. The result indicates that the adsorption process between crude

oil and the adsorbents is purely physical adsorption as the indices of purity for the crude oil remained virtually the same for the adsorbed and desorbed samples tallying with previous related works (Odozi et al., 1986; Harwood et al., 1989).

Table 3. Crude oil adsorption data

Adsorbent	wt. of adsorbent, g	Amount adsorbed, g	Adsorptive capacity, % wt.
ACC600	4.8	0.6096	12.7
ACC700	6.1	1.0492	17.2
ACC800	4.7	0.7238	15.4
ACC900	3.9	0.4602	11.8
VICOMA*	3.8	0.9348	24.6

*Commercial crude oil spillage clean up adsorbent used at the Kaduna refinery (Nigeria)

Table 4. Properties of a fresh and desorbed crude oil sample

Parameter @ room temp.	Fresh crude oil	Desorbed crude oil
Density, g/cm ³	0.9493	0.9411
API gravity	10.53	10.62
Viscosity, (cP)	1.333	1.356
Refractive Index	1.4972	1.506

4. CONCLUSION

Activated carbon adsorbents from corncobs were produced at various conditions and successfully employed in the removal of crude oil from water surface. It can be concluded that the optimum activation temperature was 700⁰C and the temperature had no definite effect on both the apparent and solid densities of the corncob activated carbons. The result of the analysis indicates the dependence of the adsorption of the crude oil on the surface textural properties of the adsorbents. Values of purity indices of the crude oil showed that the process is a physical adsorption. Even though the adsorptive capacity of the best produced adsorbent sample (ACC700) was lower than that of a commercial adsorbent (VICOMA) by about 30%, utilization of agricultural by-products to clean minor crude oil spillage is a viable approach.

It is however, recommended that future work involving the comparative economic analysis on the use of activated corncob with the commercial spillage adsorbents should be carried out. Testing on the applicability of other crop residues and analysis of the volatile organic compounds should be carried out.

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