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SORPTION POTENTIALS OF GROUNDNUT HUSK PARTICLES FOR OIL SPILL CLEANUP

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Abstract

In this study, groundnut husk particles were used to remove Escravos crude oil from seawater surface in order to assess their sorption potentials. The investigations were carried out using five different particle size ranges (4000-1000, 1000-500, 500-105, 105-53 and <53 µm) of the husk on three different oil layer thicknesses (3, 4.5 and 6 mm) over water. The particles sorbed crude oil to different degrees and at different rates but no uptake of water by the husk particles were observed. The initial sorption rates of the sorbent in the first ten minutes were the highest with the three oil layer thicknesses investigated. The maximum oil sorption capacity recorded was 9.8442g oil/g sorbent at forty minutes by particle C (500-105 µm) with 3 mm oil layer. This sorption performance compares fairly well with extant literature results for a commercial sorbent and other raw lignocellulosic plant wastes such as corn husk and kapok. The fairly good oil sorption results recorded by the particles, with no water sorption, under a dynamic experimental condition used in this work is indicative of good oleophilic property and potentials as a biosorbent. The empirical oil sorption kinetic model of raw groundnut husk particles was of inverse (decaying) exponential form which indicates a diffusion sorption mechanism.

Keywords: *Particle sizes, oil pollution, Escravos oil, sorption kinetics, biosorbent*

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1 INTRODUCTION

The spill of crude oil on fresh and marine water surfaces have always been accompanied by much devastation to the ecosystem, human health and marine/freshwater inhabitants (Rene *et al.*, 1993; Saidu, 2011; Ifelebuegu and Johnson, 2017; Agida *et al.*, 2017). Many instances of this environmental and ecological nuisance have been recorded in Brittany (France), Niger Delta of Nigeria, Arabian Gulf in Kuwait as well as Alaska and Gulf of Mexico in USA, among other places (Fiest *et al*., 1981, International Tanker Owners Pollution Federation, 2008, Saidu and Olawale, 2010, Saidu, 2011, de la Huz *et al.*, 2011, www.scientificamerican.com, 2015, Olawale *et al.*, 2020a). Oil spills are usually caused by accidents, leakages, pressure failure, and overflow of process equipment's components or sabotage to flow lines (Egwaikhide, *et al*., 2007; Agida *et al*., 2017).

Sorption method is used to remove spilled crude oil from water surfaces in areas which cannot be accessed by booms or skimmers, even as booms and skimmers do have incorporated sorbents. Other methods used in oil spill removal from water surfaces are chemical treatment, bioremediation and burning (Olawale *et al*., 2020a; Choi and Cloud, 1992). Synthetic sorbents, natural and modified organic materials and, inorganic materials are the broad types of sorbents used in oil spill cleanup operation by sorption method (Deschamps, *et al*., 2003). Sorbents derived from natural organic materials have the advantages of ready availability, low cost and biodegrability over synthetic organic sorbents and natural inorganic materials. Though synthetic sorbents usually have higher sorption capacity than the other two sorbent types, there have been increased research interests in using lignocellulosic materials (which are natural organic materials) for oil spill cleanup because of their stated advantages over the other two sorbent types. Many of the lignocellulsics are plant wastes and are available in abundance in Nigeria and other tropical countries (Odedokun, 2014 and Sanni *et al*., 2017). Some of the lignocellulsics which have been studied include rice straw, cotton, kapok, pith bagasse, barley straw, aquatic plants like *Pistia stratiotes* and *Salvinia molesta,* wool, corn husk and soya bean husk among others (Teas *et al*., 2001; Radetic *et al*., 2003; Choi *et al.*, 1993; Choi,1996; Huang and Lim, 2005; Hori *et al*., 2000; Amer *et al*., 2007; Hussein *et al*., 2009; Bayat *et al*., 2004; Sun *et al.*, 2002; Zeigler *et al.*, 2016; Olawale *et al*., 2020a; Olawale *et al*., 2020b). Some of these materials like cotton, kapok, corn husk, *Pistia stratiotes* and few others have shown good sorption capacity for oil in water bodies (Zeigler *et al*., 2016; Choi *et al*., 1993; Choi, 1996; Huang and Lim, 2005; Hori *et al*., 2000; Zheng *et al*., 2015; Deschamps

et al., 2003; Olawale *et al.*, 2020a; Olawale *et al.*, 2020b; Agida *et al.*, 2017; Dagde, 2018; Doshi *et al.*, 2018; Nwokoma and Anene, 2010). Some of the reported works treated the sorption of oils as adsorption process and some others treated the process as absorption process. As it is well known, adsorption is a surface phenomenon while absorption is a phenomenon involving the deposition of the sorbate in the bulk volume of the sorbent. The work reported here treated the crude oil removal as an absorption process considering the quantity of the crude oil intended to be removed from the water surface.

The global abundance of lignocellulosic plant wastes therefore necessitates investigations of oil and water sorption characteristics of more lignocellulosic materials to attain cost effectiveness and sustainability in oil spill cleanup. Groundnut (*Arachis hypogaea*) pod is made up of the oil-bearing nut and husk or shell; the latter constitutes about 20% of the total mass (Figure 1). It is widely grown in the tropical, subtropical and warm temperate areas in Asia, Africa, Oceania, North and South America and Europe (Freeman *et al.*, 1999). Investigation of groundnut husk for crude oil sorption performance would make it possible to identify more of the lignocellulsic wastes with sorption potentials and improve understanding of their sorption mechanism.

The outcomes of previous works on groundnut husk (Olawale and Saidu, 2010; Choi *et al.*, 1993; Choi, 1996, Dagde, 2018; Doshi *et al.*, 2018; Nwokoma and Anene, 2010) indicated the need to look deeper at the sorption potentials of this and other agricultural wastes, hence this study.



Figure 1: Groundnut pod with the nut and husk

In this study, the sorption characteristics of five particle size ranges of groundnut husk on Escravos crude oil, spilled on sea water, was investigated at about 27ºC.

2 MATERIALS AND METHODS

2.1 Pretreatment of Sorbents

Groundnut husks were collected from a farm settlement in Zaria (Kaduna State) Nigeria. They were cleansed to remove particles and other foreign materials and then sun dried. The husks were then screened for wax deposition, buoyancy and toxicity to marine life. Information were obtained from literature on wax content and toxicity of the cellulosic material. The buoyancy test was carried out as described in Section 2.2.3.

The husks were subjected to size reduction using mill and were classified 4000-1000, 1000-500, 500-105, 105-53 and <53 µm using a set of sieves (TermoFisher Scietific) to obtain the following particle size ranges: 4000-1000, 1000-500, 500-105, 105-53 and <53 µm. These particles were labelled A, B, C, D and E respectively. The lignocellulosic particulates so obtained were subjected to analysis and sorption tests.

2.2 Test and Analyses of Sorbent

2.2.1 Composition and morphology of groundnut husk

The composition of groundnut husk was determined by the (ADF) method (Van Soest *et al.*, 1991). A scanning electron microscopy (SEM) of the husk was also done with a Zeiss scanning electron microscope at an acceleration voltage of 10 kV. In addition, a Fourier transforms infrared (FTIR) analysis was carried out with a Shimadzu-8400S Fourier transform infrared (FTIR) spectrophotometer in the spectral range of 4000–500 cm^{-1}.

2.2.2 Density of groundnut husk

The method described by Kopecky (1999) was used to determine the apparent and real densities of the husk using a pycnometer. The weights of glassware, soya bean husk particles and water were measured with digital weighing balance (Adam, PW 184).

2.2.3 Buoyancy test

Buoyancy of the husk was determined by filling a 250 ml beaker with sea water, obtained from the Atlantic Ocean in Lagos, to the 200 ml mark. The density of this sea water was determined as described in Section 2.2.2. The pH and temperature of the system were then taken. Thereafter, 1 g husk (in its native form) was gently placed on the water surface and the times for partial and complete immersions of the husk in the seawater were recorded.

2.3 Analyses of Crude Oil

Escravos crude collected from Kaduna Refining and Petrochemical Company (KRPC), Kaduna was weathered for 24 h inside a fume cupboard at room temperature to drive off the volatiles in the oil.

2.3.1 Density of crude oil

The density of the oil was measured using the method described by Kopecký (1999).

2.3.2 Viscosity of the crude oil

The viscosity of the crude oil was determined with a Brookfield digital viscometer (DV-E) as described by Olawale *et al.* (2020a).

2.4 Determination of Sorption Capacity

Half a litre of seawater was measured into a 1 L glass beaker which contained a cylindrical cell made of wire gauze (12cm length x 7cm diameter). Forty (40) grams of crude oil was then measured into the beaker to form a layer whose thickness was measured as 6 mm, on top of the sea water. One (1) gram groundnut husk particles (<53µm) were then evenly spread on the oil surface. The cylindrical wire gauze was suspended such that its base was located within the water layer and below it, at the bottom of the beaker, was placed a magnetic stirrer bar.

A magnetic stirring and heating device (Stuart Heat Stir SB 162) on which the beaker was placed was adjusted to obtain a gentle stirring of the oil-particle system and to maintain a uniform system temperature of 27°C. After 10 minutes, the wire gauze cell was raised to recover the soaked sorbent particles. The recovered mass was left to drain for 5 minutes and the total weight of soaked sorbent and the cell (M_T) was obtained using a digital weighing balance (Adam, PW 184). The amount of liquid sorbed by the sorbent (M_{so}) was determined as the difference between the initial sorbent and cell weight and the weight of the soaked sorbent and cell (M_T) as given in Equations 1 and 2. A known quantity of the sorbed liquid (oil/water) was recovered with the aid of 5-10 mL petroleum ether (40-60^{0}C). Petroleum ether contained in the recovered liquid was driven off over water bath at 45°C. This was done to obtain the proportion of water (if any) that was sorbed along with the crude oil. The steps described above were repeated at sorption durations of 20, 30, 40, 50 and 60 min, using sorbent particle size ranges of 4000-1000, 1000-500, 500-105 and 105-53µm, for oil layer thickness of 6 mm. The steps described for 6 mm oil thickness layer were subsequently repeated for oil layer thicknesses of 4.5 and 3 mm..

The sorption capacities for all these variables were then calculated using Equations 3 and 4, respectively. `

$$M_{so} = M_T - (M_c + M_s) \quad (1)$$

$$M_o = M_{so} - M_W \quad (2)$$

$$SC_o = \frac{Mo}{Ms} \quad (3)$$

$$SC_W = \frac{Mw}{Ms} \quad (4)$$

where SC_o and SC_w are oil sorption capacity (g oil/g sorbent) and water sorption capacity (g water/ g sorbent) respectively. M_{so} is the mass of sorbate, M_T is the mass of the soaked sorbent and cell, M_c is the mass of cell, M_s is the mass of sorbent, M_o is the mass of oil and M_w is the mass of water (based on water proportion of the recovered sorbate and M_{so})

The data obtained in the experiments were then fitted with DataFit 9.0^R software to obtain the oil sorption kinetic model of the groundnut husk particles investigated.

3.0 RESULTS AND DİSCUSSİON

3.1 Properties of Materials

3.1.1 Physicochemical property

The analysis of the dried groundnut husk showed that it contained, on average, 36.87% cellulose, 6.73% hemicelluloses, 30.92% lignin and 25.48% others. The real and apparent densities of the husk were measured to be 0.1509 and 0.0047 g/cm^3 respectively. Groundnut husks are known to be non-toxic to marine life and contain wax deposit on its surface (Saidu, 2011)

Immersion tests of the groundnut husk showed that it floated on the sea water (pH = 6.85 and density 1.0462 g/cm^3) surface at 29°C, with no immersion whatsoever, after one week. This good buoyancy property of groundnut husk would be due to its combined low density and hydrophobic nature which is attributable to its high combined cellulose and lignin content and, the fat deposit on its fibre. These buoyancy characteristics would ensure that the husk absorbs little or no water and therefore making it, considering its reported oleophilic nature (Saidu, 2011), effective for the targeted purpose of spill oil cleanup. The average density, specific gravity, dynamic and kinematic viscosities of the crude oil were determined as 0.9002 g/cm^3 (28.4 ^{0}API), 0.885, 5 cP and 6.2 cSt respectively. water.

3.1.2 SEM analysis

The scanning electron micrographs of the groundnut husk (Figure 2) shows that the surface is porous and irregular (Das *et al.*, 2019). The SEM image confirms that the husk fibre has an irregular cross-section, non-uniform surface, some impurities with apparent minute crevices, which are typical of raw natural fibres. The porous structure of groundnut husk's fibre would help in its sorption duty.

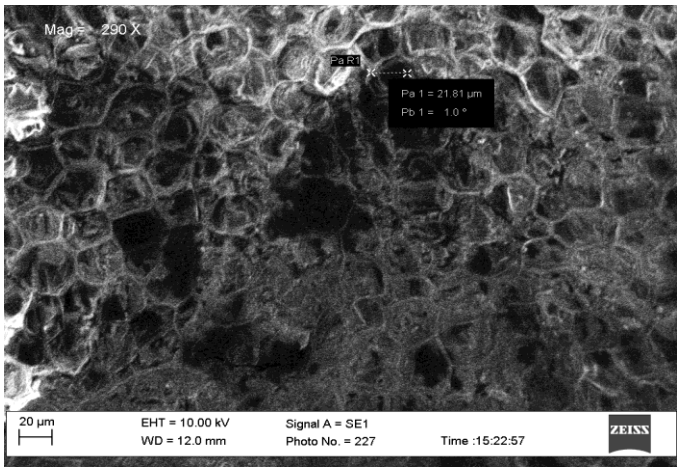

Figure 2: SEM images of groundnut husk

3.1.3 FTIR analysis

The FTIR of groundnut husk is presented in Figure 3. Some of the bands and associated functional groups are given in Table 1.

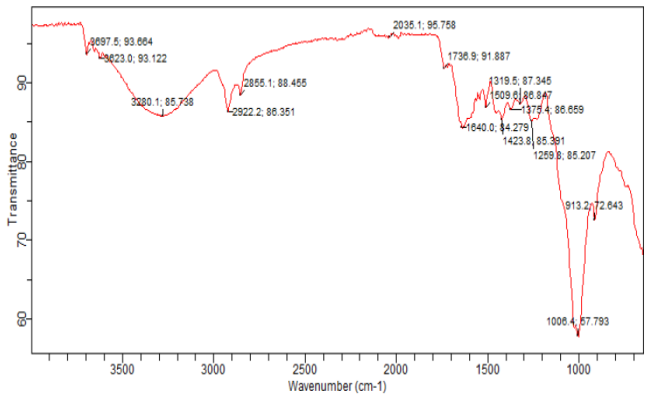

Figure 3: FTIR spectra of groundnut husk

Table 1: FTIR functiona groups and wave number of groundnut husk (Das *et al.*, 2019)

Functional group	**Wave waxnumber, cm^{-1}**
Surface–OH stretching vibrations	3280.1
Aliphatic C–H stretching	2922.2
Aldehyde C–H stretching	2855.1
Aliphatic acid C=O stretching	1736.9
Unsaturated group like alkene C=C stretching	1640
Carboxylic acid C–O stretching	1423.8
Esters C–O stretch	1259.8
Glycosidic C–H deformation with ring vibration and OH bending	1008.4

The bands in the region of 3300 cm^{-1} (Figure 3) indicate the presence of a strong hydroxyl groups in cellulose, hemicellulose and the lignin of the groundnut husk (Yeasmin and Mondal, 2015). The bands at 2922cm^{-1} and shoulder at 2855cm^{-1} were assigned to C-H asymmetric stretching and symmetric stretching of C-H of CH_2-groups respectively (Sathasivam *et al, 2005*). The bands at 1737cm^{-1} and 1640cm^{-1} were attributed to C=O stretching (hemicellulose band) and carbonyl stretching of aromatic ring (lignin). The band at 1259cm^{-1} corresponds to C-O stretching (lignin and hemicellulose) while the one at 1008cm^{-1} corresponds to C-O-C antisymmetric bridge stretching (Yeasmin and Mondal, 2015). These FTIR results lend more credence to the ADF chemical compound assay.

3.2 Sorption Capacity and Behaviour

The variation of the sorption capacity with time for various particle size ranges of groundnut husk particles spread on 3mm, 4.5mm and 6mm oil layer thicknesses (on seawater surface) are shown in Figure 3, 4 and 5 respectively, and discussed below.

3.2.1 Oil sorption capacity

Figure 4 shows how oil sorption on groundnut husk progresses with time for different oil layer thicknesses over water and different particle sizes.

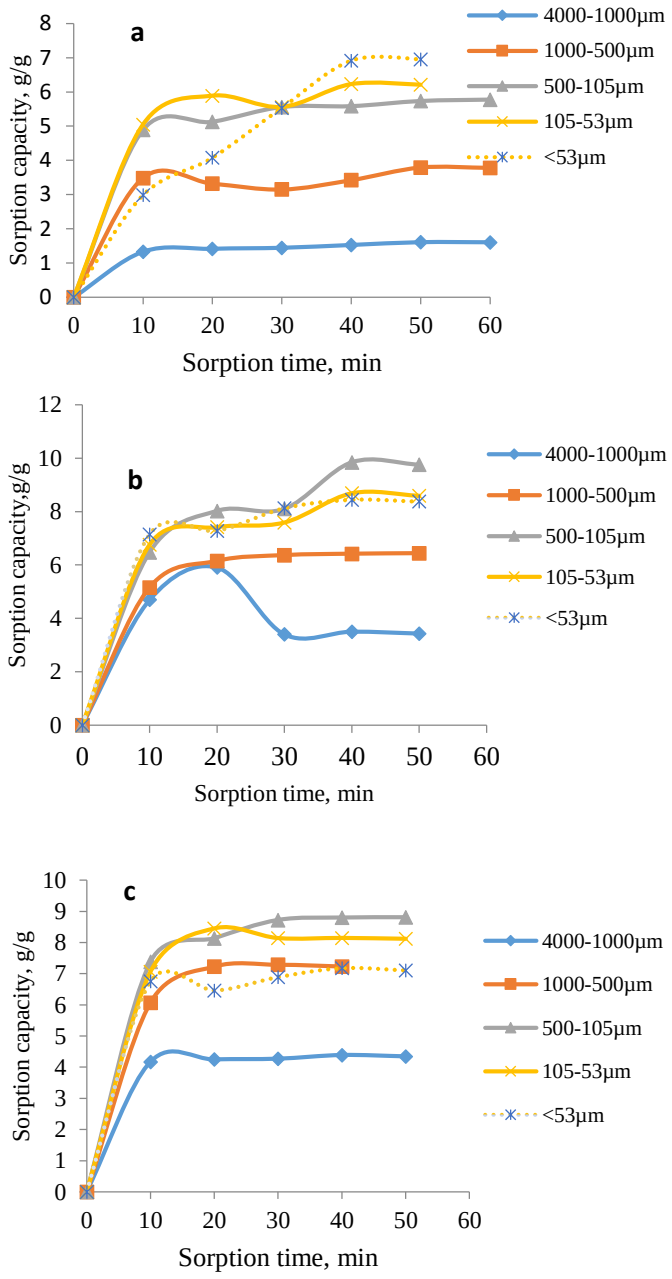

Figure 4: Variation of oil sorption capacity with time for different particle sizes: (a) 3 mm oil layer thickness. (b) 4.5 mm oil layer thickness and (c) 6 mm oil layer thickness

Figure 4a shows the variation of sorption capacity of differen particle sizes with time for 3.5 mm oil layer thickness over water. The maximum oil sorption capacity of the sorbent recorded was 9.8442 g oil/g sorbent with particle C (500-105 µm) at 40 min and the lowest equilibrium capacity for this oil layer thickness was 5.9081 g oil/g sorbent with particle A (4000-1000 µm) at 20 min. Particle E recorded equilibrium sorption value similar to particle

D (105-53 µm). The equilibrium sorption recorded by these two size ranges are not too different from that recorded by C. Particle C, D and E gave the highest initial uptake rate and particle A gave the lowest rate. The recorded equilibrium sorption capacity of particle A dropped at thirty minutes from a higher value recorded at twenty minutes and reached asymptote between thirty and fifty minutes. The average fibre diameter of groundnut husk has been measured as 21.81µm (Saidu, 2011). Since there is wax deposit on the husk surface, attraction between crude oil and this wax is expected through van der Waals forces. The sorption process would be promoted by the attraction of the oil onto the wax and also retention of the oil on the fibre surface because of its irregular structure. Thereafter, capillary action, driven by the surface tension of the oil through the cuticle of the fibre lumen, results in absorption and deposition of the oil. This capillary action should also be enhanced by the microporous lumen of the husk shown in the SEM image of Figure 2.

Figure 4b shows that with 4.5mm oil layer thickness on water the maximum oil sorption capacity of groundnut husk was 8.7240 g oil/g sorbent with particle C (500-105µm) at thirty minutes. The lowest equilibrium capacity was 4.3879g oil/g sorbent with particle A (4000-1000 µm) at forty minutes. Particle B and E recorded similar sorption capacity. Particle C (500-105 µm) gave the highest initial uptake rate and particle A (4000-1000 µm) gave the lowest initial uptake rate.

With 6mm oil layer thickness, Figure 4c indicates that maximum oil sorption capacity of groundnut was 6.9516goil/g sorbent with particle E (<53µm) at forty minutes though particles C and D recorded equally high sorption capacity. The minimum equilibrium sorption was 1.6066 g oil/g sorbent with particle A (4000-1000 µm) at twenty minutes. Particles C and D (105-53 µm) gave the highest initial sorption rate and particle A (4000-1000 µm) recorded the lowest rate.

In general, particle A gave the minimum equilibrium capacity over the three oil layer thicknesses considered. In addition, C (500-105µm) gave the highest sorption capacity for 3 and 4.5mm oil layer thickness but particle E gave the maximum sorption capacity when 6mm was used. The relative prominence of particle C appears to increase as oil layer thickness decreased. It could also be seen from the results that, in general the sorption capacity of groundnut husk increased as particle size reduced. This trend is expected because of the increase in specific surface (surface to volume) as size is reduced. This observation is supported by results of an earlier investigation by Nwokoma and Anene (2010). In addition, the decrease in inter-particle pore size as particle size is reduced is expected to enhance capillary action.

Overall, the sorption capacity of groundnut husk was observed to, initially increase with contact time but the equilibrium sorption was reached in less than thirty minutes as shown in Figures 4a-c. This implies that the crude oil was trapped fast and indicates a potential for quick cleanup of oil spill, which would prevent fast dispersal of the spilled oil (Shashwat *et al.*, 2006). The exponential decay trend displayed by the particles in oil sorption rate may be due to blockage of the fibrils' pores by the particles and/or the oil. This phenomenon might have led to the reduction/stoppage of capillary filling after a period of time. This trend was also observed when corn husk particles were used for oil spill cleanup (Olawale *et al.*, 2020a)

Furthermore, the sorption capacities of groundnut husk was observed to reduce as the amount of oil over water was increased as shown in Figure 4 a-c. A similar trend was reported in a study of corn husk particles (Olawale *et al.*, 2020a). This could be as a result of imbalance of surface forces at the husk-oil interface with attraction increasing in the direction of the oil as the oil thickness increase and the number of oil molecules increase. The oil sorption capacity was observed to decrease with oil layer thickness over water for the different particle size ranges investigated, as shown in Figures 5a – 5c. This trend has been pointed out earlier; and it might be due to the effect of the up-thrust forces originating from the water layer within the water-oil-sorbent system. The thicker the oil layer over the water the less would the convective force per area of the oil layer that is available to enhance oil transport into the particles' pores, other factors being constant.

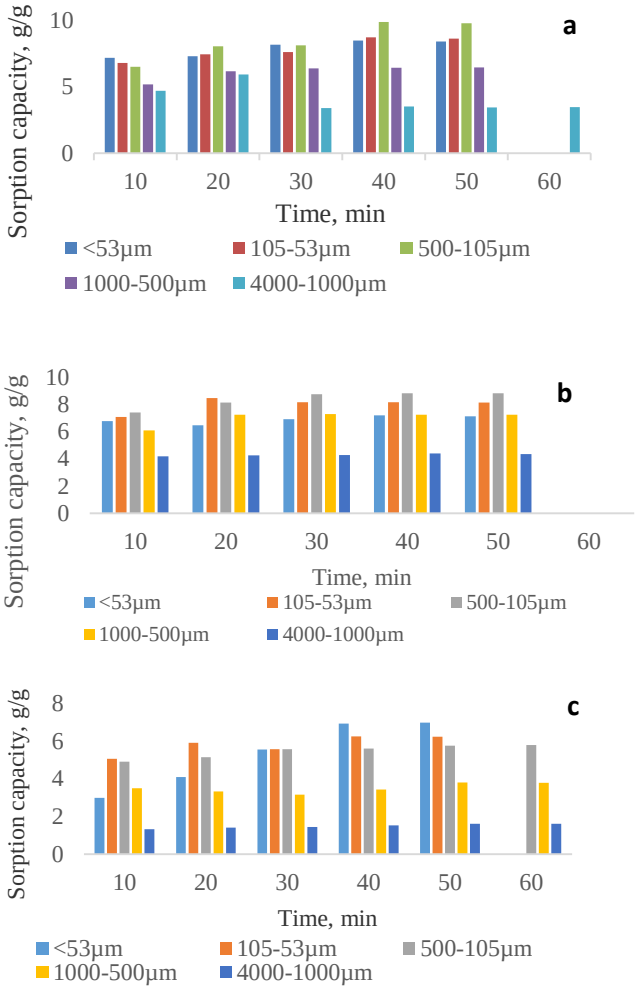

Figure 5: Time comparative sorption capacities of different particle sizes on (a) 3mm oil layer thickness (b) 4.5mm oil layer thickness (c) 6 mm oil layer thickness

No discernible trend could be seen between oil sorption capacity and particle size ranges utilized in this study, with a cursory look at Figures 4 and 5. This appears to suggest that other phenomena aside particle size related ones (such as adsorption) are involved in oil sorption by the biomass particles as suggested in the work on corn husk (Olawale *et al.*, 2020a). Further investigations are needed to correctly situate the effects of the controlling factors in the oil sorption characteristics of groundnut husk particles.

No water sorption was recorded by the five groundnut particle ranges used in this study. This would be due to the presence of hydrophobic wax deposit on groundnut husk surfaces. The results obtained for the buoyancy test of the husk also appear to support this finding.

3.3 Comparison of Sorption Capacity of Groundnut Husk and Commercial Sorbents

The maximum sorption capacity of 9.8442 g/g sorbent recorded by groundnut husk was comparable to that of the commercial sorbents (Adsorb-IT filtration fabric gray sheet) which recorded 10.15 g/g sorbent (Hussein *et al*., 2009). As natural unmodified sorbent samples were used in this work, there is potential for the biomass as a sorbent. An improved sorption performance is envisaged if the biomass is modified since porosity, surface area and other oleophilicity-enhancing factors would be increased.

3.4 Sorption Kinetics

From the results presented in Figures 4a – 4c, it is seen that oil sorption by the different particle sizes of groundnut husk displayed decaying exponential trends with time. The model of oil sorption kinetics of groundnut husk was obtained by fitting the experimental data using DataFit 9.0^{R} software. The best fit was obtained with the function given by Equation 5.

$$q = a\,(1 - e^{-t}) \qquad 5$$

where **q** is sorption capacity, **a** is the model fit parameter and **t** is the sorption time.

The parameters for kinetic model given by Equation 5 for the five particle size ranges employed for sorption over three oil layer thicknesses are presented in Table 2. The values of the model parameters, as shown in the table, follow the trend obtained for oil sorption capacities by the husk particles and so could be regarded as sorption coefficient. Particles B, C and D provided the highest coefficients on the three oil layers investigated. The coefficient of determination (R^2) recorded in all cases were higher than 0.96 except for samples E (on 6 mm oil layer thickness), samples B (on 4.5 mm oil layer thickness) and samples C and E (on 3 mm oil layer thickness) when R^2 fell to 0.66, 0.87, 0.88 and 0.81 respectively. The sorption kinetic model, which is an inverse exponential form, would indicate a diffusion mechanism for oil sorption by unmodified groundnut husk particles.

Table 2: Model parameters of groundnut husk's oil sorption kinetics for 3 oil layer thicknesses over sea water

Oil layer thickness, mm	Particle size range labels				
	A	B	C	D	E
3	3.5663	7.8097	8.4396	6.1059	2.8809
4.5	4.2843	6.4336	8.3708	7.9850	6.8770
6	1.4868	3.4920	5.4447	5.7840	5.2899

4. CONCLUSION

The oil sorption characteristics of groundnut husk were evaluated for dynamic conditions at 27°C on Escravos crude of 3, 4.5 and 6 mm oil layer thickness on water. The physico-chemical and morphological properties of the husk as well as its buoyancy on salty water were determined. Thereafter the oil sorption characteristics of the husk's particles were established to follow the exponential decay pattern. The effects of particle size and oil slick thickness on sorption characteristics were also determined. Sorption capacity of the husk particles showed good performance when compared to lignocellulsic wastes like bailey straw, soya bean husk and corn husk (Hussein *et al*., 2008; Olawale *et al*. 2022a; Olawale *et al.* 2022b). The particles in the size range of 53 – 100 µm recorded the highest sorption capacity of 9.8442 g/g sorbent, was good and comparable to the value (10.15 g/g sorbent) reported for a commercially available sorbents by Hussein *et al*., (2009). The inverse exponential function of the sorption kinetic model, which is indicative of diffusion mechanism for oil sorption by groundnut husk particles, indicates deposition of the sorbed oil in the pores of the husk's particles.

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