



# **Utilization of *Annona senegalensis* as a Sorbent for THE Removal of Crude Oil from Aqueous Media**

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## **Authors' contributions**

*This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.*

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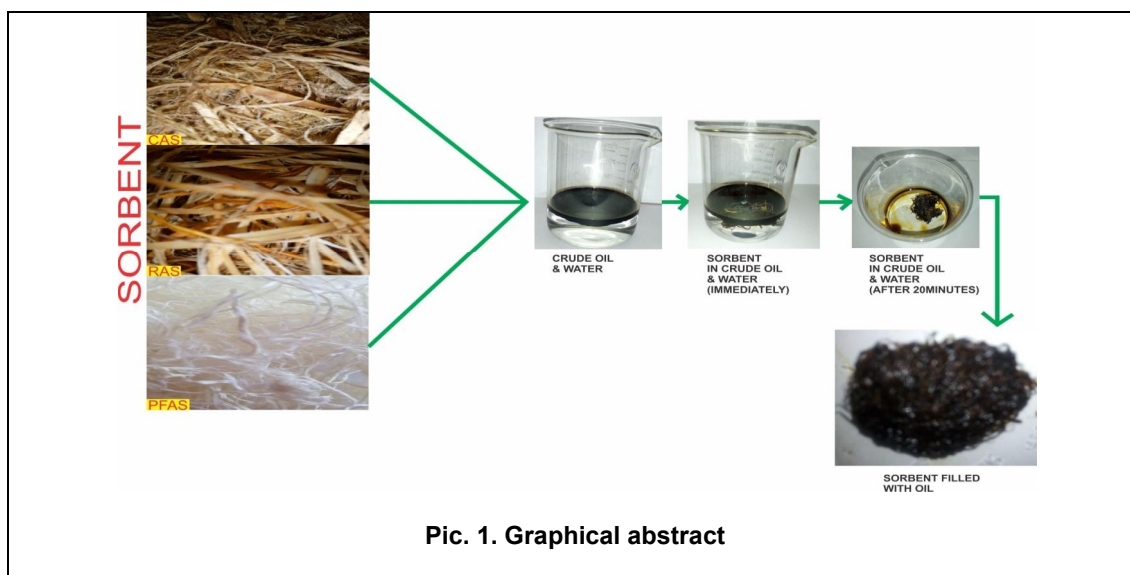
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## **ABSTRACT**

In the present study, the efficiency of *Annona senegalensis* fiber to remove crude oil from aqueous solution was evaluated. The crude *Annona senegalensis* (CAS), retted *Annona senegalensis* (RAS) and bleach *Annona senegalensis* (PFAS) were subjected to sorption studies to optimize their sorption capacity. The results revealed that the efficiency of sorbent to remove crude oil from water is related to the sorbent weight, contact time, initial oil concentration and temperature of sorption. It was found out that increase in sorbent weight led to increase in sorption capacity from 3.99-5.25g/g, 5.51-7.12g/g, and 5.01-6.72g/g in CAS, RAS and PFAS respectively. Increased in Initial oil concentration also increased the oil sorption capacity by 20-21% until it reach equilibrium. Sorption time was varied from 10, 20, 30, 40, 50, 60 and 70 minutes and the highest sorption capacity was recorded at 30 minutes before a gradual decreased was observed. Sorption capacity decreased with increased in temperature above 40°C. The sorbent exhibited good reusability after 8 cycles, with less than 50 % reduction in sorption capacity. The kinetics of crude oil sorption onto CAS, RAS and PFAS follow the second- order model with correlation coefficients higher than 0.99. The results obtained revealed that crude oil adsorption onto the *Annona senegalensis* fiber can be used as an effective adsorbent to oil spill cleanup in water bodies.

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**Pic. 1. Graphical abstract**

*Keywords: Crude oil; sorption; sorbent; Annona senegalensis; remediation.*

## 1. INTRODUCTION

The main source of energy and raw materials for synthetic polymer and chemical in the modern industrial sector is crude oil. There is variation in the amount and type of oily waste discarded from oil industry. Oil, refined products and their by-products escape from oil confinements or during transportation and spill into the environment. Due to the negative impacts of oil to the environment, it becomes imperative to take actions to improve response to oil spill [1,2].

Recently oil spills in the Niger delta region of Nigeria have escalated to serious dimensions due to pipeline vandalization and other activities in the oil industry. Most water bodies in this region are contaminated with different hydrogen carbon fraction. Oil industry spills incident rate has increase to 80% between 1976 and 2008 [3]. In Nigeria oil spills have led to loss of many lives, destruction of farmlands, fishing activities, tourist's sites and cultural areas. The greatest issue is even that of long term effect of both acute and chronic contamination that can cause diseases like cancer and also rashes in children [4].

There is need to remediate oil spill as quick as possible to avoid damage it can cause to the environment. Commercial methods such as booms, dispersants, skimmers, oil water separators and sorbents materials are all been utilized but majority of the methods are either

costly or not environmentally friendly or both causing more damage than good [5]. But sorbent has more ease of handling, fast oil uptake, good retention and reusability. A good sorbent should be biodegradable, oleophilic and reusable [6]. Hence adsorption is seen as an attractive treatment method for oily wastewater because it is environmentally friendly and has high removal efficiency, but there is need to sort for a sorbent that is effective and economical [7].

There are different types of sorbents that are used for oil spill cleanup and they are categorized as inorganic minerals (Glass, wool, sand, graphite), organic synthetic (Polypropylene, polyurethane) and organic vegetables (Straw, cotton, sugarcane bagasse, banana peel). Natural and synthetic sorbent are used for oil removal from water. Presently synthetic sorbent is given priority as sorbent because of their high sorption capacity but then non renewability and non-biodegradability of these materials cause environmental pollution this has drawn attention toward the need to develop a biodegradable material as sorbent [8]. Several sorbents have been reported as been used for remediation of oil water [9,10,11].

There is great interest in plant fiber due to their classification as renewable sources, combined with low cost availability, low density, non-toxicity and recyclability. Bast of vegetable plant is now being studied as possible replacement for some synthetic fiber [12]. Sorption techniques are

accepted due to its simplicity and relatively lower processing cost in comparison to other oil removal techniques.

Growth in oil production and processing which has led to increase in the number of oil spills resulting in more pollution in water bodies has given rise to wide application of sorbents from vegetable and animal origin. *Annona senegalensis*, commonly known as Wild Custard Apple and Wild Soursop is a shrub or small tree 2-6 m tall but may reach 11 m under favourable conditions. The bark is smooth to roughish, silver grey or grey-brown. Leaves are alternate, simple, oblong, ovate or elliptic, green to bluish green, almost without hairs on upper surface but often with brownish hairs on the lower surface. Flowers are up to 3 cm in diameter on stalks 2 cm long, solitary or in groups of 2-4, arising above the leaf axils. The fruits are formed from many fused carpels, fleshy, lumpy, egg shaped, 2.5-5 by 2.5-4 cm, ovoid or globose, unripe fruit green, turning yellow to orange on ripening. Wild fruit trees of this species are found in semi-arid to sub-humid regions of Africa. The species occur along river banks, fallow land, swamp, forests and at the coast. It commonly grows as a single plant in the understorey of savannah woodlands. It is found growing throughout Nigeria. It is very common in Northern Nigeria, primarily in Nasarawa, Kaduna, Kano, Plateau, and Niger States and in the Federal Capital Territory, Abuja and usually known as Gwándàn dàájì (Hausa) or dukuu-hi (Fulani) [13].

This work explores the use of *Annona senegalensis* fibers as sorbents in oil spill cleanup across various factors. The effect of variations in sorbent weight, contact time, initial oil concentration and temperature was examined. Water sorption capacity, sorbent reusability and oil retention were investigated.

## 2. METHODOLOGY

### 2.1 Sample Collection and Sorbent Preparation

The fibrous plant *Annona senegalensis* was collected from a farmland located in Girei Local Government Area, Adamawa State, Nigeria and identified by a Botanist from Modibbo Adama University of Technology, Yola. The plant part obtained was cut from the stem with a knife, the bark removed and washed with distilled water. It was spread on a clean polyethylene and allowed to dry in the laboratory for one week.

### 2.2 Extraction of Fiber Procedure

The fiber was extracted from the fibrous plant stem using chemical retting extraction process, giving fiber of different lengths and diameters. The fibrous plant (Sample) was treated with 6% NaOH solution in accordance with work done by Cai et al. [14]. 15g of the sample was submerged in 6% NaOH solution and heated at 100°C for 30 minutes in a water-bath. The fiber was rinsed in cold water to free fibers strands. It was neutralized with acetic acid and washed with distilled water repeatedly until all sodium hydroxide is eliminated. Finally, the fiber was dried at room temperature for 48H.

### 2.3 Bleaching of Fibers

Retted fibers were scoured in 2% NaOH solution at 100 °C for 30 minutes. Scouring of the fiber was carried out before bleaching. Dry scoured fibers were measured and submerged in a solution of 3% H<sub>2</sub>O<sub>2</sub>, with sodium pyrophosphate/sodium oxalate as buffering medium at 55 °C for 30 minutes to remove any colouring matter and white fibers was obtained.

### 2.4 Characterization of Crude Oil Sample

The properties of crude oil sample (COS) was characterized according to the method describe by Nwabueze et al. [15]. The density, viscosity, specific gravity and API gravity of the crude oil sample was investigated.

**Density:** The density of COS sample was taken by using a specific gravity bottle. The bottle was filled with oil and weighed at room temperature (28 -30 °C) and the density calculated from:

$$\text{Density} = \frac{(MS - Mb)}{Vb} \text{-----(Eq. 1)}$$

where MS = mass of oil plus bottle

Mb = mass of bottle

Vb = volume of bottle

The method was repeated in triplicate to obtain a mean value.

**Viscosity:** The viscosity for crude oil sample was determined using viscometer. The viscometer was cleansed with a non-toxic solvent and dried. A certain amount of crude oil sample was poured into a beaker, and then transferred to the viscometer. The viscometer was inserted into the water bath at the required temperature and the

viscosity was recorded in poise and converted to centistokes. This was carried out in triplicate to obtain a mean value.

**Specific Gravity:** The specific gravity of crude oil was determined from the results obtained for density. The specific gravity, being a more standard measurement was obtained by multiplying the density calculated with density of water 0.998 g/cm<sup>3</sup>.

#### American Petroleum Institute (API) Gravity

The API gravity was calculated using the formula:

$$\text{API} = (141.5 / \text{s.g}) - 131.5 \text{-----} (\text{Eq. 2})$$

where s.g = specific gravity of crude oil calculated.

### 2.5 Characterization of Crude Fibers

The physiochemical properties of the sorbents will be investigated according to the method described by Donatus et al. [16]. All the following physiochemical properties were determined: Moisture Content, Ash Content, Volatile Content, Fixed Carbon, Density, Specific Gravity and Swell ability.

### 2.6 Determination of the Amount of Water Sorption

The water content of the sorbent was determined in the laboratory using the method of centrifuge technique described by Al zubaidy et al. [17]. The sorbent was subjected to pressing to desorb the crude oil. During the pressing stage, petroleum ether was added to help extract the oil in the sorbent; the extracted liquid was collected in a centrifuge tube and placed in a water bath to break emulsion present and then, centrifuge for 20 minutes. The amount of water sorbed was weighed and recorded.

### 2.7 Test for oil Sorption Capacity by Sorbent

Factors that affect oil adsorption were investigated, namely the effect of variation in sorbent weight, contact time, oil concentration and temperature in water/oil medium and in oil medium. Tests were carried out at room temperature. The methods describe by [4] was adopted for the sorption studies. To simulate the situation of oil spill and minimize experimental

variation, the crude oil sample was held in beakers for 1 day in open air to release volatile hydrocarbon contents. The crude, retted and pure fibers were subjected to sorption studies to optimize the sorption properties.

To 100 ml of distilled water in a 250-ml beaker, 10 g of crude oil was added. A portion 0.10g of the sorbent was added into the mixture in the beaker and left unperturbed for 30 min. After 30 min, the sorbent was removed using a spatula and placed on sieving net and left to drain by hanging the net over a beaker for 10 minutes. The drained sample was weighed and recorded. This was repeated at different weights of 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 g and results recorded. This experiment was also conducted at different times of 10, 20, 30, 40, 50, 60 and 70 minutes at constant sorbent weight/ oil concentration and results were recorded. The effect of Initial concentrations of crude oil was also studied from 5, 7.5, 10, 12.5, 15, 17.5 and 20 g/100 ml of water at constant sorbent weight and time and results recorded. The effect of temperature on sorption was also investigated at different temperature (30, 35, 40, 45, 50, 55 and 60 °C) at constant weight of sorbent and time. This was also repeated in oil medium. The sorption capacity of the sorbent samples was calculated using the expression:

$$\text{Oil Sorption Capacity} = \frac{\text{New weight gain}}{\text{original weight}} \text{ g/g (Eq. 3)}$$

It was recorded as gram per gram of sorbent. The procedure was carried out in triplicates and the mean of the results reported.

### 2.8 Sorbent Reusability

The sorbent sample was used eight times and after each time the sorbent was pressed to squeeze the oil content from the sorbent and ready for further use. The sorption performance was recorded in g/g. Reusability of the sorbent sample was studied in oil medium. 8 cycles of sorption processes were performed. After each cycle, the sorbent was squeezed and re-weighed. The difference between the weight of the wet material after drainage and the initial weight of the material gives its sorption ability.

### 2.9 Oil Retention

To determine the oil retention, a known weight of sorbent was placed in 20 ml of oil for 30 min. The sorbent was removed and vertically hung, where upon the adsorbed oil began to drip from the

sorbent, the weight of the material was measured after 10, 20, 30, 40, 50, 60 and 70 min. of draining. The amount of oil retained was determined as the difference between the weight of the wet material after drainage and the initial weight of the material [18].

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of the Crude Oil Sample (COS)

The physicochemical Properties of Crude oil sample (COS) were characterized. This includes the density, specific gravity, API gravity and viscosity. The results obtained are shown in Table 1.

The physical analysis of the crude oil investigated showed viscosity of 5.04 cSt, density of 0.8651 g/cm<sup>3</sup>, specific gravity of 0.8634 and API gravity of 32.4. The specific gravity for light oil is between 0.80-0.88. The API gravity which is an important property in the classification of crude oil as heavy, medium and light revealed that the crude oil can be categorized within the range of light crude oil (31–39<sup>0</sup>) [6].

#### 3.2 Characterization of the Sorbent

The sorbent was categorized into crude *Annona senegalensis* (CAS), Retted *Annona senegalensis* (RAS) and bleached *Annona senegalensis* (PFAS), The results of the physico-

chemical properties of the sorbent are shown in Table 2.

The results of the physical properties of the raw sorbents are presented in Table 2. Considering the moisture content, of material is an index of its stability and susceptibility of microbial contamination. RAS has the highest moisture content of 12.37% while PFAS has the lowest value of 8%. This might mean that PFAS will likely have a long shelf life, low microbial contamination level because of its low moisture content [19]. Ash content indicates level of mineral in the materials. Low ash content suggests low mineral composition, which is a reflection of the inorganic content of the material. CAS has the highest value of 8%. In general ash content of fibrous raw materials has been recognized to be between 1-20%. PFAS showed a high volatile content of 60.79%. The fixed carbon content of CAS was higher than the other sorbent samples. Fixed Carbon and ash content show reduced chars of carbon content. PFAS sorbent has the lowest bulk density— 1.0041 g cm<sup>-3</sup>, this is because their structure is not dense naturally. The essence of water absorption experiment is to verify the hydrophobic properties of a sorbent. The lower the water absorbed by a sorbent, the better the potential with regards to collection of oil products from a water surface. The sorbent all adsorbed water because of their hydrophilic nature. RAS adsorbed the lowest among of water with a value of 145.72%.

**Table 1. Physicochemical properties of crude oil sample (COS)**

Properties	Values – Mean and Standard Deviation
Density (g/cm <sup>3</sup> )	0.8651± 0.01
Specific gravity (g/cm <sup>3</sup> )	0.8634± 0.01
API <sup>0</sup> gravity (30°C)	32.4 ± 0.02
Viscosity, 30°C (cSt)	5.04 ± 0.02

**Table 2. Physicochemical properties of sorbent**

Properties	CAS	RAS	PFAS
Moisture Contents (%)	12.37 ± 0.02	11.59± 0.03	8± 0.02
Ash Content (%)	8.0± 0.01	7.01± 0.02	6 ± 0.02
Volatile Content (%)	28.10± 0.02	55.88± 0.02	60.79 ± 0.01
Fixed Carbon Content	51.53 ± 0.01	25.52± 0.01	25.21± 0.01
Density (g/cm <sup>3</sup> )	1.0057±0.03	1.0043±0.02	1.0041 ± 0.02
Swell ability (%)	205.52±0.01	145.72± 0.21	171.87± 0.12

### 3.3 Effect of Sorbent Weight on Sorption Capacity of CAS, RAS and PFAS

The effect of sorbent dose on the amount of crude oil removed was studied for the different sorbent weight ranging from 0.10, 0.20, 0.30, 0.40, 0.50, 0.60 and 0.70g. As shown in Fig. 1, the sorption capacity efficiency was dependent on the weight of the sorbent in the entire sample studied. In CAS the sorption capacity increased from 3.99-5.25 g/g, RAS from 5.51-7.12 g/g and PFAS 5.01-6.72g/g. These indicate that increasing the amount of sorbent led to increase in oil sorption capacity. Increase in sorbent dosage result in more active sites, which enhances augmentation in the sportive surface area available for the oil molecules to be adsorbed. Active sites are the site where a substrate binds and products are formed. At higher dosage of the sorbent, the oil adsorbed are higher due to the availability of more empty binding sites as compared to lower dosage which has less binding sites to adsorb the same amount of oil. As the sorbent weight increased the surface area also increased and more oil is adsorbed [1,20]. The higher oil affinity of the RAS and PFAS compared to CAS is attributed to pretreatment which disrupt the fibers primary walls and exposed the microfibers causing improvement on the sorbent surface. The fact that oil is easily adsorbed into the fiber assembly of the RAS and PFAS samples due to intermolecular interaction between the oil and the

sorbent surface which has improved roughness due to pretreatment. Capillary action will also enhance the diffusion of oil through the successive fiber walls to the hollow lumen effectively in the pretreated sample [21].

### 3.4 Effect of Contact Time on Sorption Capacity of CAS, RAS and PFAS

Fig. 2 shows the effect of contact time on sorption capacity. The effect of contact time in relation to sorption capacity of sorbents was studied at different time 10, 20, 30, 40, 50, 60, 70 minutes with other experimental variables kept constant. The sorption capacity increases gradually from 10-30 minutes before a steady decreased was observed from 40-70 minutes as it reaches equilibrium. Increasing the contact time between the sorbent and oil do have effect on the percentage oil removal. Reaction time have an effect on the sorption capacity because the prolonged contact time of up till 30minutes increased the probability of effective collision between oil and sorbent. Furthermore, the longer mixing time led to better breakage of oil droplets thereby reducing the diameter of oil droplets which results to more interfacial area for oil sorption to occur and most of the residual oil are adsorbed [22,23]. The initial high rate of oil sorption may also be due to the greater bare surfaces that are available for oil uptake however as the time increased less adsorption sites were available so it affects the oil sorption [24].

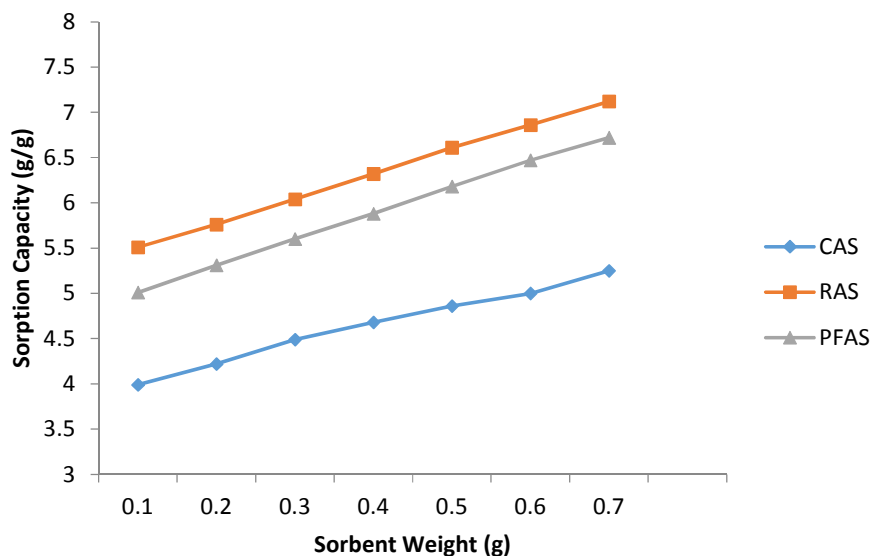
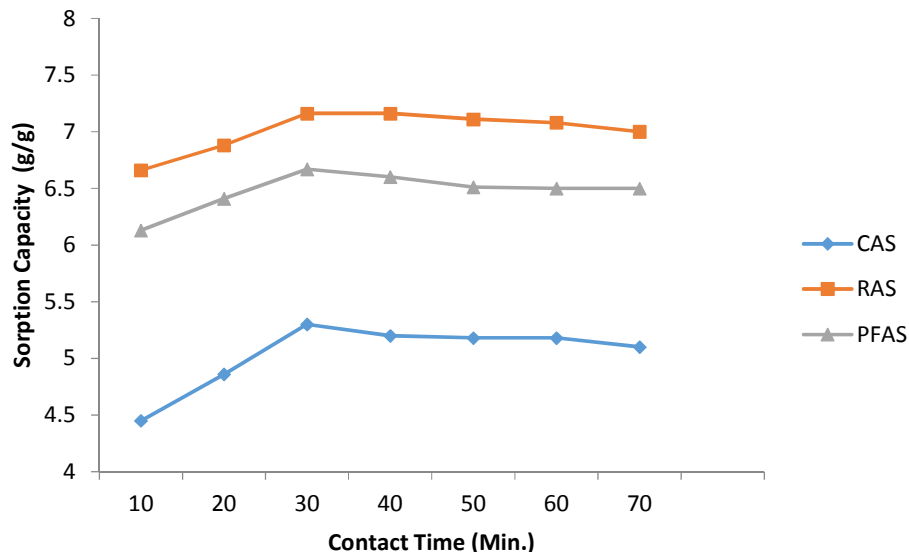


Fig. 1. Effect of sorbent weight on oil sorption capacity



**Fig. 2. Effect of contact time on sorption capacity**

### 3.5 Effect of Initial Oil Concentration on Sorption Capacity of CAS, RAS and PFAS

The initial oil concentration is imperative because the initial concentration of oil residue in solute can affect the sorption kinetics and mechanism that controls the overall reactions. Fig. 3 explains the relationship between the initial concentration and the amount of oil adsorbed by the sorbents. The effect of initial oil concentration and oil sorption capacity was studied by varying the oil concentration from 5, 7.5, 10, 12.5, 15, 17.5 and 20g/100ml of oil. The plot showed that the sorption capacity increased with increasing oil concentration up till 15g/17.5g /ml then reach equilibrium. When the initial oil concentration increased, the mass transfer driving force also increases thereby increasing the rate at which molecules pass from the bulk solution to the particle surface. This results in higher sorption capacity. And when all the sites at the sorbent surfaces becomes fill up with oil, there would be opposition to the mass transfer driving force which would lead to desorption [25]. The increases in sorption capacity can also be explain based on the fact that as oil concentration increases the oil contacting surfaces increases and the water contacting surfaces decreases hence the increases in oil pick up [26]. Slick thickness and area are key variables in oil weathering and transport models [27]. It is also evident that the sorption capacity

of the pretreated sorbent (RAS and PFAS) were higher than those of the crude sample (CAS). This is because the crude sample easily form dispersions in the water and latter settle at the base of the beaker after a while at low oil concentration, making the sorption difficult while the high sorption capacity is because at higher oil concentration, the surface of the pretreated sorbent enhances oil residue diffusion through the film surrounding the materials and into the porous network of the sorbent.

### 3.6 Effect of Temperature on Sorption Capacity of CAS, RAS and PFAS

The effect of variation in temperature on sorption capacity of the sorbents was studied from 30, 35, 40, 45, 50, 55, and 60 °C. The adsorption experiment results carried out for different temperature in Fig. 4 revealed that the sorption capacity was higher at lower temperature. The results further show that oil removal decrease with increase in temperature indicating the dependence of adsorption on temperature. As temperature increase the physical bonding between the organic compound and the active sites of the sorbent weakened [28]. This give rise to increase in the molecular interchange as molecules moves faster in higher temperature and viscosity decreased. This result in low adherence of oil to the pores walls as oil becomes light making it to drain easily during the draining steps. Sorption capacity of the oil is

inversely proportional to the oil viscosity and directly proportional to the capillary radius. Initially the cohesive forces between the molecules dominate the molecules mainly because the molecules are closely packed. When the liquid is heated the cohesive forces between the molecules reduce thus the forces of

attraction reduces which eventually reduces the viscosity of the liquids. Solubility of the oil also increased as temperature increased which makes the interaction forces between the solute and the solvent to become stronger than between the solute and the sorbent. This makes the solute more difficult to adsorb [29].

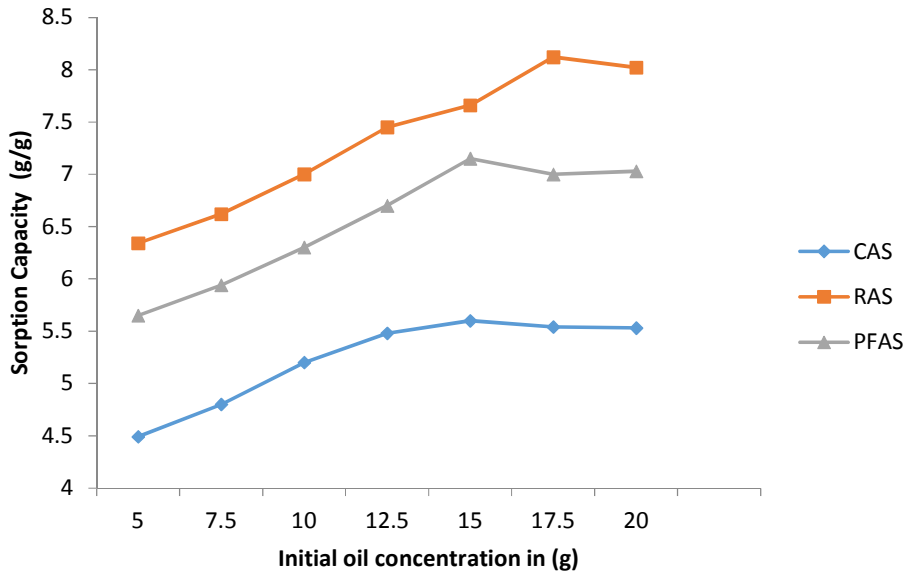


Fig. 3. Effect of initial oil concentration on sorption capacity

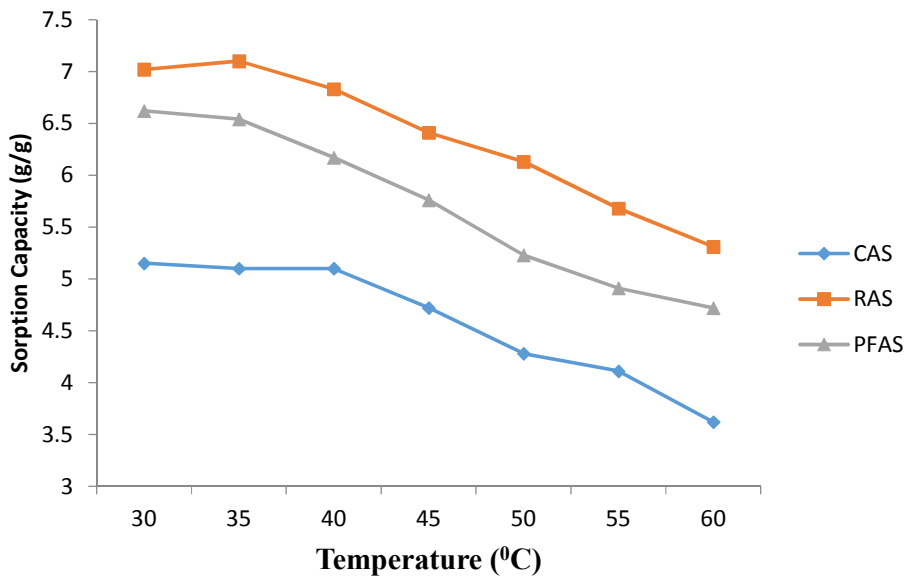


Fig. 4. Effect of Temperature (°C) on sorption capacity



### 3.7 Water Sorption Capacity on Sorption Capacity of CAS, RAS and PFAS

Fig. 5 showed the water sorption capacity of the sorbent in percentage at different sorbent weight (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7g). The water sorption capacity increased with increase in sorbent weight. Absorb water is the water that lies close to the solid surfaces under the influence of attractive forces. While increasing the amount of sorbent, large amount of oil is removed narrowing the interface between oil and water making the sorbent to adsorb high amount of water [30]. As the sorbent volume fraction increases for all the samples the initial rate of the process and the water sorption increases, this is as a result of hydrophilic nature of the sorbent. Higher sorbent content led to increase in diffusion coefficient and give rise to higher water sorption. As capillary mechanism becomes active, water molecules flow through the interface of the sorbent leading to greater diffusivity [31]. RAS has a lower value of water sorption of 179% at 0.7g of sorbent. This may be as a result of reduction in polar hydroxyl group in the fiber by replacement of OH group on the surface of the fibers by NaOH during retting [32]. Also higher bonding between the hydrophilic sites and water molecules in the untreated sorbent (CAS) leads to higher diffusion coefficient causing higher water sorption.

### 3.8 Effect of Reusability on Sorption Capacity of CAS, RAS and PFAS

Reusability is one of the major factors for selection of sorbent materials. Recyclability helps

in reducing oil cleanup costs, if the sorbent can be recycled and reused. The relationship between the number of times the sorbent was reused and its oil sorption capacity are shown in Fig. 6. The main criterion which can be used for judging reusability of a sorbent is the number of cycles it can tolerate without becoming unusable due to tearing, crushing, or other general deterioration. The results showed that decrease in sorption efficiency did not exceed 50% of the initial value after eight sorption cycles in oil without water. The amount of oil adsorbed decreases with recycling effect. Pressing causes a general reduction in the size of active site in term of porosity, so oil that goes in is consequently reduced. Loss of particle from the surface of the sorbent as a crude oil contains different types of organic and inorganic materials that can have negative effect on the bond between the sorbent and the oil can also lead to reduction in sorption capacity [33]. Decreased in sorption capacity with increased in number of reused is also observed due to the fact that the squeezing of the fiber assembly will lead to the reduction of effective clearance in the fiber bundle and the deformation of partial hollow lumen [34]. There may be deformation due to wearing and tearing residual oil might still be presents giving less space for more oil to be adsorbed. Full recovery of the void fraction may not be obtained and these prevent more oil from entering the fiber assembly. Pretreated sample RAS and PFAS retained 80% of its sorption capacity because the sorbent surfaces is very effective to improve its reusability due to more stable liquid bridge between pretreated sorbent compared to the raw sorbent (CAS).

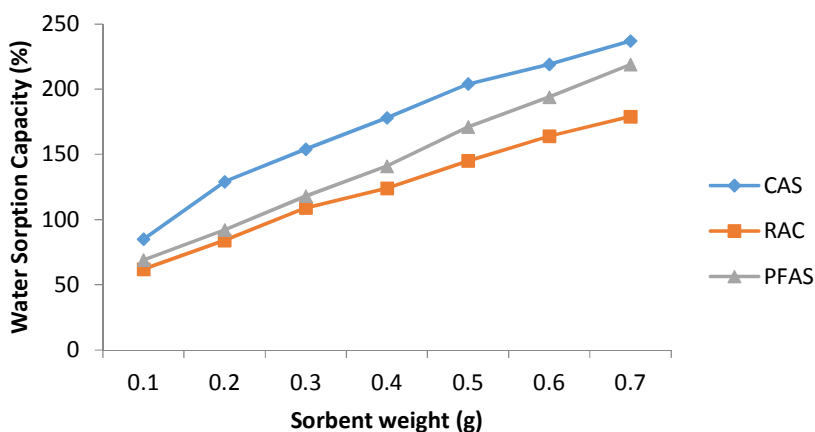


Fig. 5. Water sorption capacity (%) of sorbent

### 3.9 Oil retention of Sorbent

Oil retaining ability of a sorbent is a major concern in oil sorption. Oil retention is the amount of time that oil stay inside the sorbent material. Even if the sorption capacity is high, it ability to hold oil for a long period is paramount. Good retaining ability means that the adsorbed oil will not be lost during handling of the sorbent. The effect of oil retention with time 10, 20, 30,40, 50 60, and 70 minutes for CAS, RAS and PFAS were studied. The quantities of adsorbed oil as remains in sorbent were shown in Fig. 7. CAS, RAS and PFAS losses 33%, 25% and 27% of the initial adsorbed respectively. Reduction in oil retention with time can be as a results of

instantaneous dripping out of oil from the external surface of the sorbent assemblies and surfaces of the reacting system in the first stage then further draining is observed due to oil draining out from the extra-lumen liquids which continue for a period slowly. The draining in the extra –lumen liquids occur because the capillary pressure was insufficient to hold the weight of the oils retained in the sorbent [35]. The pretreated sample (RAS and PFAS) has higher retention capacity than the raw sample (CAS) because it has more stability of capillary pressure within the materials hence the edge in oil retention capacity [36] and the oil bridges formed among the bundles would have been easier to destabilized in the raw sample [37].

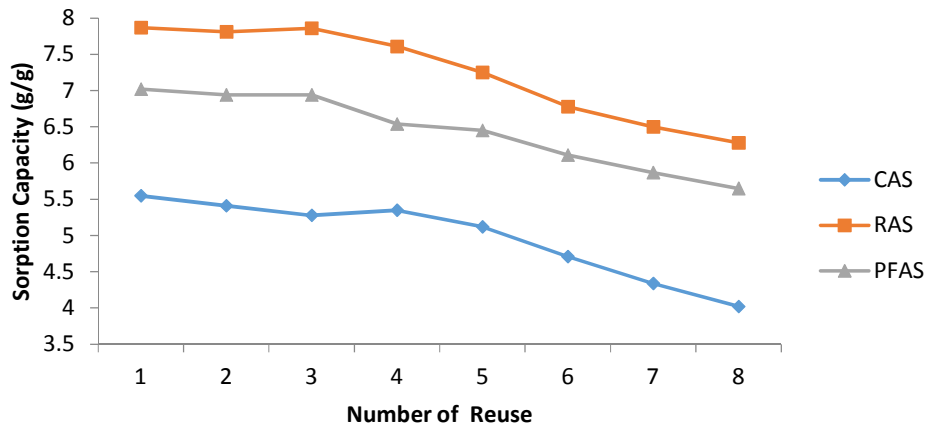


Fig. 6. Effect of sorbent recyclability on sorption capacity

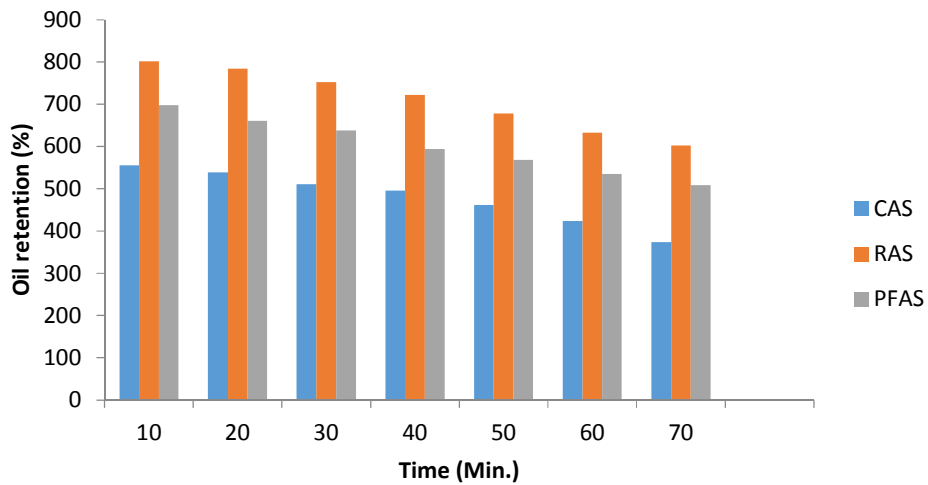


Fig. 7. Oil retention (%) of sorbent

### 3.10 Kinetic Modeling of the Oil Sorption Process

The studies of sorption kinetics are important in determining the effectiveness of sorption; however, there is relevance in identifying the types of sorption mechanism in a given system. To understand the sorption process, a kinetic study was conducted. The sorption kinetic models were applied to the experimental data to analyze the rate and mechanism of crude oil sorption onto the sorbent. The kinetic models applied to this study are the Lagergren pseudo first-order and then Ho and McKay pseudo-second-order models. The pseudo-first-order kinetic model, which is also known as the Lagergren equation, is expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 \dots \dots \dots \text{(Eq. 4)}$$

Similarly, the pseudo-second-order kinetic model proposed by Ho can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots \dots \dots \text{(Eq. 5)}$$

where  $q_t$  and  $q_e$  are the amounts of crude oil adsorbed onto the sorbent at time  $t$  (s) and

equilibrium, respectively, in g/g.  $k_1$ (1/min) is the rate constant of pseudo-first-order adsorption, and  $k_2$ (g g<sup>-1</sup>/min) is the rate constant of pseudo-second-order adsorption.

### 3.11 Kinetic Studies for Annona Senegalensis (CAS, RAS, PFAS)

The values of the kinetic parameters are generally determined from the slope and intercept of  $t$  versus  $\ln(q_e - q_t)$  as shown in Fig. 8 (a), 9 (a) and 10 (a). The plot of  $\ln(q_e - q_t)$  vs. time gives a plot with slope equal to  $-k_1$  and intercept of  $\ln(q_e)$ . The plot of  $\frac{t}{q_t}$  versus time gives a straight line with the slope  $\frac{1}{q_e}$  and intercept of  $\frac{1}{k_2 q_e^2}$  as shown in Fig. 8 (b) 9 (b) and 10 (b). The pseudo-second-order kinetic expression resulted in a higher  $R^2$  value (i.e., 0.9985, 0.9994 and 0.9995 for CAS, RAS and PFAS, respectively). The straight lines in the plots prove a good agreement of experimental data with the second-order kinetic model. If the plot is linear, then the sorption process may be described as chemisorption [38].

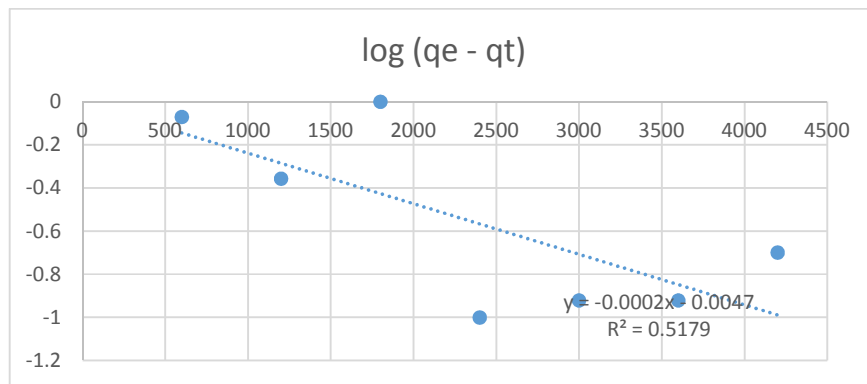


Fig. 8 (a). First- order kinetics CAS

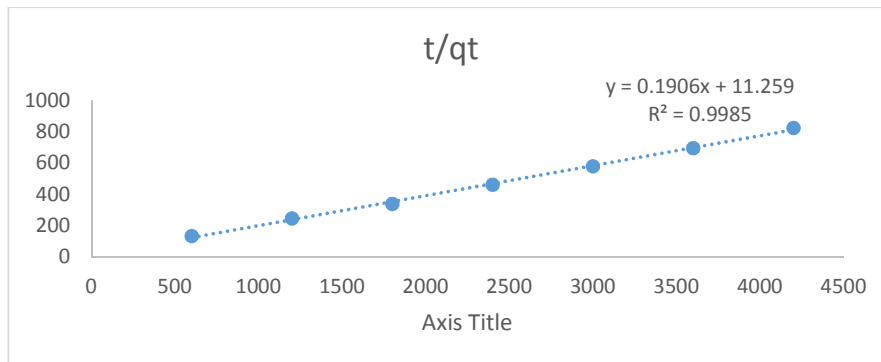


Fig. 8 (b). Second- order kinetics CAS

The calculated parameters namely  $R^2$ , slope, intercept,  $k_1$  and  $k_2$  for the pseudo first order and pseudo second order kinetics for CAS, RAS and PFAS are presented in Table 3. Based on the results in Table 3, the pseudo-second-order expression provided a good fit to the experimental data based on the high

regression coefficient ( $R^2$ ) values, which were close to 1. It can be also concluded that the adsorption process was controlled by chemisorption, which involved valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate [39].

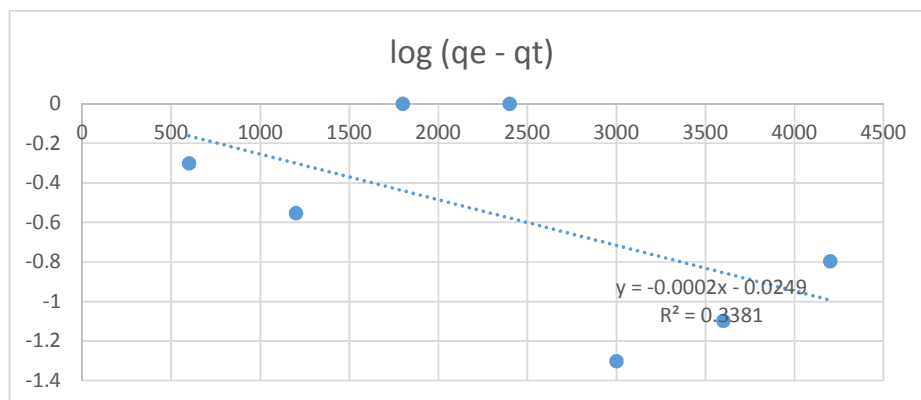


Fig. 9 (a). First- order kinetics RAS

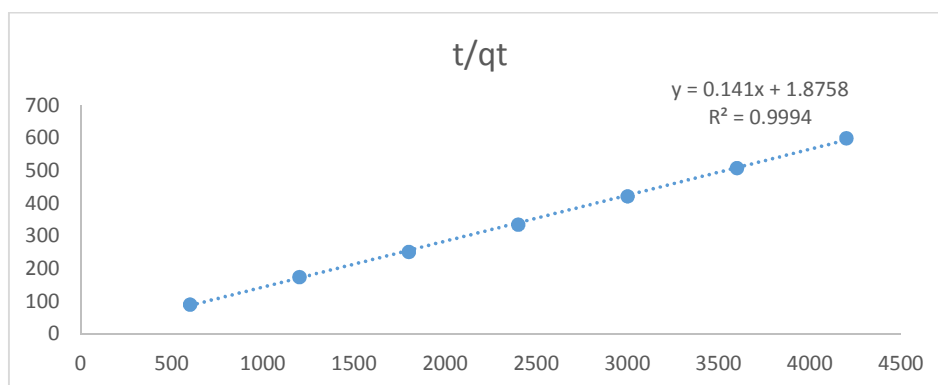


Fig. 9 (b). Second- order -kinetic RAS

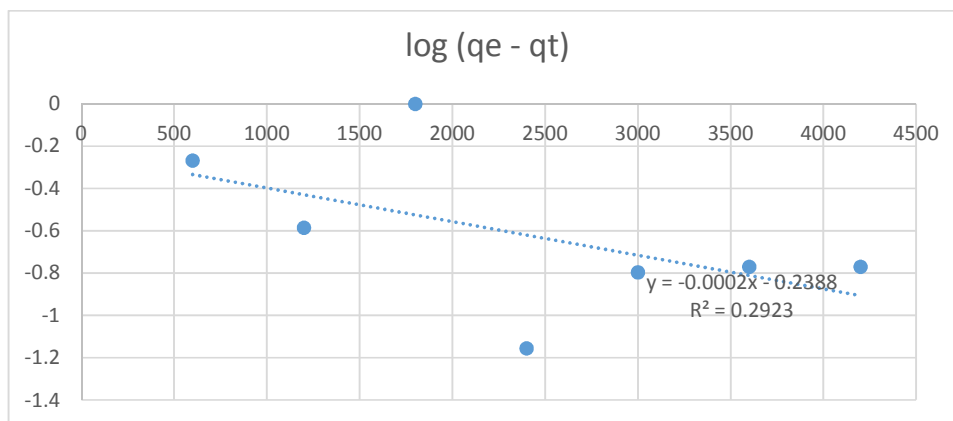


Fig. 10 (a). First- order kinetic PFAS

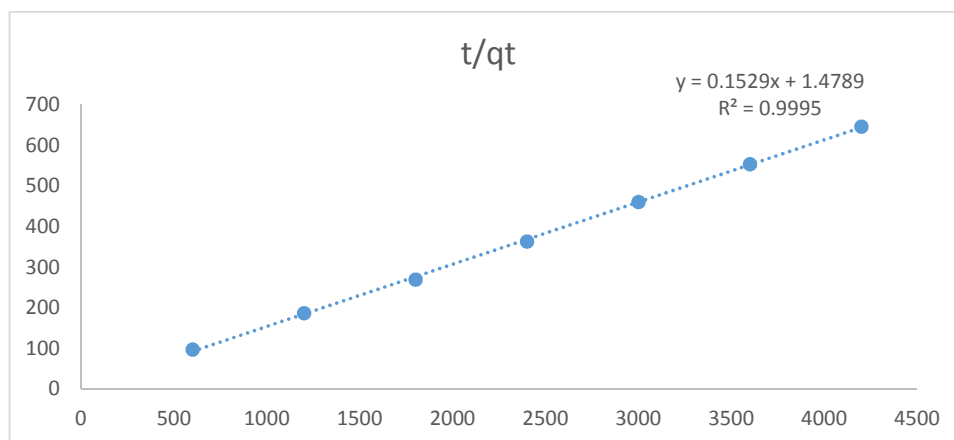


Fig. 10 (b). Second-order kinetic PFAS

Table 3. Summary of kinetic parameters for crude oil sorption

Sorbent	Kinetics	Slope	Intercept	R <sup>2</sup>	k <sub>1</sub> (min <sup>-1</sup> )	k <sub>2</sub> (g g <sup>-1</sup> min <sup>-1</sup> )
CAS	First order	0.0002	-0.0047	0.5179	0.000461	
	Second order	0.1906	1.1259	0.9985		0.0032
RAS	First order	-0.0002	0.0249	0.3381	0.000461	
	Second order	0.141	1.8758	0.9994		0.0106
PFAS	First order	-0.0002	-0.2388	0.2923	0.000461	
	Second order	0.1529	1.4789	0.9995		0.0158

#### 4. CONCLUSION

In this study, the efficiency of *Annona senegalensis* fiber as sorbent for crude oil adsorption from aqueous solution was investigated. The results indicate that the adsorption of oil onto *Annona senegalensis* fiber is dependent on the sorbent weight, contact time, initial oil concentration and temperature as all the factors affects the sorption capacity of the sorbent. The experiments above showed that increased in sorbent weight and initial concentration led to better sorption capacity. Contact times of 30 minutes gives higher sorption capacity and temperature of less than 40°C was chosen for the sorption studies. CAS, RAS and PFAS sorbent exhibited good reusability and oil retention. The pseudo-second-order model well represents adsorption kinetics in this study indicating that the rate limiting step may be a chemical interaction between the oil compound and the sorbent surface that it is due to the monolayer formation. This implies that the sorbent can be transported and handle without the oil draining off since there is a chemical bond between the oil and the sorbent materials. *Annona senegalensis* fibers with their desirable

qualities have the potential to be an effective sorbent for oil-water separation.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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