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Optimization studies on the sorption of crude oil onto silver nano composites of pineapple crown

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Abstract
Oil spillage has posed a tremendous negative effect to the world today, as it has challenged the world's economy and ecosystem. The world's governing bodies and scientists have been on a quest to develop new low-cost and effective techniques in the area of addressing this challenge. This study compared the performance of raw and acetylated silver nano-composites of pineapple crown (AgNRPA and AgNAPA) as an eco-friendly and effective material for the sorption of crude oil from aqueous medium. The sorbents characterization using FT-IR spectrum showed functional groups that enabled the sorption process. The kinetic study done revealed that the sorption process was governed by pore and surface penetration, as well as chemisorption, justified by the R^2 values of 0.945 and 0.992 for AgNRPA and AgNAPA as best fitted to pseudo second order model while the isotherm study done generated data of 1.000 and 0.999 for AgNRPA and AgNAPA respectively as best fitted to Temkin isotherm haven sampled three isotherm models; Langmuir, Freundlich and Temkin models thus revealing the sorption process as multilayer and endothermic. Thermodynamic study described the sorption process chemisorption and endothermic in nature as seen by data generated for the enthalpy as 82.6 and 25.5 (KJ/mol). Its positive values observed in the entropy change showed that there is an increase in the degree of disorderliness of the system while the negative values of the Gibb's energy revealed that the absorption process was spontaneous in nature. The statistical analysis done using SPSS version 26 successfully created predictive equations for the oil sorption capacities under varying conditions and revealed the existing relationships between the variables in this study. There-fore the successful application this material in their modified nano-composite form as seen in this study can be use in addressing the problem of oil spillage in the marine regions.

Keywords: crude oil spillage, adsorption, pineapple crown, acetylation, silver nano-composite

Introduction

The discovery and exploration of crude oil has driven human evolution till date, leading to the sustenance of civilization and industrialization. Thereby exposing the environment to its negative effect from the direct or indirect release of liquid crude oil as a result of human activities surrounding the its exploration (Adeyanju, 2004) [3] and (Raimi, Sawyerr, Ezekwe, & Salako, 2022) [27]. This release of liquid crude oil is known as oil spillage. Although the importance of crude oil cannot be over emphasized, its negative effect is felt, in the health of the ecosystem and the biota especially in the coastal regions. Areas affected with oil spillage are known to have very high mortality of the plants and animals, which translates to the health and occupation of the human in that region (Bamidele and Agbogidi, 2007; Osuji, Erondu and Oguli, 2010) [6, 26]. Therefore the necessity to decontaminate our water bodies from this pollutant should not be undermined.

Over the years, responds methods for the treatment of this oil spillage in the affected coastal region ranges from the use of skimming, booming, burning to application of dispersants (Sueiro, Garrido, & Araujo, 2011) [32] and (Tamis, Jongbloed, Karman, Koops, & Murk, 2012) [35]. But recently there is a growing use of adsorbents due to their high adsorptive capacity on sorption process. Various literatures have review great potentials in the use of organic sorbent material for sorption procedures due to their biodegradable nature, easily availability and low cost (Adebajo, Frost, Kloprogge, Carmody & Kokot; 2003) [2]. Such material like groundnut shell, banana stalk, oil palm fruit fiber, rice husks, mango peels, cocoa pod husks (Olasehinde, Abegunde & Adebayo, 2020) [24] and even the use of the by-products of pineapple as seen in this study have been effectively use in treatment processes.

This 21st century has brought to light the remarkable potentials in the use of nanoscience and nanotechnology for the treatment of environmental pollution (Rickerby & Morrison, 2007) [28] and (Brumfiel, 2003) [9]. This is as a result of its improved surface area, much higher efficiencies and faster adsorption rates in water treatment (Sadegh, Ghoshekandi, Masjedi, Mahmoodi & Kazemi, 2016) and (Dil, Ghaedi & Asfaram, 2017) [30, 13]. Literatures has revealed its successful application in the treatment of industrial effluents, groundwater, surface water and drinking water (Sadegh, Ghoshekandi, Masjedi, Mahmoodi & Kazemi, 2016) [30] and (Savage & Diallo, 2005) [31], without altering both the physical and chemical properties of the area of its application. Scientists have further enhanced it performance ability by combining nanoparticles with agro-waste as recorded in (Murgueitio, Cumbal, Abril, Izquierdo, Debut, & Tinoco, 2018) [21] and (Akpomie & Conradie, 2021) [4]. Its successful application is taking environmental treatment procedure to a whole new level. Hence this study combined pineapple crown in its raw and acetylated forms with silver nanoparticles for the removal of oil spillage from aqueous medium with the aim of evaluating its efficiency. The success of this study brings to birth a new, low-cost and effective means of addressing the issue of oil spillage in the coastal regions.

Materials and Methods

1. Sample preparation

The Pineapple Crowns were obtained from a Local Market (New Market) in Enugu metropolis, Nigeria. The sorbent was thoroughly washed and dried in Sunlight for 28 hours (4hours for 1 week) and then in the oven at 60ºC for 4 hours, in order to remove fungi, dust and reduce moisture content before processing 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 carried out using 10g of the Crude oil in a 100ml of the water and then stirred gently for some hours at room temperature and pressure. The other reagents and chemicals were obtained from British Drug House (BDS).

1.1. Acetylation of the Sorbent

Pre-treatment of the Sorbent was done using method described by (Nwadiogbu, Ajiwe, & Okoye, 2016) [22] while acetylation was done using method prescribed by (Sun, Sun, & Sun, 2004) the process was carried out in the presences of 1% N-bromosuccinimide (NBS) using acetic anhydride, by combining the pre-treated extract with the acetic anhydride in a ratio of 1:20 at a temperature of 100ºC, for duration of 1 hour, after which the excess reagent decanted and sample was 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.

1.2 Synthesis of Silver Nano Composite

The synthesis was done following method described by (Akpomie & Conradie, 2021) [4]. 100ml of 25mM $AgNO_3$ solution was poured into a beaker, stirred for 30minutes with a magnetic stirrer at 30ºC. Then 10g of the raw and acetylated powder samples were measured and added to the $AgNO_3$solution with continuous stirring for about 2hours to biogenic reduction and stabilization of the $AgNO_3$ to silver nanoparticles. Then chemical reduction done by adding 3ml of 1% trisodium citrate and stirred for another 8 hours, then allowed to rest for 30minutes. The solution was centrifuged for 1 hour at 8000rpm, after which the composites were washed with excess water until the pH was neutralized, then centrifuged again. They were oven dried for another 24hours at 70ºC. The samples were then pulverized to fine powder before been sieved through a 100µm mesh screen.

2. 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}.

3. Batch Adsorption study

The sorption procedure was carried out using method reported by (Banerjee, Joshi, & Jayaram, 2006). Oil sorption as;

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

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 this study the effect of time was studied by varying time from 1minutes to 20minutes, Dosage from 0.2g to 1.0g while temperature from 30^0C to 50^0C.

4. Statistical analysis

Statistical package for the social sciences (SPSS) version 26 was used for the statistical analysis of obtained data.

5. Kinetic study

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;

$$In\,(q_e - q_t) = Inq_e - K_1 t \quad (3)$$

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)

The pseudo second order expressed as (Ho & McKay, 1999) [17]

$$t/q_t = \frac{1}{K_2 q_e^2} + t/q_e \quad (4)$$

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)

Elovich model is mathematical expression is seen as;

$$q_t = 1/\beta\, In\,(\alpha\beta) + 1/\beta\, Int \quad (5)$$

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

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

$$q_t = K_d . t^{1/2} + C \quad (6)$$

And the liquid film diffusion which its equation can be expressed as (Taffarel & Rubio, 2009) [34]

$$In(1 - F) = -K_{fd} . t \quad (7)$$

where k_d(mg/g$s^{1/2}$) is the rate constant for intraparticle diffusion model where the slope is 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 showing the thickness of the boundary layer, hence as the value of the intercept increases, the boundary layer effect is greater (Kavitha & Namasivayam, 2007) [20]. While F is the fractional attainment of equilibrium liquid film diffusion model and its obtained from, q_t/q_e. K_{fd}

($meq^{-1}s^{1/2}$) is the rate constant derived from a plot of In(1-F) against t.

6. Equilibrium study

In this study, three models were applied for the evaluation of the sorption process. They are; Langmuir, Freundlich and Temkin isotherm models.

The langmiur isotherm model is mathematically expressed as; (Malik, 2004)

$$\frac{1}{q_e} = \frac{1}{k_l q_m} \cdot \frac{1}{c_e} + \frac{1}{q_{max}} \quad (8)$$

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). These are obtained from the plot of $1/C_e$ against $1/q_e$

The separation factor R_L which is a fundamental characteristic of Langmuir, mathematically expressed as; (Hameed, Chin & Rengaraj, 2008) [16].

$$R_L = \frac{1}{1 + K_L C_o} \quad (9)$$

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 $R_L = 0(irreversible)$.

Freundlich isotherm model equation as expressed by (Burton, Stensel, Metcalf, & Eddy Inc Tchobanoglous, 2003

$$logq_e = logK_f + \frac{1}{n} logC_e \quad (10)$$

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.

Temkin isotherm model is mathematically expressed as (Temkin & Pychev 1939);

$$q_e = BIn(A) + BIn(C_e) \quad (11)$$

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.

7. Thermodynamic study

The thermodynamic parameters of Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are used in the determination of the nature of the sorption process as data used are obtained from the study of the effect of temperature. Its mathematical expression is obtained from; (Huang, Chen, He, Tang, Zhu, & Zhang, 2015) [18]

$$\Delta G = \Delta H - T\Delta S \quad (12)$$

Where T is the temperature in Kelvin, R is the ideal gas constant (8.314 J/molK).

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. ΔH values below 20 (KJ/mol) indicates physisorption, 20 to 80 (KJ/mol) indicates both physisorption and chemisorptions while above 80(KJ/mol) is only chemisorptions (Fabian, Aloysius, & Abiola, 2014) while a negative or positive of ΔH implies the nature of the reaction is either exothermic or endothermic reaction (Edet & Ifelebuegu, 2020) [14]. ΔS (entropy) elicits the degree of randomness of the reaction.

Results and discussion

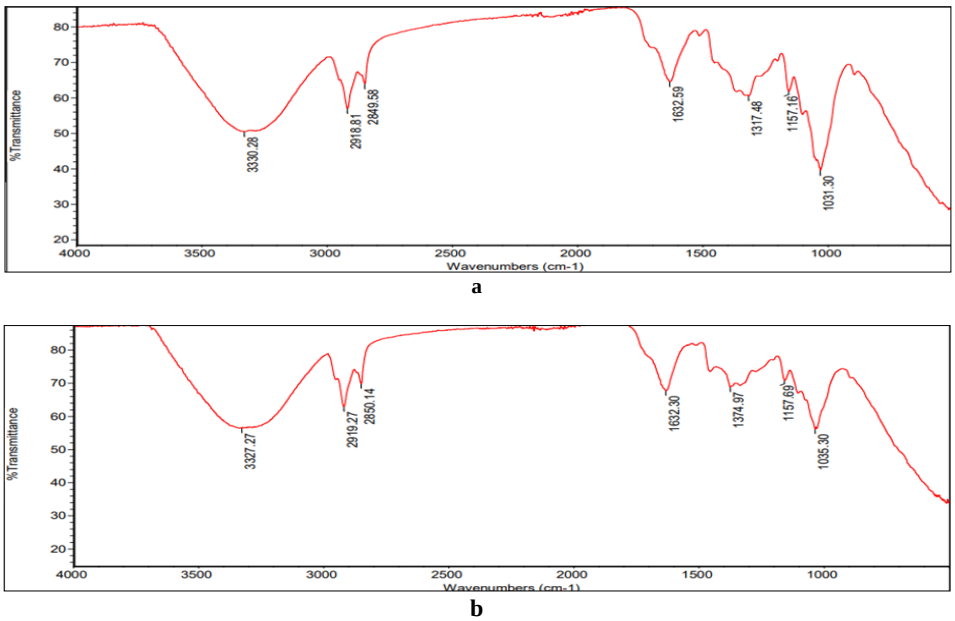

Fig 1: a and b: FT-IR Spectrum of AgNAPA and AgNRPA

Table 1: IR Spectra Results of AgNRPA and AgNAPA.

Band Positions (cm^{-1})		
AgNRPA	**AgNAPA**	**Proposed Signal Group**
3327	3330	-OH, stretching of the hydroxyl group
2919	2918	C-H stretching of alkane group.
2850	2849	C-H stretching of alkane group.
1632	1632	C=O carbonyl group of ester off the alkene group.
1374	1317	C-H of a carboxylic group
1157	1157	C-O-O anti symmetry bridge from the carboxylate.
1032	1031	C-O stretching vibration of a primary alcohol.

Table 3.1, Fig 3.1(a) and (b) seen above represents the IR spectra results for AgNAPA and AgNRPA composites of the pineapple crown. The result showed strong and broad vibration peaks of the hydroxyl group (-O-H) at 3327-3330 cm^{-1}, consistent with cellulosic material. C-H (methyl group) stretching of the alkane group at 2919-2918 cm^{-1} and 2850-2849 cm^{-1} of the cellulose. The carbonyl group (C=O) of the ester out of plane of the alkene associated with the hemicelluloses seen at 1632 cm^{-1}in both samples. 1374-1317cm^{-1}peak presenting the methyl group (C-H) out of plane of a carboxylic group. C-O-O of the carboxylate group of the cellulose and the hemicelluloses seen at 1157cm^{-1} observed in both samples and finally 1032-1031 cm^{-1} which is the C-O stretching in the primary alcohol of the cellulose and hemicelluloses (Nwadiogbu, Ajiwe & Okoye, 2016). The slight shift in the band position observed in 3327-3330 cm^{-1}, 2919-2918 cm^{-1}, 2850-2849 cm^{-1},1374-1317 cm^{-1}1032-1031 cm^{-1} show modification from the Raw sample to Acetylated sample (Devi & Saroha, 2014). The consistence seen in the peak 1632 and 1157 cm^{-1} present major points of attachment of the silver nanoparticles (Abd Almawgood, El Tohamy, Ismail, & Samhan, 2021) [1]

1. Study of the Optimal Operational Conditions of the Sorption Process.

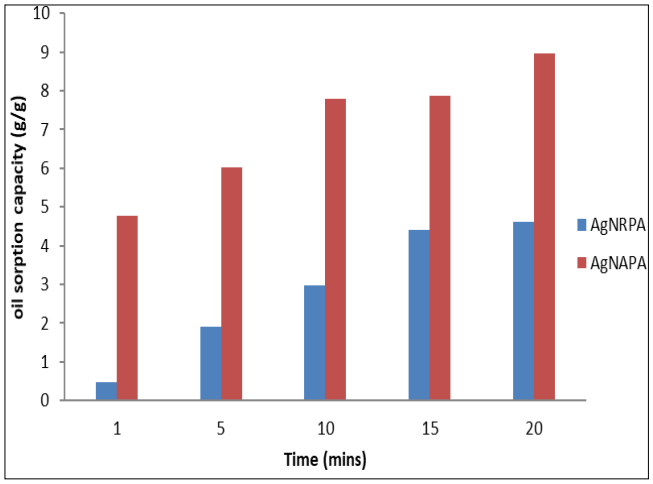

Fig 2: OSc against Time for AgNRPA and AgNAPA

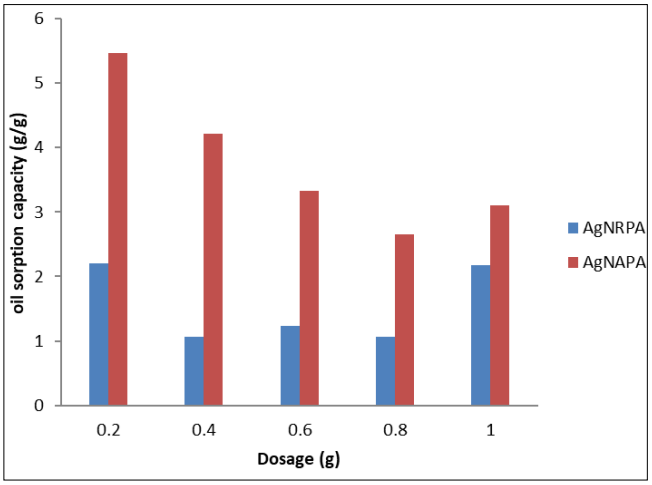

Fig 3: OSc against Dosage for AgNRPA and AgNAPA

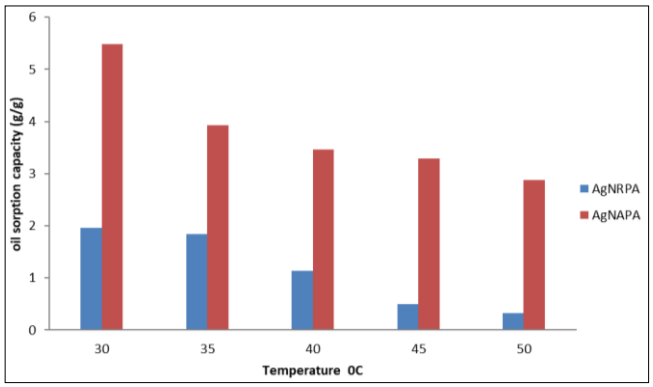

Fig 4: OSc against Temperature for AgNRPA and AgNAPA.

The study of the optimal operational conditions of the sorption process studied the effect of contact time, effect of varying the dosage of the sorbent and the variation of temperature on the sorption process. The result obtained is reflected in Fig 3.2, 3.3 and 3.4.

It is observed that varying the contact time from 1 minute to 20 minutes showed steady increase in the oil sorption capacities from 0.47 to 4.61 g/g and 4.71 to 8.95 g/g for AgNRPA and AgNAPA respectively. This indicates the present of available attachment sites even at 20 minutes, that is to say that saturation has no occurred at the time of maximum contact in this study. Similar results are seen in (Dawodu & Akpomie, 2014) [11].

The study of the effect of dosage revealed steady decrease from 2.20 to 1.07 g/g and 5.47 to 2.66 g/g of the oil sorption capacities from 0.2 to 0.8 g, and then an increase of 1.07 to 2.18 g/g and 2.66 to 3.11 g/g for AgNRPA and AgNAPA accordingly is seen from 0.8 to 1.0 g. This pattern is most likely due to accumulation at the adsorption sites (Dawodu & Akpomie, 2014) [11], but the study of temperature showed that increase in temperature from 30 ºC to 50 ºC has no influence on the sorption as oil sorption capacity showed a steady decrease from 1.96 to 0.32 g/g and 5.48 to 2.88 g/g with increase in the temperature for AgNRPA ana AgNAPA respectively, this could be due to the nature of the sorbate material under study. This patter is similar to th study done by (Olufemi & Otolorin, 2017) [25]. The study showed better performance in the AgNAPA composites of pineapple crown, this is as a result of the chemical modification (acetylation) done on the composites to enhance the hydrophobic nature of the material (Bayat, Aghamiri, Moheb & Vakili-Nezhaad, 2005 [8].

2. Statistical analysis

The statistical analysis done using SPSS version 26, developed a predictive equation using linear regression model similar to that prescribed by ((Nwadiogbu, Okoye, Ajiwe & Nnaji, 2014) [23], where OSc represents the oil sorption capacities of AgNRPA and AgNAPA under the study of the effect of time (t), dosage (So/D) and Temperature (T). The amount of oil sorbed was represent by Sd. The Model summary of the regression model gave values for the R^2 which indicates the strength of the linear equation developed while the standard error of the estimate (SEE) gave the error margin which is the degree of accuracy of the predicted OSc values. Pearson's correlation was also used to reveal the relationships between variables.

$$OScAgNRPA_{(time)} = -0.003t + 4.977Sd - 12.965So + 2.632 \ , \ R^2 = 1.000, \text{SEE} = 0.004 \quad (13)$$

$$OScAgNAPA_{(time)} = -0.304t + 8.398\,Sd - 430.502So + 86.398 \ , R^2 = 0.994, \ \text{SEE} = 0.253 \quad (14)$$

$$OScAgNRPA_{(dosage)} = 1.367Sd - 2.552So + 1.792 \ ; R^2 = 0.879, \text{SEE} = 0.266 \quad (15)$$

$$OScAgNAPA_{(dosage)} = 2.014Sd - 9.464So + 5.250; R^2 = 0.864, \text{SEE} = 0.639 \quad (16)$$

$$ScAgNRPA_{(temperature)} = -0.004T + 4.772Sd - 5.154So + 1.220; R^2 = 1.000, \text{SEE} = 0.006 \quad (17)$$

$$OScAgNAPA_{(temperature)} = 0.001T + 5.048Sd - 17.202So + 3.343; R^2 = 1.000, \text{SEE} = 0.005 \quad (18)$$

Table 2: Pearson's Correlation of Time, Dosage and Temperature on AgNRPA and AgNAPA.

	OSc		**Sd**		**So**		**t**		**T**	
	AgNRPA	AgNAPA	AgNRPA	AgNAPA	AgNRPA	AgNAPA	AgNRPA	AgNAPA	AgNRPA	AgNAPA
Time										
OSc	1	1	1	0.989	-0.035	-0.824	0.975	0.964	-	-
Sd	1	0.989	1	1	-0.023	-0.780	0.976	0.956	-	-
So	-0.035	-0.824	-0.-023	-0.780	1	1	-.0.004	-0.924	-	-
T	0.975	0.964	0.976	0.956	-0.004	-0.924	1	1	-	-
Dosage										
OSc	1	1	0.557	-0.595	0.098	-0.778	-	-	-	-
Sd	0.557	-0.595	1	1	0.862	0.956	-	-	-	-
D	0.098	-0.778	0.862	0.956	1	1	-	-	-	-
Temperature										
OSc	1	1	1	1	0.390	-0.485	-	-	-0.975	-0.916
Sd	1	1	1	1	0.414	-0.457	-	-	-0.971	-0.926
So	0.390	-0.485	0.414	-0.457	1	1	-	-	-0.311	0.174
T	-0.975	-0.916	-0.971	-0.926	-0.311	0.174	-	-	1	1

Linear equation 13 and 14 are for the study of time, which reveals that for every 1minute increase in time, there are 0.3% and 30.4% rise in the oil sorption capacities of both AgNRPA and AgNAPA with respect to the multiplying factors of the other variables and the constants of each equation. The model summary of the regression equation shows very strong R^2 values of 1.000 and 0.994 for both AgNRPA and AgNAPA accordingly while AgNRPA had lower SEE value of 0.004 compared to AgNAPA value of 0.253, therefore indicating a higher accuracy level in the predicted OSc value when compared with the calculated OSc value. Table 3.2 reveals strong positive regression values of 0.975 and 0.964 for AgNRPA and AgNAPA between time and OSc, hence the strong positive influence increment in time had on the oil sorption capacities of both sorbents as seen in the responds patterns of these two sorbent materials under the study of the effect of time. Similar relationship is also seen between time and the amount of oil sorbed.

Equation 15 and 16 above is the predictive regression equation developed for the study of the effect of dosage, it is seen from these equations that the values, 2.55 and 9.464 (AgNRPA and AgNAPA) are the multiplying factors for every 1g increase in the dosage with respect to all other multiplying factors of the developed equations in corresponds to the predicted OSc values. The model summary show R^2 values of 0.879 and 0.864 for AgNRPA and AgNAPA, thus reflecting the strength of these developed equations. AgNRPA shows lower SEE in value of 0.266 compared with that of AgNAPA as 0.639. Pearson's correlation values shown in Table 3.2 reveals regression values for AgNRPA and AgNAPA as 0.098 and -0.778 presenting the relationship between dosage and OSc. This means that increase in dosage does not have good or positive influence over the oil sorption capacities however, the inverse is seen in the relationship between dosage and the amount of oil sorbed.

Linear equation 17 and 18 above were developed for the study of Temperature, giving 0.004 and 0.001as the multiplying factors of every 1^{o}C rise in temperature with cognizant of every other multiplying factors as factors that influence every degree rise or fall in oil sorption capacities of AgNRPA and AgNAPA respectively. The model summary revealed very strong R^2 values of 1.000 for both sorbents and very low SEE values of 0.006 and 0.005 for both AgNRPA and AgNAPA, thus implying the existence of very high accuracy level for these predictive equations. Table 3.2 of the Pearson's correlation also showed very strong but negative regression values of -0.975 and -0.916 for both AgNRPA and AgNAPA for the relationship

between temperature and OSc, similar that value are seen between temperature and the amount of oil sorbed as -0.971 and -0.926, hence the decline pattern seen in the adsorption of the crude oil under the study of the effect of temperature for these sorbents under study.

3. Kinetic Study

Table 3: kinetic Results of silver nanocomposites of Raw and Modified Pineapple Crown.

Kinetic Models	AgNRPA	AgNAPA
$q_{e\ exp}$ (mg/g)	4705	8990
Pseudo first order		
$q_{e\ calc}$ (mg/g	6734.5	5340.1
K_1 (s^{-1})	0.195	0.169
R^2	0.877	0.984
Pseudo second order		
$q_{e\ calc}$ (mg/g)	-	-
K_2 (s^{-1})	-	-
R^2	0.945	0.992
Elovich		
B (g/mg)	0.0007	0.00072
α (mg/g/mins)	1.6 x10^3	4.1 x10^3
R^2	0.933	0.948
Intraparticle diffusion		
Kd (megg^{-1}s$^{1/2}$)	1275.0	1226
R^2	0.983	0.973
C	-840.5	3749
Liquid film diffusion		
Ked (megg^{-1}s$^{1/2}$)	0.197	0.169
R^2	0.899	0.984

The Kinetic study results shown in Table3.3 above, placed data generated for both AgNRPA and AgNAPA as best fitted to pseudo second order model as regression coefficient values generated (R^2) as 0.945 and 0.992 were higher and closer to the value 1 compared with the R^2 values generated from the application of pseudo first order model as 0.945 and 0.992 for both AgNRPA and AgNAPA respectively. This showed that the sorption processes were governed by chemisorptions. The application of Elovich model was invalid for the classification of the sorption as chemisorptions due to the R^2 values generated as 0.933 and 0.948 for AgNRPA and AgNAPA were lower than those generated from pseudo second order, however with very strong R^2 values seen in the application of this Elovich model, it could be an indicator that the sorption is multilayer in nature. (Riyanto & Prabalaras, 2019) [29] and (Atef & Waleed, 2009) [5] showed results similar to these in this study. The sorption process of AgNRPA seem to be by pore penetration, as R^2 value generation for intraparticle diffusion as 0.983 is higher than that of liquid film diffusion 0.899 while AgNAPA sorption process is more of surface penetration as its R^2 value for liquid film diffusion 0.984 is higher than that of intraparticle diffusion 0.973. However the very large deviation from the origin as -840.5 and 3749 of the intercepts of both AgNRPA and AgNAPA actually reveals that pore penetration for AgNRPA and surface penetration for AgNAPA are not the only limiting steps in sorption process each of these sorbents. Therefore it could be concluded that the sorption for both sorbents is governed by both pore and surface penetration.

Table 4: Isotherm Results

Isotherm Models	AgNRPA	AgNAPA
Langmuir		
q_o	0.046	1.230
B	1.665	0.699
R_L	0.000006	0.000014
R^2	0.304	0.192
Freundlich		
K_f	5.5 x 10^{14}	0.534
1/n	-2.34	0.874
R^2	0.335	0.265
Temkin		
B(KJmol^{-1})	-48.83	-45.21
A(Lmg^{-1})	3.162	3.163
R^2	1.000	0.999

The application of these three isotherm models; Langmuir, Freundlich and Temkin seen above in Table 3.4, showed data generated as best fitted to Temkin isotherm model as regression values of AgNRPA and AgNAPA were 1.000 and 0.999 which were greater than those of Langmuir as 0.304 and 0.192 and those of Freundlich isotherm model as 0.335 and 0.265. This means that the sorption is multilayer which is correlation with the assumption given by the results of Elovich. The negative values seen in B (heat of sorption) implies that sorption is endothermic in nature. Similar result was seen (Idan, Abdullah, Choong, & Jamil, 2018). The R_L values of both sorbents AgNRPA and AgNAPA as 0.000006 and 0.000014 are values greater than zero both lesser than, thus indicating that the sorption process is favourable.

Table 5: Thermodynamic Study Results

						ΔG(KJ/mol)		
Samples	**ΔH(KJ/mol)**	**ΔS(KJ/molK)**	**R^2**	**303K**	**308K**	**313K**	**318K**	**323K**
AgNRPA	82.6	0.300	0.939	-8.90	-9.80	-11.30	-12.80	-14.80
AgNAPA	25.5	0.103	0.892	-5.71	-6.22	-6.74	-7.25	-7.77

Thermodynamic result for both AgNRPA and AgNAPA seen in Table 3.5 above showed positive values of enthalpy (ΔH) as 82.6 and 25.5 kj/mol k. This reveals that the sorption process is both endothermic and chemisorptions, thus agreeing with the Temkin isotherm and Pseudo second order results seen in this study. The positive values of entropy (0.300 and 0.103) indicate increase in the degree of disorderliness and high level of affinity between the sorbate and the sorbents. While the negative values seen in Gibb's energy (ΔG) shows the spontaneous nature of the sorption process onto sorbents AgNRPA and AgNAPA. (Atef & Waleed; 2009) [5] recorded results similar to those seen in this study.

Conclusion

This study has unveiled great efficiency and effectiveness in use of silver nano-composite of pineapple crown in the sorption crude oil from aqueous medium. The further enhancement of the silver nano-composites with acetic anhydride has favored better performance as seen in

AgNAPA, with the sorption process of both sorbent been governed by both pore penetration and surface penetration. The studied of effect variable; time, dosage and temperature, showed that only time had a positive influence over the oil sorption capacities of the sobents. The data generated for kinetic study of both AgNRPA and AgNAPA showed that the sorption process were chemisorptive in nature as it fitted perfectly to Pseudo second order model. The isotherm study showed results best suited to Temkin isotherm model haven sampled three model; Langmuir, freundlich and temkin isotherm model, thus revealing the multilayer sorption and endothermic process involved in the sorption of crude oil onto these sorbents. The thermodynamic study showed results of the enthalpy, entropy and Gibb's energy as chemisorption, endothermic, increased level disorderliness and spontaneity of the sorption process, hence confirming the kinetic and isotherm results of this study. Therefore this study has brought to light the potential in the use of nanotechnology in combination with agro-waste for the treatment of crude oil spillage in aqueous medium.

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