



**REMOVAL OF CRUDE OIL FROM CONTAMINATED WATER BY ACETYLATED
ORANGE PEEL FIBERS**

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ABSTRACT

Oil spill is one of the most serious pollutants having negative effects on the ecosystem and marine life, with environmentalists facing major challenges in its treatment and in developing alternative methods for its cleanup at low cost. Among different sorbents, agriculture waste is widely used for oil cleanup due to its biodegradability, low cost and availability. This research investigated crude oil sorption from water using acetylated and unacetylated orange peels under mild conditions. The acetylated (treated) and unacetylated (untreated) orange peel sorbents were used to sorb oil from water, and their sorption capacities and isotherms were compared. The effects of adsorbent dosage, contact time, the initial oil concentration and temperature on the oil sorption were studied and results showed higher sorptive capacities by the acetylated orange peels compared to the unacetylated orange peels. Generally oil sorption capacities increased with increasing weight of adsorbents, contact time, oil concentration and decreased with increasing temperature. Equilibrium studies showed that the Langmuir isotherm was the best fit isotherm for oil removal by orange peels.

Key words: Acetylation, adsorption isotherms, hydrophobic, oil sorption capacity, oil spillage, orange peels.

INTRODUCTION

Oil spill is currently viewed as one of the most significant worries on the planet, as it represents an extraordinary danger to natural and marine life. It is from many sources, such as oil transportation, waste disposal, accidents and oil production [1]. When oil is explored, transported, stored and its derivatives are used, there is a danger of spillage that can have a critical ecological effect [2]. Because of its dangerous properties, the whole character of the area

is harmed once a territory has been polluted with oil. Therefore pollution by petroleum oils affects sea life, economy, tourism and leisure activities due to the coating properties of these materials [3].

In Nigeria, oil exploitation has increased the rate of environmental degradation and has perpetuated food insecurity as a result of death of fish and crops as well as loss of farm lands and viable rivers for fishing activities leading to loss of livelihood [4]. The chronic nature of the oil pollution and its associated environmental and social impacts may have an insidious impact on one's physical health (sustained systemic toxicity by oil-related contaminants) and mental health (such as increased risk for high levels of distress) which are different from those of discrete traumatic events [5]. Nigeria's oil industry at present is heavily dependent on foreign experts, international oil companies and other foreign organizations to handle large-scale waste, thus there is an urgent need to develop an indigenous cost-effective method for cleaning up oil based on the environmentally friendly low cost agro-by products.

Nowadays, there is a growing interest in sorbent production from natural organic sorbents for oil spills removal, such as barley straw, rice straw, rice husk, pith bagasse, banana trunk, garlic, onion peel and so on. The direction of interest in developing alternative materials, such as agriculture wastes is the result of the restrictions of other types of sorbent products [6, 7]. Natural plant fibers are lignocellulosic which are comprised of lignins, hemicellulose and cellulose having hydroxyl groups of different reactivity, and its surface is hydrophilic due to the presence of hydroxyl groups [8]. The downsides of these plants fibers when used as sorbents are their poor buoyancy, hydrophilicity and low oil sorption capacity compared to synthetic sorbents [9]. The effectiveness of the sorbents in saturated environments would be enhanced when the density of the hydroxyl functionalities is decreased [10]. When the density of hydroxyl functions reduces, the viability of the sorbents in immersed conditions would be upgraded.

Acetylation reaction has received considerable attention more than any other chemical modification technique known, it consist of chemical reactions between the reactive constituents of the natural fibers (hydroxyl groups) and a chemical reagent forming a covalent bond between the two [11]. This chemical modification promotes the substitution of polar hydroxyl groups found on fiber cell wall by the less polar acetyl groups [12]. Agricultural waste sorbents such as orange peels are abundantly available in different parts of Nigeria, and due to its abundance and easy accessibility, this material can be used as a cheap adsorbent for crude oil sorption in

aqueous medium. To the best of our knowledge, no studies on the sorption of oil using acetylated orange peels and the mechanism of the sorption process have been reported. Therefore the aim of this study is to modify the surface structure of Orange peel fibers by acetylation and to enhance their surface hydrophobicity for subsequent applications as sorbents in crude oil spill cleanup.

MATERIAL AND METHOD

Orange peel fibers were collected from fruit sellers in Sabon Gari local government Area of Kaduna State, Nigeria. The samples were thoroughly washed with distilled water to remove foreign materials and water-soluble components. The washed samples were initially air dried for 12 hrs and then oven-dried to a constant weight at 65 °C for 36 hrs.

After drying, the samples were cut and ground, then sieved with laboratory sieves to obtain homogenous particle sizes using a mechanical sieve shaker which was used to separate the sorbent into the desired particle size of 300 µm.

Sample pre-treatment

To reduce the influence of the fiber extract on acetylation, the sieved materials were extracted with a mixture of acetone and n-hexane (4:1, v/v) as solvents for 5 hrs. The extraction was carried out to remove extractable components from the fibers. After extraction, the samples were dried in a laboratory oven for 16 hrs.

Acetylation of the agro-waste

A portion (20 g) of the sorbent was placed in a 250-mL conical flask containing 120 mL of acetic anhydride and 6 g (1% of the solvent) *N*-bromosuccinimide (NBS). The flask was placed in a temperature-controlled water bath set at 70 °C for 90 min. Then, the conical flask was removed from the water bath and the hot reagent was decanted. The sorbents were thoroughly washed with ethanol and acetone to remove unreacted acetic anhydride and acetic acid by-product. The products were allowed to dry in an oven set at 60 °C for 16 hrs and later cooled in a desiccator and stored in a plastic container prior to analysis and crude oil sorption studies [13].

Oil sorption capacity

The raw and acetylated samples were subjected to crude oil sorption test. In order 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.

To 1 liter of distilled water, 50 g of crude oil was added. A portion (1.5 g) of the sorbent was added into the mixture in the beaker and left unperturbed for 10 min in a water bath at 35°C. After 20 min, the sorbent was removed using sieving net and left to drain by hanging the net over the beaker in an oven for 4 hrs at 60 °C. The drained sample was weighed and recorded. This was varied at different sorbent dosages (1.5, 2.5, 3.5, 4.5 and 5.5 g) at different times, (10, 15, 20, 25 and 30 min) also at different initial concentrations of crude oil (25, 37.5, 50, 67.5 and 75 g/L of water) and at different temperatures (25, 30, 35, 40 and 45°C) [13].

The sorption capacity of the sorbent samples was calculated using the expression

$$\text{Oil Sorption Capacity} = \frac{\text{New Weight Gained (g)}}{\text{original weight (g)}} \dots\dots\dots (1)$$

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

RESULTS AND DISCUSSION

Effect of Adsorbent dosage on crude oil sorption capacity

Results as given in Figure 1 showed that the oil sorption capacities increased readily with sorbent dose as dosage increased from 1.5 g to 3.5 g for both raw and treated orange peel fibers. This was due to the fact that the number of available sorption sites and surface area increased by increasing the sorbent dosage therefore resulting in increase in the amount of sorbed crude oil [14]. There was an initial rapid increase in the amount of crude oil sorbed by modified orange peel fibers from 8.72 g/g to 10.63 g/g as the sorbent dose increased from 1.5 g to 2.5 g. The increase in the oil sorption capacity progressed slowly to 11.12 g/g as the dosage increased further to 3 g. This slow increase could be as a result of less exposure of the remaining available sites for adsorbate binding to occur [15]. Afterwards, this increase slowly proceeded to 11.12 g/g as the dosage increased from 3.5 g.

In general, the oil sorption capacities of the treated orange peel fibers (TOPF) were higher than the untreated fibers (UOPF) as the sorbent dosage increased. This could be due to the

sufficient amount of acetyl groups available for attachment at the hydroxyl group (-OH) sites in the cellulose. As the sorbent dosage increases, the same amount of acetyl groups are available for attachment to the increasing hydroxyl group sites (-OH) sites, hence the oil sorption capacity will increase as the ratio of the acetyl groups to hydroxyl groups (-OH) decreases [13]. The increase in the number of acetyl groups increases the hydrophobicity of the fibers which in turn increases the crude oil sorption.

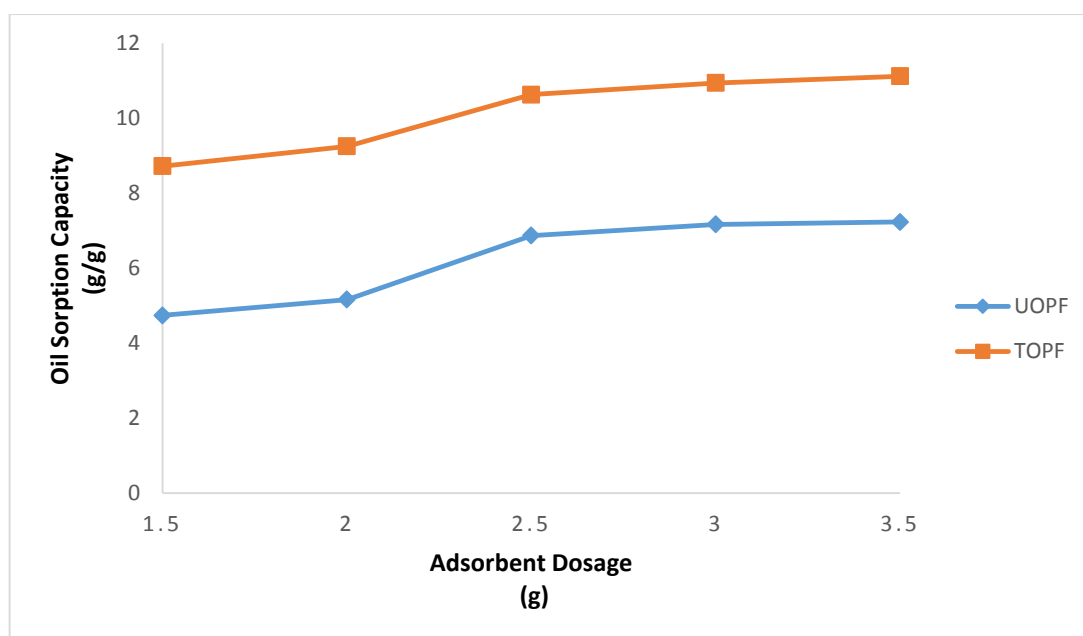


Figure 1: Effect of Adsorbent dosage on the crude oil sorption capacity (OSC) of the sorbents

Effect of contact time on crude oil sorption capacity

The effect of contact time on the sorption of crude oil by untreated and treated orange peel fibers was investigated from 10 – 30 minutes. Figure 2 reveals the oil sorption capacities of both the raw and treated orange peel fibers with respect to contact time. As the contact time increased, there was a corresponding increase in the oil sorption capacity in both raw and treated orange peel fibers. The oil sorption capacity of the treated orange peel fibers increased progressively from 10.22 g/g to 11.84 g/g as the contact time increased from 10 to 30 minutes and its equilibrium was attained at 30 minutes corresponding to 11.84 g/g. The equilibrium sorption may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of the adsorbent [16].

The oil sorption capacity of the raw (untreated) orange peel fibers increased from 6.28 to 7.58 g/g as the contact time increased from 10 to 25 minutes. However, after 25 minutes, the rate of sorption decreased slowly to 7.54 g/g. This could be explained that a large number of vacant surface sites and microscopic voids were available for sorption during the initial stages of the sorption process and after the equilibrium time, there were fewer available vacant sites and would be difficult to be occupied due to repulsive forces between the oil molecules on the solid and bulk phases [17, 18]. Thus, maximum sorption of 7.58 g/g was achieved at 25 minutes for the raw orange peel fibers depicting the optimum time for sorption. Further increase in time after 25 minutes did not bring about any significant improvement because at that time, the sorbed oil residue starts to clog the pores near the outer surface so oil residue can no longer diffuse to the active sites deep within the interior surface. In general, the oil sorption capacities of the treated fibers were higher than the untreated (raw) fibers as the contact time increased.

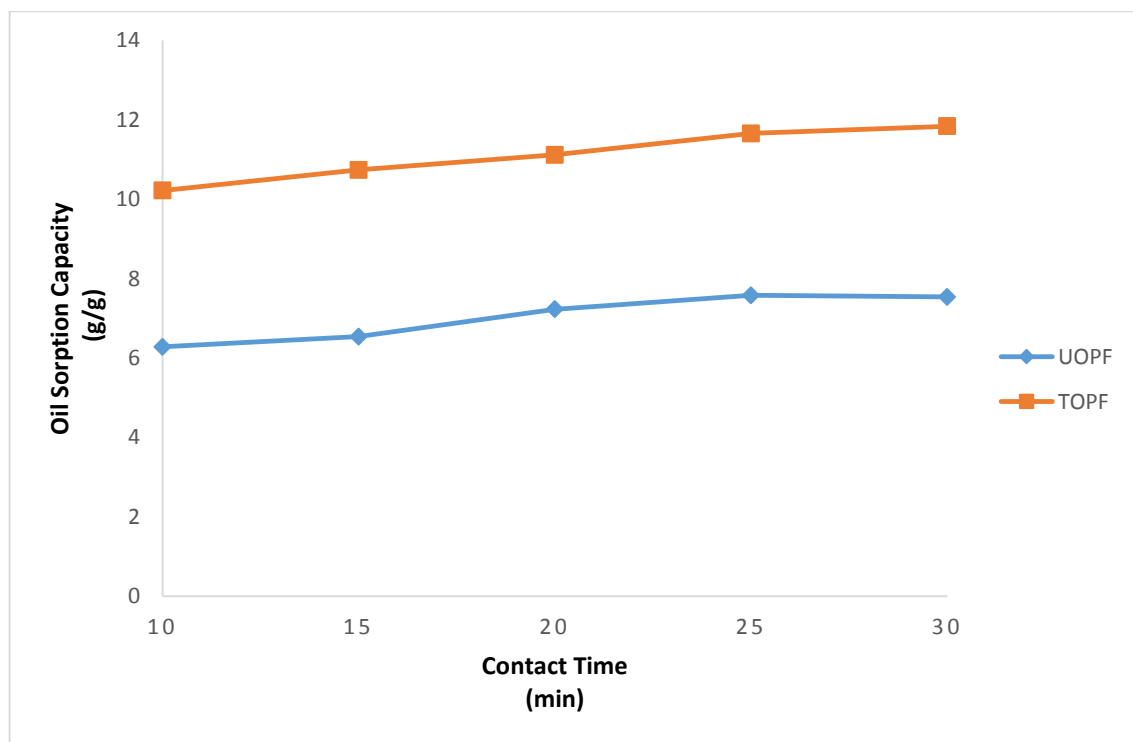


Figure 2: Effect of Contact time on the crude oil sorption capacity (OSC) of the sorbents

Effect of Initial crude oil concentration on crude oil sorption capacity

Figure 3 showed that the oil sorption capacity of the sorbents (untreated and treated) generally increased with increase in the initial crude oil concentration. Untreated (raw) Orange peel fibers achieved equilibrium at 7.85 g/g after which there was a decrease in the oil sorption capacity as the initial crude oil concentration was increased. The decrease experienced by the untreated sorbents after equilibrium could be attributed the fact that at higher concentrations, the oil molecules themselves may be clustered into micelles making the adsorption process more difficult in some of the adsorbent pores [19].

It was also evident from the figure, that the sorption capacities of the treated orange peel fibers were higher than that of the untreated orange peel fibers. The reason for the higher increase in oil sorption capacity of the treated samples can be attributed to absorption of crude oil molecules at the hydrophobic reactive sites and also diffusion into the pores or hollow lumen of the sorbents [20].

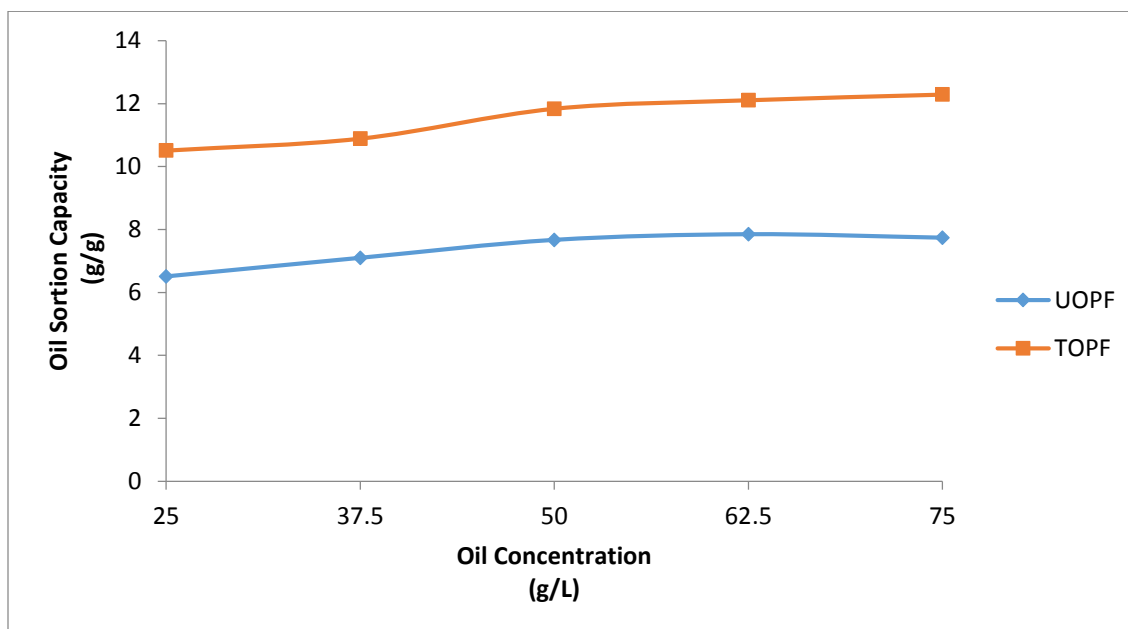


Figure 3: Effect of Initial oil concentration on the crude oil sorption capacity (OSC) of the sorbents

Effect of temperature on crude oil sorption capacity

The effect of temperature on the crude oil sorption capacity of the raw and treated orange peel fibers was investigated over a temperature range of 25°C to 45°C. Since temperature varies in

different areas and seasons, it is a significant factor to be studied in oil spill treatment [21]. It was observed that there was an initial increase in the sorption capacity with increasing temperature for the sorbents. This increase may be due to the decrease in the oil viscosity at higher temperature suitable to penetrate pores and rest between surface roughness until it reached maximum value of oil sorption at 35°C. The increase in oil sorption capacity with increasing temperature could also be due to better interaction between the sorbents and the crude oil, leading to increased diffusion at higher temperatures, with an increase in the temperature resulting in an increase in segmental mobility of the fibers, which would increase the sorption capacity [22].

After equilibrium, a further increase in the temperature led to a decrease in the oil sorption capacity. This may be due to the oil being very light (as a result of increased temperature) which led to its release from the treated sorbent particles again. It may be due the fact that as the temperature rises, the viscosity of the crude oil reduces, its liquidity also increases, and the random motion of the crude oil particles increases which could promote the crude oil particles and the sorbents to collide with each other and may lower the opportunity to oil droplets to be attached on adsorbent surface [23, 24].

In general the oil sorption capacities of the treated fibers were higher than the untreated (raw) fibers as the temperature increased. This could be due to the fact that during the acetylation process, the fiber swells as the reaction proceeds, requiring disruption of the hydrogen bonding network. In addition, the hydroxyl groups of the cell polymers form extensive hydrogen bonding networks with the matrix, and the reaction of the anhydride with the hydroxyl group requires the breaking of a hydrogen bond. So, increasing temperature favors breaking such hydrogen bonds, swelling the fibers, diffusing the esterifying agent and moving the reactant molecules, thus enhancing the reaction rate [25].

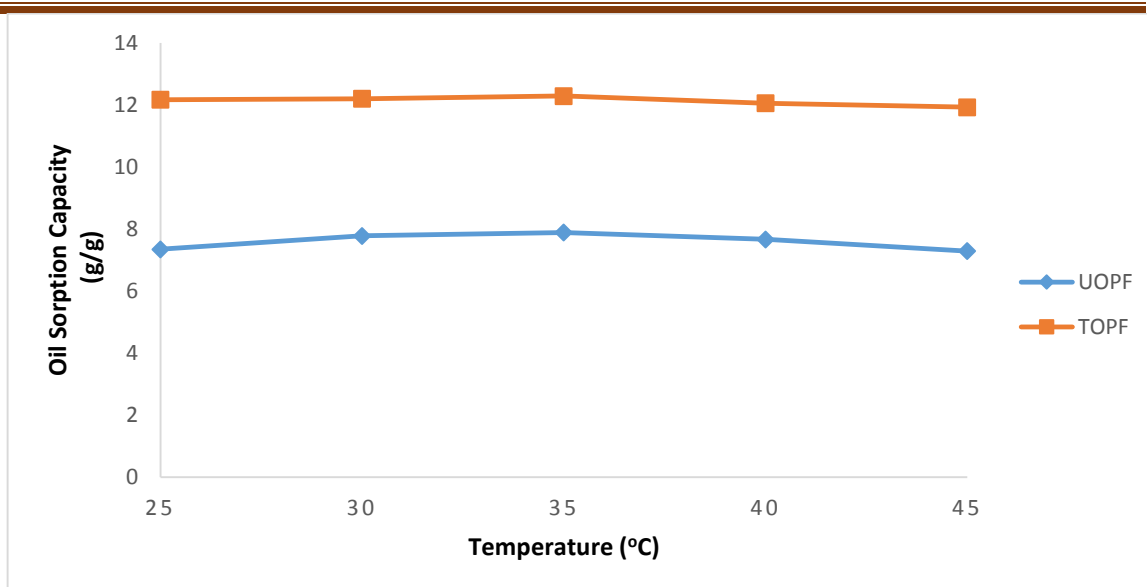


Figure 4: Effect of Temperature on the crude oil sorption capacity (OSC) of the sorbents

Equilibrium adsorption studies

Langmuir Adsorption Isotherm

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model represents the equilibrium distribution of adsorbate molecules between solid and liquid phases, suggesting the formation of monolayer sorption and also energetically homogeneous surfaces [26]. It also assumes that adsorption occurs uniformly on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at that site. Based upon these assumptions, Langmuir represented the following equation

$$qe = \frac{qmaxbCe}{1+bCe} \quad (2)$$

The Langmuir adsorption parameters were determined by transforming the Langmuir equation into linear form:

$$\frac{1}{qe} = \frac{1}{qmax} + \frac{1}{bqmax Ce} \quad (3)$$

Where; q_e is the amount of adsorbate adsorbed per gram of dried adsorbent at equilibrium, q_{max} is the maximum monolayer coverage capacity (g/g), C_e is the amount of oil in water at equilibrium, b the Langmuir constant related to the energy of sorption, is the ratio of

sorption and desorption rates [27]. The values of q_{max} and b were calculated from the intercept ($\frac{1}{q_{max}}$) and slope ($\frac{1}{q_{max} b}$) of the plot $\frac{C_e}{q_e}$ against C_e [28].

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter, R_L , which is a dimensionless constant referred to as separation factor. It is given by

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

Where C_0 is the highest initial concentration of sorbate, and b is the Langmuir constant. The values of R_L indicate the shape of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [29]. The Langmuir isotherm parameters for both raw and treated orange peel fibers are given in Table 1.

The R_L values of the raw and treated fibers for this sorption process were all between 0 and 1, indicating the favourable sorption of crude oil on the fibers. But with the treated fibers having lower R_L values than the untreated fibers, it meant more favourable sorption of the crude oil unto the treated fibers.

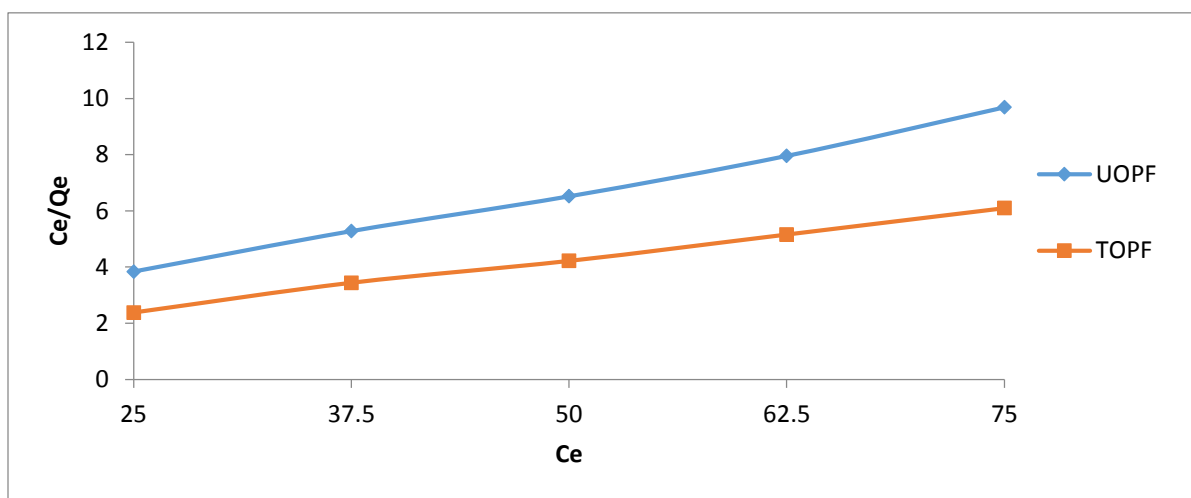


Figure 5: Langmuir Isotherm for the Oil Sorption by the Orange Peel sorbents

Table 1: Langmuir Parameters for the Untreated and Treated Orange peel fibers (OPF)

	R ² value	<i>b</i>	<i>Q max</i>	R _L
Treated OPF	0.9984	8.13	1.67	0.0016
Untreated OPF	0.9967	7.89	1.1	0.0017

Freundlich sorption model

The Freundlich isotherm was applied to estimate the sorption intensity of the sorbent towards the sorbate. One major characteristic of the Freundlich isotherm is its ability to give an appropriate description of equilibrium data over a restricted range of concentration [27, 30]. This isotherm gives an expression which defines the surface heterogeneity and the exponential distribution of active sites and their energies [31]. Crude oil is a mixture of several chemicals and therefore a multicomponent system of interest. The model assumes that the removal of crude oil molecules occurs on a heterogeneous sorbent surface and can be applied to multilayer sorption. The equilibrium data were treated with the linearized Freundlich isotherm by plotting a chart of log *q_e* against log *C_e* as shown in Figure 6. The linearized form of Freundlich sorption isotherm was used to evaluate the sorption data and is represented as

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (5)$$

The magnitude of *K_F* and *1/n* shows easy separation of the crude oil from the contaminated water and high sorption capacity, it determines the steepness and curvature of the isotherm. The *1/n* values should be between 0.1 and 1 or its ‘*n*’ values should be in between 1 and 10 for favorable sorption. In the present study the “*n*” values of the untreated OPF was 5.72 while the treated OPF had *n* values of 6.58. These *n* values indicated favorable sorption for the sorbents (both untreated and treated), but the higher *n* values of the treated fibers indicates much favorable sorption than the untreated fibers and also implies that the treated fibers have a higher affinity for crude oil.

In general, the R² values of the treated OPF were higher than that of the untreated while for both isotherms indicating more favorable sorption by the treated sorbents while the Langmuir

isotherm were higher than the R^2 values of the Freundlich isotherms, indicating that the manner of sorption is monolayered and that the surfaces of the fibers are predominantly homogeneous.

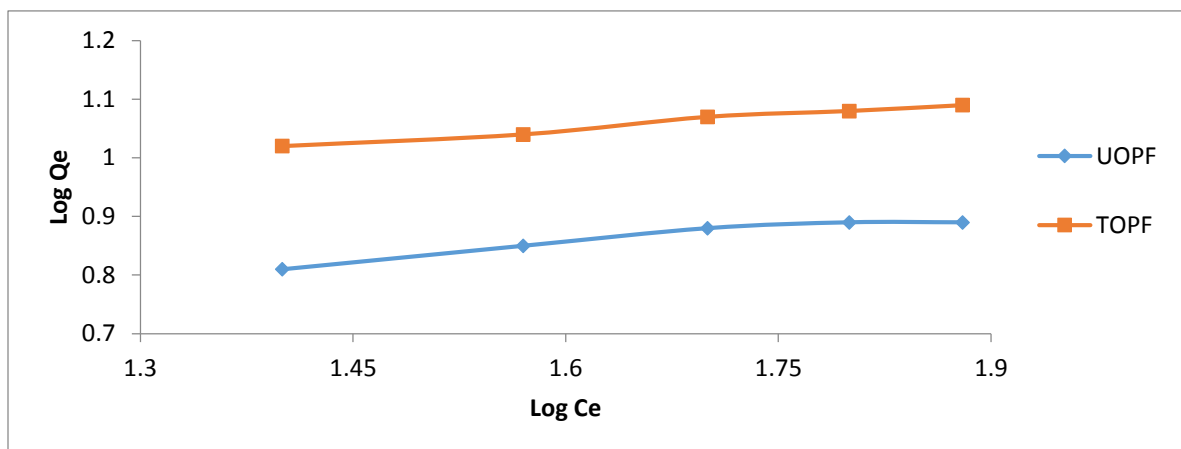


Figure 6: Langmuir Isotherm for the Oil Sorption by the Orange Peel Sorbents

Table 2: Freundlich Parameters for the Untreated and Treated Orange peel fibers (OPF)

	R^2 value	$1/n$	n	K_F
Treated OPF	0.9831	0.15	6.58	6.402
Untreated OPF	0.9365	0.17	5.72	3.734

CONCLUSION

Orange peel fibers were successfully modified by acetylation and used to remove crude oil from water, with the treated (acetylated) peels having higher oil sorption capacity compared to the untreated peels. The crude oil sorption from water using treated and untreated peels was found to be dosage, time, initial oil concentration and temperature dependent, and its sorption process being a monolayered one. Over all, it can be seen that sorption capacity of orange peels gives good result as a new and low cost agriculture waste for oil spill cleanup. Subsequently, the use of orange peels as sorbent not only helps in the lowering of environmental contamination, but also helps in the reduction of agriculture wastes.

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