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Adsorption study on the sorption of crude oil from water using raw/modified pineapple crown

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Abstract
The effect of Crude oil spillage is felt in every aspect of human civilization. Its treatment procedure still remains a challenge to the developing world due to the very high cost of implementation of the existing techniques. In this study, Pineapple Crown which is an eco-friendly, Cheap and easily available agro-waste was chemically modified (APA) for the treatment of oil spillage in aqueous medium and its performance compared with the raw sample (RPA). The characterization of the sample using FT-IR, revealed the suitability of the sorbents for acetylation and sorption process, giving the extent of acetylation as 1.68. Date from the study of the effect of time, dosage and temperature was employed for the study of the kinetic models which then suggested that, sorption process occurs through both pore and surface diffusion mechanisms, the R^2 value generated for RPA was best fitted to Pseudo first order while APA was best fitted to Pseudo second order. The Isotherm study done generated R^2 values best fitted to Temkin with values of 1.000 and 0.999 for RPA and APA respectively thus depicting that the sorption process were both multilayer sorption and endothermic in nature. The thermodynamic study confirmed the physisorption and chemisorption's nature of RPA (18.0KJ/mol^{-1}) and APA (30.7 KJ/mol^{-1}) in the sorption process as well as the endothermic nature as seen the values of enthalpy. The negative value seen in Gibb's energy correlates to the spontaneous nature of the sorption process. The results presented and discussed in this study conclusively projects the acetylated pineapple crown as preferred sorbent material in the treatment of crude oil spillage.

Keywords: crude oil spillage, acetylation, pineapple crown, sorption capacity, kinetic, isotherm, thermodynamics

Introduction

Decontamination of our water sources from Crude Oil pollution is of very high priority due to its modulating effects on the physical and chemical properties of the affected environment. Crude oil as a World energy source has found its usefulness in every aspect of the economy, building the sustenance of civilization and industrialization, through the continuous establishment of manufacturing industries.

The growing demand for Crude Oil amidst feasible renewable energy sources have led to a progressive increase in its exploration hence the heightened level of crude Oil spillage in the environment. Crude oil spillage is considered as an intentional or accidental release of liquid crude Oil to the environment mainly from anthropogenic activities surrounding its processes to its usage (Raimi, Sawyerr, Ezekwe, & Salako, 2022) [31], which are; exploration, extraction, transportation, refining and storage (Nwadiogbu, Okoye, Ajiwe & Nnaji, 2014) [27, 28]. Its presence is an emphatic negative repo-effect on the environment, economy, social, human and organisms (Welch & Joyner, 2010) [42], that must be addressed with effective and efficiency treatment methods (Broekema, 2016) [9]. Some of these treatment techniques employed in the decontamination process are; burning, skimming, use of dispersants and sorbent materials (Sueiro, Garrido, & Araujo, 2011) [37] and (Tamis, Jongbloed, Karman, Koops, & Murk, 2012) [40].

The use of sorption techniques have been considered as the most effective approach for decontamination, therefore evaluation of the nature of the sorbents to be employed based on its oleophilic and its hydrophobic properties (Teas, Kalligeros, Zanikos, Stournas, Lois, & Anastopoulos, 2001) [41] other properties such as its endurability, reusability, biodegradability, high uptake capacity and high selectivity of oil must be considered. However recently, the use of nature sorbent (agro based waste materials) such as; rice straw, peat moss, wood, cotton and many others as sited by (Choi & Cloud, 1992) [11] and (Deschamps, 2003) [13].

Scientist have employed methods such acteylation, cynathylation, benzeylation and methylation (Rowell, Simonson, & Tillman, 1990) [33], of which acteylation has received more recognition than other chemical modification methods known (Rowell, Hess, Placket, Cronshaw, & Dunningham, 1994) [32] as property enhancement procedures dealing with the setbacks imposed by its nature.

This study employed Pineapple Crown as a low cost, easily available and biodegradable agro-waste to be understudied for the efficient application of it as a sorbent material, through optimization of its performance as a sorbent material in the treatment of oil spillage. This research will contribute successfully to addressing the treatment of oil spillage in the environment.

Materials and methods

1. Material preparation

The Pineapple Crowns were obtained from a Local Market (New Market) in Enugu metropolis, Nigeria. The Pineapple crowns were thoroughly washed and dried in Sunlight for 28 hours (4hours for 1 week) and then in the oven at 60^{o}C for 4 hours, in order to remove impurities and moisture content before grinded into powdered form and then sieved using British Standard Sieve (BSS sieve). The Crude Oil was obtained from the Creeks of Delta State, Nigeria and Laboratory simulation of the spilled oil was done using 10g of the Crude oil in a 100ml of the water and then stirred gently for some hours at room temperature and pressure.

2. Pre-Treatment of the sample/ acetylation

The Pre-treatment was done using method described by (Nwadiogbu, Ajiwe, & Okoye, 2016) [26]. Acetylation of Sample. **(**method described by (Sun, Sun, & Sun, 2004) [38] The process was done in the presences of N-Bromo succinimide (NBS) using acetic anhydride, by the combining the pre-treated substrate with the reactant in a ratio of 1:20 (a dried substrate/ml acetic anhydride) at 100ºC, for duration of 1 hour and 1% of catalyst. After heating, the remaining reagent was decanted and sample washed with ethanol and acetone to remove excess acetic anhydride and other by-products. The new product was then dried in the oven at 60ºC for 16hours ready for analysis. The extent of acetylation (EA) was estimated from the region of the vibrational signal of C=O and C-O of the infra-red spectra. It is expressed as the ratio of the intensities (I) of region of C=O and C-O.

3. Batch adsorption protocol

The sorption procedure was carried out using method reported by (Banerjee, Joshi, & Jayaram, 2006) and Oil sorption capacity (g/g) calculated as

$$Sc = \frac{S_{st} - S_o}{S_o} \quad (1)$$

Where S_o is the initial weight of the sample (g), S_{st} is the weight of the sample and oil (g). The amount of oil adsorbed q_e (mg/g) is the calculated using,

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

Where C_o is initial concentration in (mg/l), C_e is concentration at equilibrium (mg/l), V is volume of solution L, M is weight of dry adsorbent in g and q_e is adsorption capacity (mg/g).

Under the batch absorption study of the effect of contact time was done varying time from 1 minute to 20 minutes, study of dosage was done by varying dosage from 0.2g to 1.0g while temperature was done by varying temperature from 30 ºC to 50 ºC, as other variable were left constant.

4. Fourier transform infrared spectroscopy

Characterization of the Raw and Acetylated samples were done at the National Research Institutes for Chemical Technology using FT-IR Shimadzu 8400s spectrophotometer in the of 4000 – 400 cm^{-1}.

Results and discussions

1. Infra-red spectroscopic studies

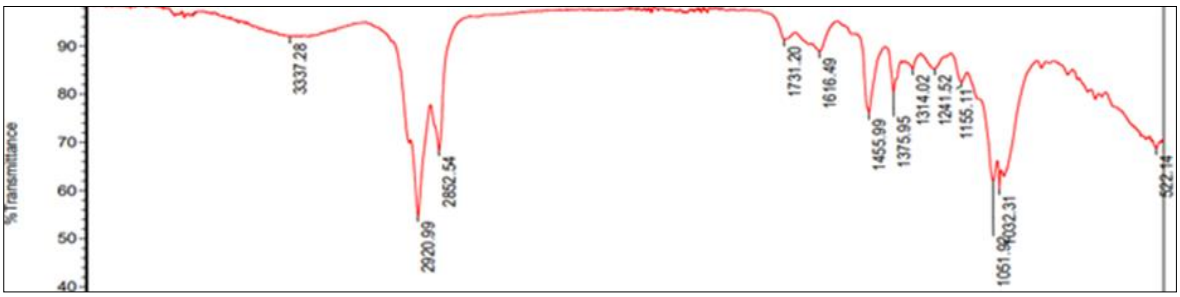
The infra-red spectrum of RPA and APA are represented in Fig 3.1a and b which shows the proposed assignments of the signal bands also represented in Table 3.1 below. The FT-IR results revealed major changes, seen in the spectrum of the acetylated sample as compared with that of the raw sample. An increase in the carbonyl absorption bands at 1731 cm^{-1}(C=O ester ascribed to the hemicelluloses), 1455 cm^{-1} (C=C of the alkene), 1314 cm^{-1} (C-H of –C-CH_3) and 1241 cm^{-1} (C-O of the acetyl group) suggest the formation of ester from acetylation process (Bodirlau & Teaca, 2009) [8]. The observed shift in band regions of the –OH group seen in 3333 – 3337 cm^{-1}, 1633 – 1616 cm^{-1}, 1317 – 1375 cm^{-1}, 1159 – 1155 $cm^{-1}$and 1032 – 1051 cm^{-1} indicates bond breakage or formation, thus confirming the occurrence of a chemical reaction. (Devi & Saroha, 2014). The –OH out of plane at 1455, 1314, 1155, 1159, 1032 and 552 cm^{-1} are indicates that reduction took place at the hydroxyl group after reaction (Adebajo & Frost, 2004)). The extent of acteylation calculated from the spectrum of the acetylated pineapple crown sample is given as;

$$EA = \frac{I\,1731}{I\,1032} = 1.677 \quad (3)$$

The value 1.677 is the extent of acetylated calculated for pineapple crown, which is close that recorded for corncob by (Nwadiogbu, Okoye, Ajiwe & Nnaji, 2014) [27, 28] and consistence with various results reported by literatures.

Table 1: Results of the FT-IR Spectra

Band Positions (cm^{-1})		
RPA	**APA**	**Proposed Signal Group**
3333	3337	-OH stretching of the hydroxyl group of cellulose
2917	2920/2852	C-H stretching of CH_3-O group of the cellulose
-	1731	C=O of ester ascribed to the hemicelluloses
1633	1616	C=O of ester.
-	1455	C=C of alkene.
1317	1375/1314	C-H out of place of O-C=O-CH_3 group of acetyl
-	1241	C=O stretching of acetyl group of lignin.
1159	1155	C-O-O anti symmetry bridge from the carboxylate Group stretch of cellulose / hemicelluloses.
1032	1051/1032	C-O stretching vibration of the cellulose, Hemicelluloses and primary alcohol.
-	552	-OH out of plane bending



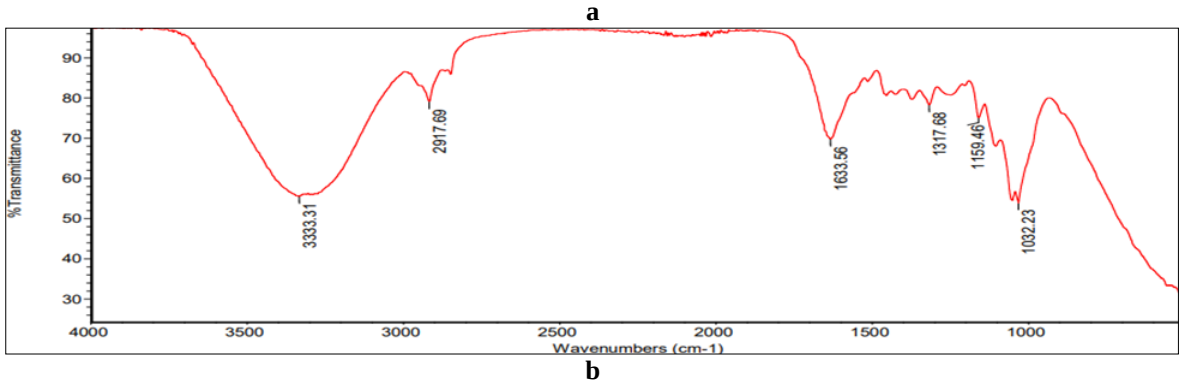


Fig 1: FT-IR spectrum of a) APA and b) RPA

2. Effect of Contact Time, Dosage and Temperature

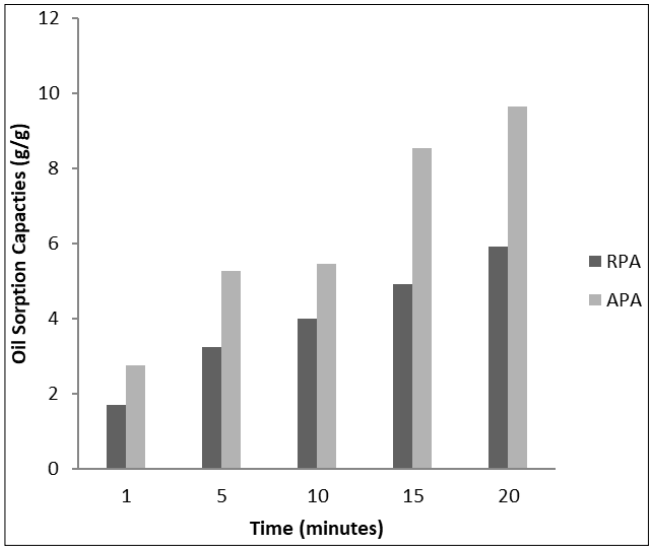


Fig 2: OSc against Time for RPA and APA

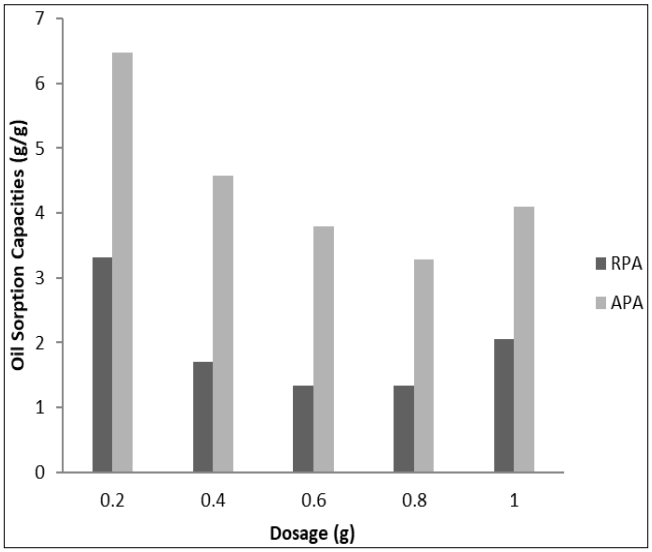


Fig 3: OSc against Dosage for RPA and APA

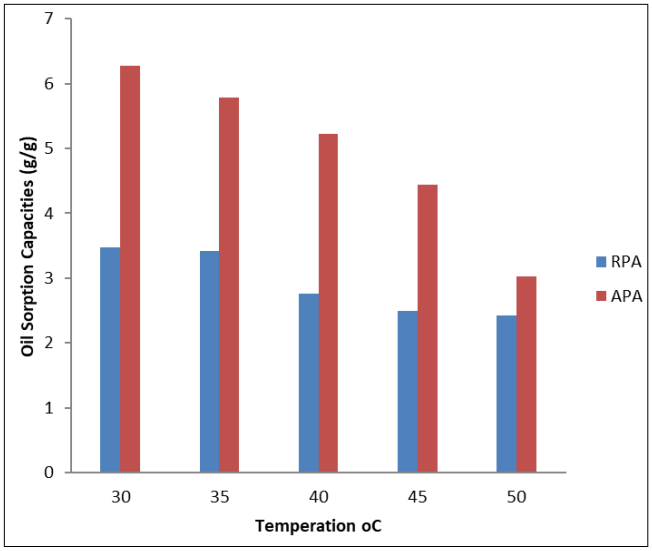


Fig 4: OSc against Temperature for RPA and APA

Fig 3.2 represents the trends of crude oil sorption onto the sorbents RPA and APA. A steady increase in the sorption capacities is observed as the sorption contact time increases from 1minute to 20 minutes. The maximum OSc was observed at the maximum contact time 20 minutes for RPA and APA as 5.91 g/g and 9.66 g/g, this is as a results large amount of available attachment sites and the movement of the sorbate into the inner microscopic pore of the materials. (Dawodu & Akpomie, 2014). For the entire period sorption, APA had a better performance with higher sorption capacities at each recorded time compared with that of RPA. This must be due to the enhanced hydrophilic properties, thus creating more room for oil-sorbent attachment. (Bayat, Aghamiri, Moheb & Vakili-Nezhaad, 2005) [7].

The relationship between Time and oil sorption capacity is expressed using a statistical predictive tool involving regression as seen in (Nwadiogbu, Okoye, Ajiwe & Nnaji, 2014) [27, 28] using SPSS version 26, thus showed strong R^2 values 1and lower Standard error of standard (SEE) for RPA as 0.012.

$$OScRPA = 0.003t + 4.804Sd - 20.577So + 4.252\ ,\ R^2 = 1,\ SEE = 0.012 \quad (3)$$

$$OScAPA = 0.052t + 4.020Sd - 13.831So + 3.402,\ R^2 = 1,\ SEE = 0.241 \quad (4)$$

The study of the effect of dosage on the sorption of crude oil was represented in Fig 3.3 observing the trend of OSc against dosage for both RPA and and APA, a steady decrease is seen from 0.2 to 0.8 g, this could be as a result of overlapping or accumulation at the adsorption sites (Dawodu & Akpomie, 2014). At 0.8 to 1.0 g an increase was seen, this is due increase in available active binding sites as result of increase in dosage (Zafar, Nadeem & Hanif, 2006) [43]. However the maximum sorption capacities

were observed at 0.2g as 3.32 g/g and 6.48 g/g while minimum sorption capacities was seen at 0.8 g as 1.33 g/g and 3.29 g/g for RPA and APA respectively An overview of the general performance of both sorbents places APA as a better sorbent material, this is due the chemical modified of the sorbent material giving it an enhanced hydrophobic nature. The statistical predictive tool developed from linear Regression showed the relationship between Dosage and Oil Sorption Capacities of both Sorbents as;

$$OScRPA = 1.217sd - 4.078\,So + 3.272,\ R^2 = 0.418, SEE = 0.889 \quad (5)$$

$$OSCAPA = 1.552Sd - 6.603So + 1.792,\ R^2 = 0.874, SEE = 0.558 \quad (6)$$

From equation 5 and6 stronger R^2 and lower SEE value is seen in APA compared with those of RPA.

The tends as observed in Fig 3.4, showed that increased temperature was not favorable to the entire sorption process due to the declined pattern observed in the oil sorption capacities with increased temperatures for both sorbents (RPA and APA). The maximum sorption capacities were at 30ºC with values of 3.48 g/g and 6.27 g/g. However this observed pattern was as a result of the nature of the absorbate (Crude oil) having its volatility in the presences of heat been the major factor. Critical evaluation of the entire sorption process revealed that APA had a lead on performance when compared with RPA. Similar trend was observed with (Olufemi & Otolorin, 2017) [29] in the sorption of crude oil using mango shell and mango shell activated carbon. Strong R^2 and very low SEE are observed in the predictive equation 7 and 8 below.

$$OSc\,PA_{(R)} = 0.010T + 5.703Sd - 9.113So + 0.989,\ R^2 = 1.000, SEE = 0.0036 \quad (7)$$

$$OScPA_{(A)} = -0.003T + 4.756Sd - 21.953So + 4.741, R^2 = 1.000, SEE = 0.0118 \quad (8)$$

3. Kinetic studies

This study analyses the rate and mechanisms involved in the sorption of crude oil onto RPA and APA samples. Five kinetic models were applied in this study; Pseudo first order model, Pseudo second order, Elovich, intraparticle diffusion and liquid film diffusion models.

Pseudo first order model represented by this equation;

$$In\,(q_e - q_t) = Inq_e - K_1 t \quad (9)$$

Where q_t (mg/g) is the amount of absorbate adsorbed at time t (minutes) and q_e is the amount of absorbate adsorbed at equilibrium. The graph of $In(q_e - q_t)$ was against time t (minutes) is plotted and the slope and intercept obtained as a function of this graph to generate the rate constant q_e and other values.

The pseudo second order model can be expressed as (Ho & McKay, 1999) [20]

$$T/q_t = \frac{1}{K_2 q_e^2} + t/q_e \quad (10)$$

Where k_2 (g/mg s^{-1}) is the rate constant of this pseudo second order, q_e and k_2 values also calculated from the slope and intercept of a linear plot of t/q_t against time t (minutes)

The involvement of Elovich model which is mathematical expression is seen as;

$$q_t = {}^1/_\beta\, In\,(\alpha\beta) + {}^1/_\beta\, Int \quad (11)$$

Where q_t(mg/g) is the adsorption capacity at time t(mins), α(mg/g/min) is the initial rate of adsorption. B(g/mg) is the adsorption constant. A plot of q_t against Int gives a linear equation where α and β are determined from the slope and intercept.

The Intraparticle diffusion model can be expressed as (Weber Jr & Morris, 1963)

$$q_t = K_d . t^{1/2} + C \quad (12)$$

where k_d(mg/g$s^{1/2}$) is the rate constant and the slope obtained from a plot of q_t against $t^{1/2}$ and C is the intercept obtained from the linear plot of q_t against $t^{1/2}$ which indicates the presences of boundary layer effect, it shows the thickness of the boundary layer, hence as the value of the intercept increases, the boundary layer effect is greater (Kavitha & Namasivayam, 2007). Another important mechanism involved in movement of the adsorbate from liquid phase to solid phase is the liquid film diffusion which its equation can be expressed as (Taffarel & Rubio, 2009)

$$In(1 - F) = -K_{fd} . t \quad (13)$$

Where F is the fractional attainment of equilibrium and its obtained by this, q_t/q_e and K_{fd} ($meq^{-1}s^{1/2}$) is the rate constant derived from a plot of In(1-F) against t.

Table 2: Kinetic results

Kinetic Models	RPA	APA
$q_{e\ exp}$ (mg/g)	5995	9805
Pseuso first order		
$q_{e\ calc}$ (mg/g)	4760.0	10016.6
K_1 (s^{-1})	0.105	0.169
R^2	0.964	0.741
Pseudo second order		
$q_{e\ calc}$ (mg/g)	-	12500
K_2 (s^{-1})	-	-
R^2	0.943	0.827
Elovich		
B (g/mg)	0.00076	0.0005
α (mg/g/mins)	4.1 x 10^3	8.9 x 10^3
R^2	0.934	0.768
Intraparticle diffusion		
Kd (megg$^{-1}s^{1/2}$)	1178	1838
R^2	0.987	0.874
C	578.4	1328
Liquid film diffusion		
Ked (megg$^{-1}s^{1/2}$)	0.105	0.169
R^2	0.965	

Table 3.2 represents the kinetic study results for RPA and APA. It is observed from the Table above that the coefficient regression value for RPA of Pseudo first order 0.964 is higher than the R^2 value for Pseudo second order as 0.943, thus implying that the sorption for the raw pineapple crown is physisorption, similar to results reported by (Liman, M., Pendo, Yakubu, & Umaru, 2022) while APA had R^2 value for Pseudo second order as 0.827 higher than that of Pseudo first order 0.741, hence indicating that the absorption process for the acetylated was governed by chemisorptions. This similar to results seen in (Adegoke,

Adekola, Olowookere, & Yaqub, 2017) [2]. This shift from pseudo first order in the raw to Pseudo second order in the acetylated must be due the chemical modification of the pineapple crown. The R^2 values of Elovich model (0.934 and 0.768 for RPA and APA respectively) were lower than those of Pseudo first and second order model so it cannot be used to classify the sorption process as chemisorptions but with values greater than 0.5 could be an indicator that the sorption process might be multilayer sorption.
Intraparticle diffusion revealed R^2 values for RPA and APA as 0.987 and 0.874 which were greater than that of Liquid film diffusion as 0.965 and 0.742 thus indicating that the absorption is more of pore penetration than that of surface diffusion. Although the large intercept observed RPA and APA as 578.4 and 1328 show that intraparticle diffusion is not the only limiting step in the sorption process, it is also governed by surface diffusion.

4. Isotherm studies
In this study, sorption of crude oil onto the composites were evaluated using three models; Langmuir, Freundlich and Temkin isotherm models.
The langmiur isotherm model was used to describe the adsorption phenomena and is based on the assumption that adsorption occurs uniformly on the active sites of absorbent, also once an adsorbate occupies a site no further sorption can occur at that site (Nwadiogbu, Ajiwe & Okoye 2016) [26].
It classifies the sorption into a monolayer adsorption process and its equation is mathematically expressed as; (Malik, 2004

$$\frac{c_e}{q_e} = \frac{1}{K_l q_m} + \frac{1}{c_e} \quad (14)$$

Where q_e is the amount adsorbed per a unit weight of adsorbent at equilibrium (mg/g), C_e is the concentration of crude oil(mg/l), q_m is the max adsorption capacity and K_L is the adsorption equilibrium monolayer constant (L/mg).
A plot of $1/C_e$ against $1/q_e$ gives a linear equation from where the factors of the equation are obtained as;

$$R_L = \frac{1}{1+K_L C_o} \quad (15)$$

Where C_o is the initial concentration of the crude oil, K_L is the Langmuir constant. This R_L value signs the nature of the adsorption as;
$R_L > 1(unfavourable), 0 < R_L < 1(favourable)$ and $R_L = 0(irreversible)$

The second model, Freundlich has its equation as expressed by (Burton, Stensel, Metcalf, & Eddy Inc Tchobanoglous, 2003

$$logq_e = logK_f + \frac{1}{n} logC_e \quad (16)$$

A linear graph of log qe versus log Ce gives the slope and intercept, from where 1/n and log K_f is obtained respectively. Where q_e is the quantity of adsorbate per mass unit of the adsorbent (mg/g) C_e is the equilibrium concentration of the adsorbate (mg/l) while K_f is the affinity of the adsorbate towards adsorbent $(L/mg)^{1/n}$ and 1/n is the adsorption intensity or surface heterogeneity. The value 1/n ranges between 0 and 1, so the adsorption becomes more heterogeneous as 1/n value gets closer to zero.

Finally, Temkin isotherm model equation is expressed as (Temkin & Pychev 1939);

$$q_e = BIn(A) + BIn(C_e) \quad (17)$$

Where $B = \frac{RT}{b}$ (j/mol) as Temkin constant related to the heat of sorption, A is the Temkin isotherm equilibrium binding constant (L/g). R is the universal gas constant (8.314 j/mol) and T is absolute solution temperature (^oK). the constant A and B are calculated from the intercept and slope of the linear graph of qe versus Inc_e.
However, positive values of B indicates an endothermic reaction while negative values indicates exothermic reaction in a sorption process (Edet & Ifelebuegu, 2020) [15].

Table 3: Isotherm Results

Isotherm Model	RPA	APA
Langmuir		
q_o	0.152	0.413
B	0.615	0.579
R_L	0.000016	0.00073
R^2	0.107	0.458
Freundlich		
K_f	$3.72x10^{38}$	$3.x10^6$
1/n	-7.167	-0.643
R^2	0.597	0.003
Temkin		
B(KJmol^{-1})	-46.98	-45.72
A(Lmg^{-1})	3.163	3.163
R^2	1.000	0.999

The Isotherm study generated regression values (R^2) for RPA and APA as seen in Table 3.3 above as best fitted to Temkin isotherm model with values ranging from 1.000 to 0.999 which are greater than those of Langmuir and Freundlich as 0.107/ 0.597 and 0.458/0.003 for RPA and APA. This implies that the sorption process was multilayer sorption. The negative value observed in the B values (heat of sorption) is an indicator that the sorption process is governed by endothermic reaction.

5. Thermodynamic study
The thermodynamic parameter of Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are used in the determination of spontaneity of the adsorption process, the nature of the adsorption process and also the adsorbent applicability.
The parameters of thermodynamic are evaluated using this expression seen in (Huang, Chen, He, Tang, Zhu, & Zhang, 2015) [21],

$$\Delta G = -RTInK \quad (18)$$

$$\Delta G = \Delta H - T\Delta S \quad (19)$$

The values of ΔH and ΔS are calculated from the slope and intercept of the linear plot of Ink versus 1/T.
A negative value of ΔG (Gibb's energy) at all temperatures in indicates spontaneity of the adsorption process while

otherwise indicates non-spontaneity in the adsorption process. Also values below 20 (KJ/mol) in the value of ΔH indicates physisorption, 20 to 80 (KJ/mol) indicates the presence of both physisorption and chemisorptions while above 80(KJ/mol) is only chemisorptions (Fabian, Aloysius, & Abiola, 2014) [16] while a negative of ΔH implies the nature of the reaction is exothermic while if the value is positive it is an endothermic reaction (Edet & If elebuegu, 2020). ΔS (entropy) elicits the degree of randomness of the reaction, if a positive value is obtained; this implies increased randomness and good affinity.

Table 4: Thermodynamic Results

				ΔG (KJ/mol)				
Samples	ΔH	ΔS	R^2	303K	308k	313k	318k	323k
RPA	18.0	0.081	0.967	-6.54	-6.95	-7.35	-7.76	-8.16
APA	30.7	0.117	0.895	-4.75	-5.34	-5.92	-6.51	-7.09

The results seen in Table 3.4 above, showed ΔH enthalpy as positive with value of 18.0 KJ/mol^{-1} for RPA hence confirming the sorption process as physisorption and APA as 30.7 KJ/mol^{-1} thus making the process chemisorptions. The positive value seen in the enthalpy is an indicator that the process is endothermic, this is in correlation with the results obtained from the isotherm study. Similar results are recorded (Shokry, Elkady, & Salama, (2020) and (Fabian, Aloysius, & Abiola, 2014) [16]. The entropy ΔS, showed a positive-values of 0.081 and 0.117 for RPA and APA respectively, this shows increases in disorderliness or randomness of the system with great affinity between the sorbent and sorbate. ΔG Gibb's energy reported negative values thus showing the spontaneous nature of the sorption thus similar to those in (Atef & Waleed; 2009) [3]

Conclusion

This study unveils the potential in Pineapple crown as a good sorbent of an agro by-product for the treatment of crude oil spillage. The enhancement of the hydrophobic nature using acetic anhydride further confirms better sorption behavior in the field of environmental treatment procedures. The sorption of crude oil is observed to occur by both surface and pore penetration, as well as multilayer sorption, as seen in the data generated in the isotherm study been best fitted to Temkin isotherm model. The results also indicated that after acetylation the sorption process shifted from physisorption as reflected by the data generated for RPA to chemisorptions, as data for APA were in correlation with Pseudo second order reaction. The thermodynamic study conclusively confirms the sorption process of RPA and APA as physisorption and Chemisorption respectively, governed by endothermic reaction as elicited by the enthalpy data. The observed negative values of Gibb's energy (ΔG) showed the spontaneous nature of the sorption process. Hence better adsorption performance seen in the acetylated pineapple crown makes it a feasible, effective, low cost and eco-friendly sorbent alternative in the treatment of crude oil spillage.

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