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Sorption Kinetics and Intra Particulate Diffusivity of Crude Oil on Kenaf (*Hibiscus cannabinus* L.) Plant Parts

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Abstract: The Kinetics of sorption and intarparticute diffusivity of crude oil using kenaf (*Hibiscus cannabinus* L.) plant parts was studied. The amount of crude oil adsorbed increased with time. The amount of crude oil adsorbed were 11. 86, 9.92, 7.54 and 7.10 mg mL^{-1} for the roots and stems respectively. The fractional attainment of equilibrium, values showed that the stem parts research equilibrium point before the root parts. This study has showed that the sorption of crude oil on kenaf (*Hibiscus cannabinus* L.) plant parts is particle diffusion controlled. The rate coefficient for particle diffusion were 0.015 and 0.007 mm^{-1} for the root parts and stem parts, respectively.

Key words: Intraparticute diffusivity, crude, kenaf (*Hibiscus cannabinus*)

INTRODUCTION

The research into the use of agricultural by products and their modified products as adsorbents for the removed of pollutants such as crude oil films from aqueous environment has been on increase. Some of these agricultural by- products in clued corres ponding author. Straws, rice-husks, saw dusts, modified cellulose and kenaf (*Hibiscus cannabinus* L.)[1, 2].

This is because these agricultural-by products are naturally occurring, hence they are abundant, available at little or no cost. They are have advantages over conventional adsorbents like charcoal, activated carbon, Sanol, Foam, because they are easily biodegradable, low cost, abundan and easy available.

Crude oil pollution is any impairment of the environmental quality with crude oil as major pollutant. This phenomenon is on the increase in most crude oil producing nations as well as crude oil consuming nations[3,4]. Crude oil polluting arises as a result of either accidents involving oil tankers on the road, rail ways, ricers, cakes, sea estuaries[5], or accidents involving factures of pipe lines, bulk storage tanks and vandalization of oil pipelines[3] incidents of crude oil or its products pollution from leaks from pipelines, careless stocking and handling of crude oil, washing from contaminated surfaces, illegal dumping of oil contaminated wastes from industries[4].

The effects of crude oil and its refined products pollution are enormous. These effects however, differ from one environment to another, subject to such physical features such as land, sea, surface water, recreational water, estuaries, lakes ricers. For instance, crude oil spills on sea and other water bodies can cause the destruction of aquatic life cycles, toxicity to marine lives, clogging of power plants amenities of recreational facilities[6,7]. There are several factors that influence the effects of crude oil or its refined products on marine lives. These are; type of crude oil spilled such as cresol, phenol, chlorinated hydrocarbons, duration of the spill prior to remediation efforts, quantity of crude oil spilled, frequency of spills state of crude oil prior to spill, season of they and habitat of the marine organisms at a particular ecosystem[8,9]. There are two distinctive remediation processes used in crude oil and its products spills controls. There are natural control mechanisms of dissolution, evaporation, spreading and applied methods of containment, sin king, burning and sorption process,[10]. The sorption-controlled mechanism of crude oil spill is the trust of this work.

Kenaf (*Hibiscus cannabinus* L.): This is a herbaceous plant that belong to the family of *malvacae.* And of is native to East control Africa. Kenaf plant is a fast-growing warm season, multipurpose annual plant with slender straight stems[11]. Probably originated in Africa, where it was first d omesticated as early as

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4000 BC, in western Sudan[12]. The first scientific work on the uses of kenaf (*Hibiscus cannabinus* L.), plant originated in India around A.D 1800[11]. Kenaf has a high potential for use an sound absorption panels and thermal resistor due to its low density. It is one of the cheapest available organic. biomass adsorbent known. it has high hydrophobic property due to its surface be coated wax,[13] kenaf (*Hibiscus Cannabinus* L.) plant supplies crude for hand, craft purposes, leaves and stems for foods, it is used as crude oil adsorbents due to its preference for oil to the exclusion of water in crude oil water mixture. It is used as natural, non-toxic, completely biodegradable agricultural biomass for crude oil adsorption from aqueous environment[13].

Equilibrium studies: The fractional attainment of equilibrium is the rate of the amount of adsorbates such as meta-lion, crude oil films, or other adsorbates removed from water surface after a certain time, to that removed when sorption equilibrium is attained.

$$\frac{(M_o)}{(M^t)} = \frac{Ct}{C_o} ----(i)^{[14]}$$

Where C_t = amount of adsorbate such as crude oil films adsorbed on adsorbent such as kenaf (*Hibiscus cannabinus* L.) plant parts.

C_o = initial concentrations of adsorbate such as crude oil spilled in a simulated crude oil spill on a synthetic sea water environment.

It would be definitely expected that factors such as the number of the reactive sites on the substrate and the bulkiness of substrate would affect the rate of sorption of adsorbate such as crude oil films. However a great deal of information is obtained from factional attainment of equilibrium. The rate of attainment equilibrium may be either film diffusion controlled, particle diffusion controlled, even though these two different mechanisms cannot be sharply differentiated[15]. For particle diffusion controlled process the fractional attainment of equilibrium and is a function of:

$$\frac{Dt}{Dr_0{}^2} ------(2)$$

Where D is the diffusion coefficient of the adsorbate such as crude oil on the water surface, Dt = the distribution coefficient of the adsorbate such as crude oil film and r_0 is the particle radius of the adsorbent such as Kenaf (*Hibiscus cannabinus* L.) plant parts. Therefore, the sorption of a high amount of adsorbate such as crude oil films on water surface is facilitated by a reduction in the size of adsorbate such as crude oil films[16, 9]. Hence, the time needed to attain a given uptake level is not dependent only on the variables such as concentrations, particle size of the adsorbents.

A linear driving force concept was used to develop the relationship:

$$In\ (I - \alpha) = -Kpt ----(3)$$

For a particle-diffusion controlled sorption processes[15] α is the fractional attainment of equilibrium, kp is the rate coefficient for particle – diffusion controlled process, corresponding to particle size of the sorbent t is time and in is a measure of infraparticulate diffusivity. If a plot of in (1-α) versus time results in a linear relationship, then sorption process is particle controlled and diffusivity of adsorbate such as crude oil films onto adsorbent surface is independent of the extent of the sorption.

This study, therefore, reports on the sorption kinetics and intraparticulate diffusivity of kenaf (*Hibiscus cannabinus* L.) plant parts as crude oil films adsorbent on a synthetic sea water environment.

MATERIALS AND METHODS

Sample collection: Kenaf (*Hibiscus cannabinus* L.) plant parts were collected from the botanical garden at Abia State University Uturu. The Kenaf plant parts were identified by a botanist Mr. Chinedu and deposited at plant herbarium until required for analysis crude oil sample (250 mL) was collected from oil flow station at Oguta, Imo state, courtesy of shell petroleum development company, Nigeria. The crude oil sample was identified by SPDC petroleum Chemist as light crude oil with the following characteristics; sulphur content (< 10%), pour point in degree Celsius (-3.5-2.5). All chemical reagents were analytical grades from BDH chemicals, London.

Sample preparation: Crude oil sample (250 mL) was used neat. Kenaf (*Hibiscus cannabinus* L.) plant parts were separated into roots and stems manually. Both roots and stems were air-dried for 72 h. Each portion (root and stems ground into fine power using mortar and pestle. Each kenaf power was sieved using 2 mm-steel sieve and stored in a plastic bottle labeled powered root and stem respectively until required for analysis.

Synthetic sea water: Fifty grams of sodium chloride crystals was weighed and added into one-liter volumetric flask the to the sample was dissolved, use 1 liter of distilled water the one flask was made up to mark to obtain a 5% synthetic sea water.

Adsorption studies: Effect of contact time on crude oil films binding: simulated crude oil spills were carried out using 30 mL each of the 5% synthetic sea water and varying volumes of crude oil. Five glass vessels were set up each containing 30 mL 5% synthetic sea water. Each of these five glass vessels was labeled and each received 0.2, 0.4, 0.6, 0.8 and 1.0 mL of crude oil respectively corresponding to 7, 13, 20, 27 and 30 mg mL^{-1} crude oil simulation spills, respectively. One gram of sieved powdered kenaf plant root each was measures out and uniformly spread over the crude oil films floating in each of the five glass vessels set up. Contact time of 25 min was allowed for each of these five experiment set up. At the each of 25 min contact time interval, the floating adsorbent with its content (s) was scooped into a separating flask and the adsorbed crude oil desorbed using 20 mL chloroform. The desorbed crude oil extracts from each of the five experimental setup was determined using spectrophotometer at 500 nm wavelength[17]. The above experiments were repeated exactly using one gram each of sieved powdered stem part of kenaf plant as the adsorbent. The amount of crude oil adsorbed in mg mL^{-1} in each of the experimental setup was calculated by a direct comparison with standard method approach[18,19].

Equilibrium sorption studies: The equilibrium sorption was studies by calculating the fractional attainment of the equilibrium α for both kenaf root and stem. The fractional attainment α of the equilibrium which is the ratio of the amount of crude oil films adsorbed from the synthetic sea water surface after a certain time t to that removed when sorption equilibrium was attained was obtained using Eq. 1 .The intra particulate diffusivity was also calculated for the two adsorbents namely kenaf root and kenaf stem, respectively.

RESULTS AND DISCUSSION

The results of the uptake level of crude oil as time increase from zero to thirty minutes are shown in Fig. 1, it could be seen that the uptake level of the crude oil by kenaf root increased steady whereas the uptake level of crude oil by kenaf stem increased for a while before it decreases. From Fig. 1 it was observed that the uptake rate increases with time for root to a peak showing that sorption was steady and reached maximum at about thirty minutes. But the uptake of crude oil by the stems decreases with time. Table 1 gives the fraction or ratio of the amount sorbed at any given time (Ct) to the initial concentration (C_o). Table 1 it is easy to calculate the percentage of sorption. The value for root at 20 min, 26.2% is higher than that of stem 20%. It is clearly seen
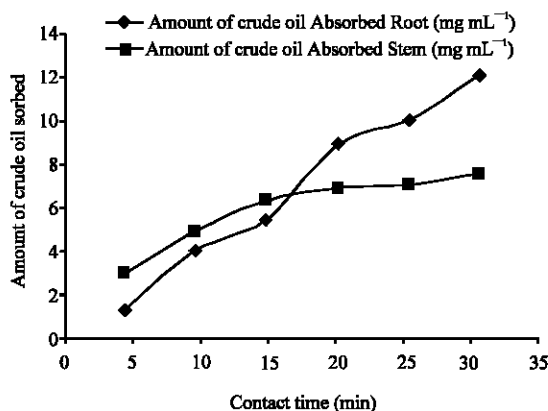

Fig. 1: Effects of Contact time on the Sorption of Crude oil onto kenaf (Hibiscus Cannabinus L.) plarts (mg mL^{-1})

Table 1: Fraction of the amount of crude oil sorbed onto kenaf (*Hibiscus cannabinus*) plant parts

Time (min)	c_t/c_o	
	Root	Stem
5	0. 046	0. 014
10	0.222	0.148
15	0.164	0.188
20	0.262	0.200
25	0.294	0.220
30	0.352	0.224

The data are mean value of four determinations

that at 30 min 35.2% of crude oil spill has been sorbed by the roots of kenaf compared to 22.4% sorbed by the stem of the kenaf. Differential sorption of crude oil by different parts of kenaf (root and stem) has been ascribed to (1) different in the morphology of root and stem of the kenaf plant (2) differences in the storage capacity of roots and stems of kenaf plant.

The fraction attainment of equilibrium (α) was calculation from relationship

$$\alpha = \frac{(M_t)}{(Mo)} = \frac{C_t}{C_o} \ ----(1)$$

Where $(M)_t$ is the concentration of crude oil film at anytime t and (M) is the concentration of crude oil film at infinity, that is equilibrium. The plot of α against time t is shown in Fig. 2. From this figure, it is observe that the value of α change with time t increased from 5 to 30 min. it can be seen that α is higher for root than stem. This value of α has shown that root sorbed more crude oil than stems that also mean that the rate of crude oil sorption by the root of kenaf plant was faster, compared to the stem.

A plot of in (1-α) against time (not shown) for crude oil for the two parts of plant (root and stem) showed straight lines. This means that the sorption process for
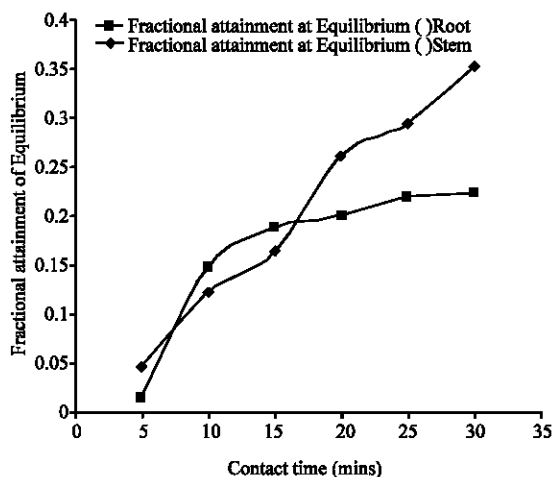
Fig. 2: Fractional attainment of equilibrium (alpha) Vs time for the sorption of crude oil films in kenaf (*Hibsicus cannabinus*) plant parts

Table 2: Rate coefficient for particle-controlled sorption for crude oil onto kenaf (*Hibiscus cannabinus*) plant parts

Crude oil	Root	Stem
Kp $(min)^{-1}$	0.015	0.007

root and stem is particle diffusion controlled. The values of the rate coefficient for particle-diffusion controlled sorption (Kp) is shown in Table 2.

The rate for particle-diffusion controlled sorption of crude oil for stem root are 0.007 and 0.015 min^{-1}, respectively. This gives a measure of the diffusion rate of the crude oil indicating that diffusion rate also affection sorption rate of crude oil using kenaf root and kenaf stem.

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