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INVESTIGATING THE PROPERTIES OF *PANSEKE* TO DETERMINE THE ADSORBENCY FOR SOLUBLE CRUDE OIL

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Abstract:
Panseke (The flamboyant tree; Delonixregia) a low cost agricultural forest product was assessed to investigate the feasibility of the materials to be used as adsorbents for soluble crude oil by determining their moisture content, buoyancy, water adsorbency and oil absorbency. The study also determines the relationship between dissolved oil absorbency and other factors time of adsorption, concentration dosage. In addition, relation between soluble crude oil adsorbency and three other factors of time of adsorbency, concentration of spill and dosage of the adsorbent were determined. The result values of moisture content of 4.84%, buoyancy of range: 8 – 17 %, water adsorbency of range 1.49 – 4.26 % and Langmuir values of $R_L = 0.0213$, q_m= 1.527 mg/g and K_L= 0.0632L/mg. The result of the study shows that Panseke powder is an effective absorbent for the removal of soluble oil from water upon oil spillage.

Keywords
Panseke, Bio-adsorbent, Bio-Remediation, Soluble crude oil

1. Introduction:

Crude oil consists of different hydrocarbons that range from a light gas to heavy solid. When oil spills on water, the physical and chemical properties of oil change progressively, [1]. This process is referred to as weathering which includes evaporation, dissolution, adsorption onto suspended materials, agglomeration e.t.c [2]. The adverse impact of oil spill on the ecosystem and the long term effect of environmental pollution calls for an urgent need to develop a wide range of materials for cleaning up oil from oil impacted areas especially as the effectiveness of oil treatment varies with time, the type of oil and spill, the location and weather conditions [3].

Large amount of agricultural waste (corn cob, corn husk, plantain peel, plantain pseudostem, bread fruit seed husk, borassus coir e.t.c) are produced in many countries of the world. However, many of these waste materials are not reused. One of the features of these organic materials is that it can absorb by capillary forces an amount of oil and/or water greater than it' s own weight [4]. Furthermore, these natural materials can be completely degraded in nature by biological, physical, chemical and photochemical processes. [5].

In Nigeria, many of natural products and products from agricultural waste are possible alternative choice for cheaper adsorbents which also support natural degradation. However, data in oil adsorption capacity of natural adsorbent is still rare. Therefore, more studies and information gathering on this is required for further development. Despite the abundance of cleanup techniques and effective ways of combating oil spills, there still remains a problem of the remediation of soluble crude oil. This study tends to use natural materials; pig dung, panseke and African walnut as adsorbent for soluble crude oil with our personal concentration on panseke.

2. Materials and Methods:

2.1 Collection of Materials and Equipment's.

Collection ofthe adsorbents, *Panseke* (the flamboyant tree: delonixregia) was obtained from a forest in Lapai, Niger state, Nigeria. Crude oil was obtained from Shell Petroleum Development Company, Warri, Delta state, Nigeria. Equipment's used for the analysis are digital weighting scale, measuring cylinder, beaker, conical flask, magnetic stirrer stirring rod, dropper, stop watch, sample bottles, sieve mesh, shakertable, mortar and pestle, grinding stone, oven, filter paper and crucible were all obtained in chemistry and physics laboratory of the university of Abuja, Nigeria.

2.2 Preparation of Sample.

In this study, the natural material is prepared to eliminate or minimize the effect of external factors that can cause a deviation from accurate readings. These factors are impurity, size effect and change of contact angle. The stems are manually harvested (the flamboyant tree: delonixregia). And then its impurities are removed by washing thoroughly with clean water. It is then chopped into approximately 1 cm of length then sundried for days until weight remains constant. It is then stored in plastic bag to prevent moisture from air. The dried piece is then grinded into powered from by a mortar or grinding stone and then it is sieved to collect only the finest of its powered. This powder is then stored in air tight containers to prevent moisture from air and will be used adsorbent for soluble crude oil.

2.3 Determination of Moisture Content.

In this study the tested material is exposed to room's temperature for 24 hours before investigating their moisture content and other characteristics. The procedures of determining moisture content are described below.

Place 4 g of the powdered *panseke* 24 hours exposed adsorbents in the crucible (the resolution must be + 0.01 g) and define it as W. Oven dry it at 103^{o}c until its weight remain constant. Totally transfer the dried adsorbents from crucible. Record the sorbent weight and denote it as w_d. Calculate the moisture content in adsorbents by using the equation;

$$Moisture\ Content = \frac{W1-Wd}{Wd} \times 100 \quad (1)$$

2.4 **Buoyancy Test.**

In the situation where adsorbents are used for combating oil spill incident recovering (or harvesting) of soaked materials is an important step to reduce their impacts on aquatic resources. Though, it is possible that some adsorbents may not be collected during the recovering process due to sinking. This effect can be expressed in term of "Buoyancy" (Wang, 2014). However, in the case of soluble oil remediation the material has to pass through the entire depth of the water body for remediation to be effective. And since this adsorbent is biodegradable, there will be no deleterious impact to water body, or its aquatic life [6].

2.5 Determination of Water Adsorbency.

Water absorbency of materials is determined after the materials have been exposed in a room's temperature for 24 hours [7]. The procedures for determination of water adsorbency are shown below.

Weigh 1 g of the powdered *panseke* 24 hours exposed adsorbent and define it as W_o. Transfer it to 10ml water filled test cell. Place the test cell cover on its opening and place it on a shaker table and Set its frequency to 200 rev/min. Shake for 5 min adsorption period (during the process, investigate its appearance and changes on both adsorbent and water). Let it be settled for 2 minutes and then drain the content for 30 seconds. Weigh the drained sample and record it as $w_{drained}$ and calculate the water absorbency by using this equation.

$$\text{Water absorbency} = \frac{\text{Wdrained} - \text{Wo}}{Wo} \quad (2)$$

2.6 Soluble oil absorbency.

Soluble oil adsorbency is the amount of soluble oil adsorbed on 1 g of adsorbent. Materials used for oil spill adsorbent should have oil adsorbency more than 5 g oil / g adsorbent. In this study, adsorbate or oil to be investigated is crude oil. The procedures for the determination of soluble oil adsorbency are listed below:

i. Standard solution of crude oil in water
ii. Adsorption capacity in variation with time
iii. Adsorption capacity in variation with concentration
iv. Adsorption capacity in variation with dosage

2.7 Regeneration of Adsorbents.

Regeneration being the process of renewal or restoration is an important process in the use of an adsorbent. It entails that an adsorbent can be reused after remediation. However, in the case of remediating soluble crude oil, where the adsorbent has to go through the entire depth of the water body, recovery of adsorbents is more or less an impossible feat [8].

Nevertheless, in a case where adsorbents can be recovered, a regeneration process is required. Hence, here is a set of procedures for the regeneration of adsorbents.

200ml of water is measured into a beaker and 1g of crude oil is added to the beaker. The solution is stirred for 30mins at a temperature of 40^oc. The solution is filtered into a conical flask and 10ml of filtrate is measured into a shaking bottle. 0.1g of adsorbent was added to the filtrate and then placed on a shaking table for 50mins at a shaking frequency of 200rpm. The sample was filtered into a bottle with the residue of adsorbent left on the filter paper. The paper containing residue was washed into beaker with 10ml of water and allowed to settle and then decanted into a sample bottle and labeled "1" cycle. 10mil of water was added again to the residue and allowed to settle then decanted again and was labeled "2" cycle. The process was repeated up to the 5^{th} cycle and the residue was then placed in an oven to dry until the weight became constant.

3. Result and Discussion:

3.1 Moisture Content.

After careful experimental test using the detailed steps mentioned in materials ad methods above over a range of 15 samples and using the statistical analysis presented below, it is concluded panseke has a moisture content of 4.84% moisture with a standard deviation of 0.11.

Table 1: moisture content of adsorbent

Adsorbent	Mean	N	Std	Minimum	Maximum
Panseke	4.83732	15	11084	4.623	4.968

3.2 Buoyancy.

Buoyancy of adsorbent is investigated by studying its variation in time of adsorption. Just as stated earlier, the buoyancy of an adsorbent to be used for remediation of crude oil spill should be about 90% to be considered effective (not more than 10% of adsorption should sink) however, in the case of remediating soluble crude oil, the adsorbent is required to pass through the depth of the entire water body, therefore a buoyancy of 10% or less would be considered effective (about 90% of adsorbent will go through the water body).

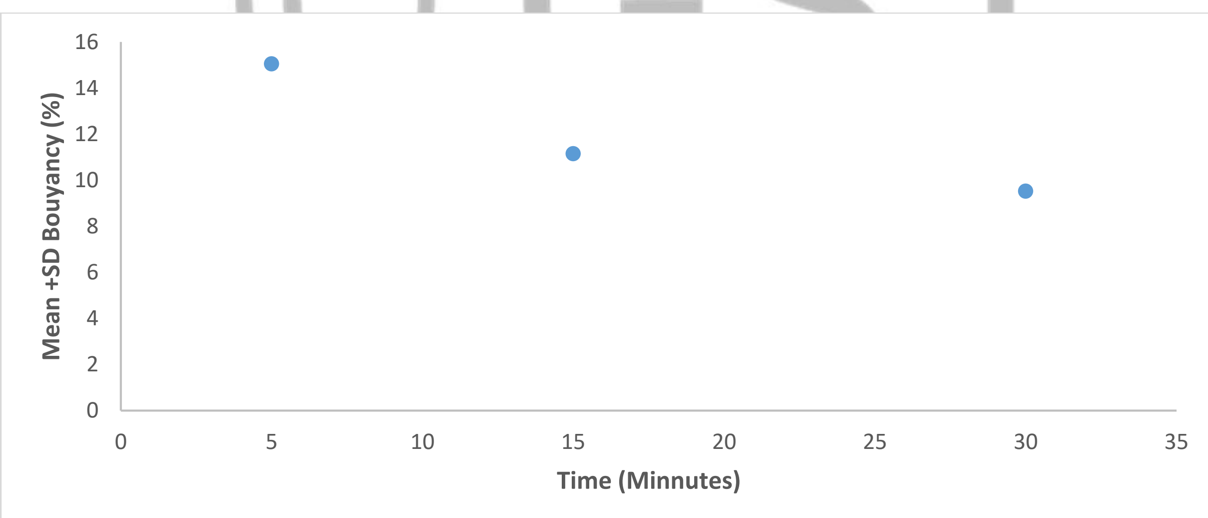

Figure 1: Buoyancy of Panseke with Time of adsorption

Buoyant of panseke varies in range of 8% to 17% at 0mins (upon introduction of adsorbents) it is already at 80%. At 5mins it is at 15.04% with a standard deviation of 2.001. At 15mins buoyancy is 11.14% with a standard deviation of 0.68 and lastly at 30mins buoyancy is 9.52% with a standard deviation of 1.63.

3.3 Water Absorbency.

Amount of water (g) absorbed into 1g of absorbent "water absorbency" of the materials was investigated. The schematic plot between water absorbency and time of absorption of the absorbent is shown in the figure 2.

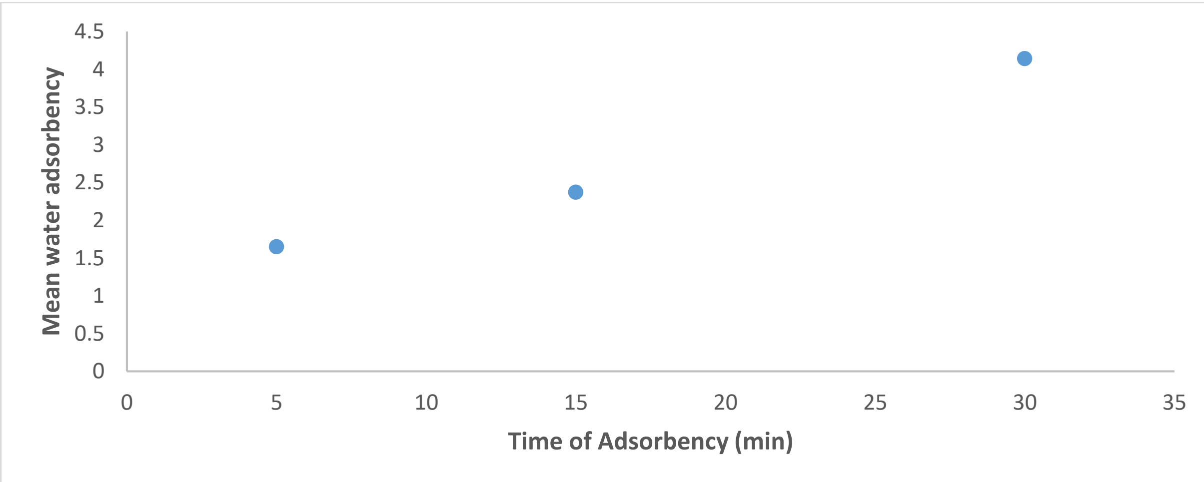

Figure 2: Water adsorbency of Panseke with time of adsorption

Water absorbency of *panseke* at time interval of (5 min., 15min, and 30min.) varies in range of 1.49 to 4.26. At 5 minutes, an average of water absorbency is 1.65 with standard deviation of 0.11. At 15 minutes, the average of water absorbency is 2.37 with standard deviation of 0.08. Lastly, at the time of absorption of 30 minutes, the average of water absorbency is 4.114 with standard deviation of 0.08.

3.4 Soluble oil absorbency.

From the experimental procedure stated in materials and methods, soluble oil absorbency was carried out as absorption capacity was varied over three factors namely time, dosage and concentration. After spectroscopic analysis of samples and reviewing, results was obtained, the following were observed:

• Absorption capacity in variation with concentration

In the case of varying absorption capacity with concentration of crude oil, samples were created using a spill of 0.15g, up to 0.75g of crude oil and 0.1g of absorbent was used in remediation of 10ml of each sample.

The effect of initial spill concentration in the range of 0.05 to 0.75g on absorption (investigated under the specified conditions; contact time of 30 min; absorbent dosage of 0.1g; and temperature of 40˚C) is shown below. The amount of adsorbate (soluble oil concentration) relating to the lower initial spill concentration of crude oil was just about the same with the amount when higher concentration was used. It is seen that the removal of soluble oil was not dependent on the concentration of the spill but on the percentage solubility in water of the type of crude oil as the decrease in the initial concentration had no effect in the amount of soluble oil removed; this is in line with the results of [9]. While the amount of spill concentration was varied, the soluble oil concentration remained the same at 30±0.02mg/L.

• Absorption capacity in variation with time

After absorbents were introduced, the samples were placed on a shaker 5mins, 10mins and 20mins up to 100mins for different samples. The spectroscopic consult shows meaningful absorption and gradual change in sample properties up until 10mins.

Absorption of soluble crude oil was measured at given contact time for a constant spill concentration of 1g of crude oil to 200ml of water (10000mg/L), and 5g of absorbent to 10ml of its filtrate (500mg). From figure 3, the plot reveals that the rate of percent soluble oil removal is higher at the beginning. This is probably due to larger surface area of the absorbent powder being available at the beginning for the absorption. Most of the maximum percent soluble oil removal was attained after about 40 min of shaking time. The increasing contact time increased the soluble oil absorption and it remains constant after equilibrium is reached in 30 min.This depicts that it takes about 30mins for absorption of soluble crude oil by *panseke* to take place after which the absorbent becomes saturated if all of the soluble crude oil hasn't been absorbed.

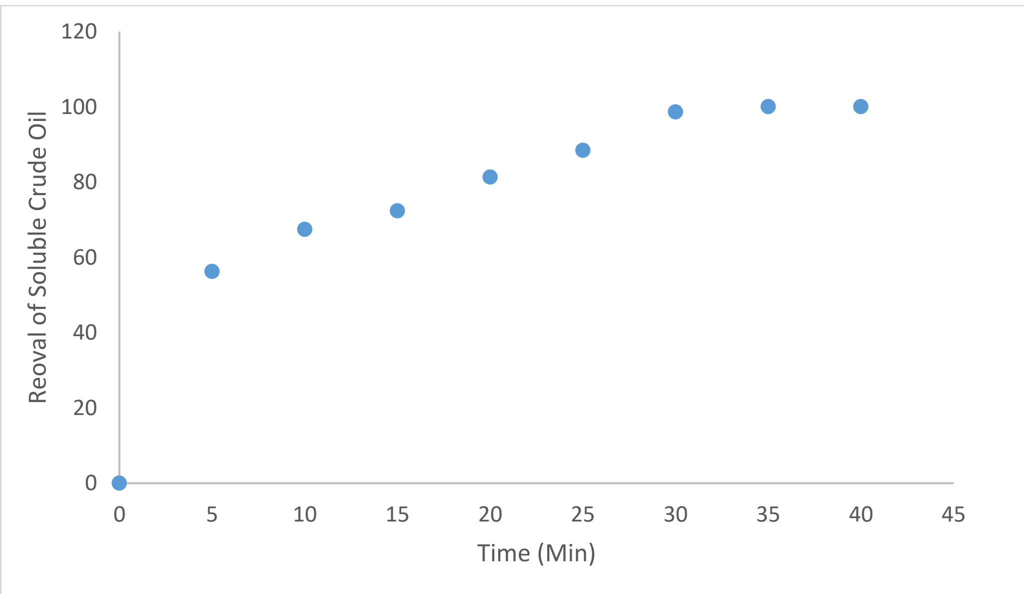

Figure 3: effect of contact Time on Adsorption

• **Absorption capacity in variation with dosage**

Spectroscopic result analysis shows that the absorption of soluble crude oil increases rapidly with increase in the amount of *panseke* powder due to greater availability of the surface area at higher concentration of the absorbents ascertained elsewhere [10]. The significant increase in uptake was observed when the dose was increased from 0.3 to 0.6g. any further addition of the absorbent beyond this did not cause any significant change in the absorption. This may be due to overlapping of absorption sites as a result of overcrowding of absorbent particles. From the results, it is revealed that within a certain range of initial soluble oil concentration, the percentage of soluble oil absorption on 0.3g of *panseke* powder is determined by the sorption capacity of the absorbent. The maximum removal of soluble oil was obtained in the absorbent dose of 0.6g. It is also observed that with increased dose of absorbent, water was found to be more reddish.

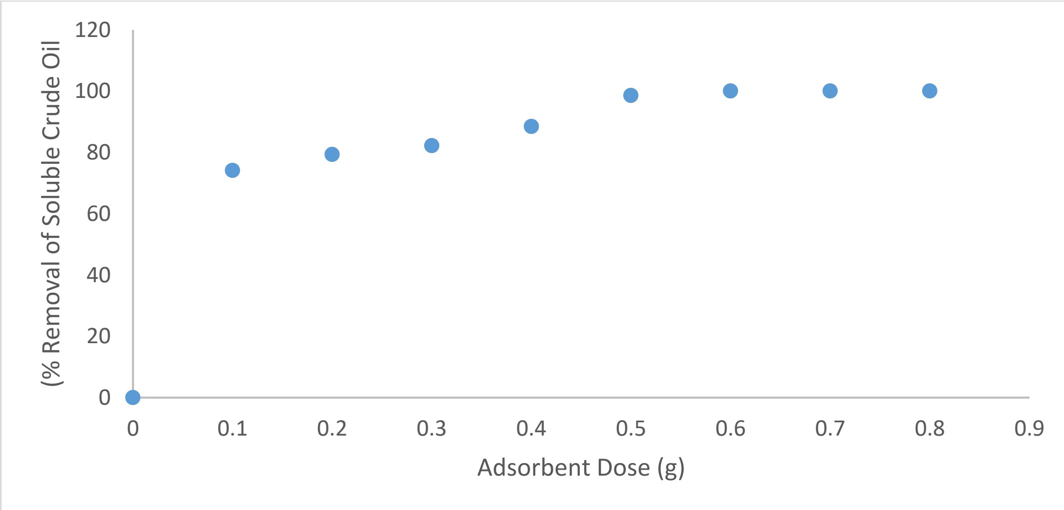

Figure 4: Effect of Adsorbent Dose

3.5 Regeneration of absorbents.

From the experimental procedures in 3.3.6, concerning regeneration of absorbents, after the regeneration process, the second hand absorbents were found to be relatively lighter that the first hand ones, furthermore; the particles appear to be looser than the first hand absorbents. It also appears to have lost a lot of its coloration and has increased water absorbency soluble oil absorbency.

3.6 Equilibrium study.

Having looked at the absorption process as it relates to different time frame, different concentration of soluble oil, and different doses of absorbent; lets now review the equilibrium study of adsorption itself. Absorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and absorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of absorbents, the type of coverage and possibility of interaction be the adsorbate species [11]. Adsorption data are by describe by adsorption isotherms, such as Langmuir, Freundlich and Temkin isotherms. These isotherms relate soluble oil uptake per unit mass of absorbent, $q_e$to the equilibrium adsorbate concentration C_e.

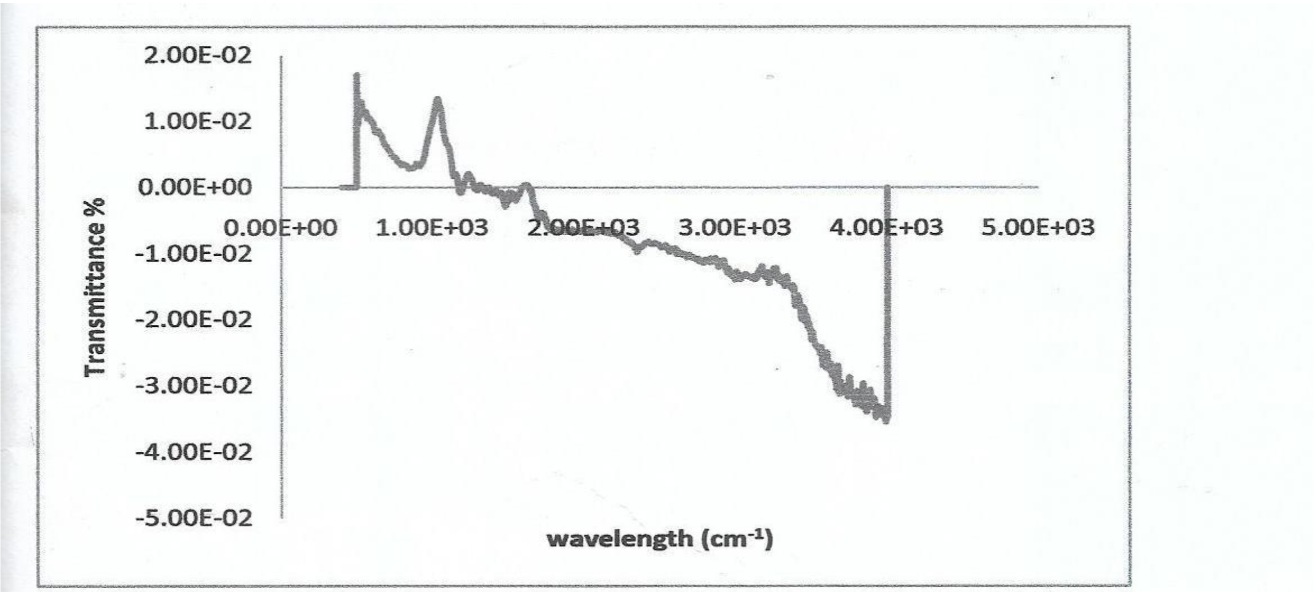

Figure 5: Spectrogram of adsorbent

Absorption isotherm is the relation in a constant temperature between partial pressure of adsorbate and amount of absorbed substance at its equilibrium condition. In the experiment, adsorbate is the soluble oil in liquid state. Thus, concentration of soluble oil, and amount of absorbed substance at equilibrium condition.

4. Conclusion:

Panseke powder is an effective absorbent for the removal of soluble oil from water upon oil spillage. From the studies it is observed that absorption of soluble oil is very rapid in the initial stage and decreases while approaching equilibrium. It also shows that the equilibrium time will increase with increase in initial soluble oil concentration. The percentage removal of soluble oil increase with the increase in absorbent dosage and decreases with increase in initial adsorbate concentration.

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