

Thermodynamics, Kinetics and Optimization Studies of Crude Oil Sorption Using Modified and Unmodified Husks of Bambara Nut (*Vigna subterranea*)

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ABSTRACT

Oil spillage in water bodies constitutes environmental burden to coastal cities around the world in view of the escalating cases of the pollution with the consequential damages to humans and aquatic lives. Sorption of oil spillage using agricultural biomass has attracted recent research attention partly due to the simplicity of the process and the availability of the sorbents. This work estimated the kinetics, isotherm and thermodynamics parameters of oil sorption using modified and unmodified bambara nut (*Vigna subterranea*) husks as sorbents. The modification was carried out using the acetylation method, which increased the hydrophobicity of the sorbent, and the sorption study was in batch process using a UV-Vis spectrophotometer to measure oil absorbance as a direct correlation to residual oil concentration. Analysis of the sorption kinetics indicated that the pseudo second order model fitted more than the pseudo first order model with average R^2 values of 0.902 and 0.960, for the modified and unmodified sorbents. The Weber-Morris model equally predicted the kinetics with high correlation coefficient, but the intercept of the model deviated from zero with average values of 2.58 and 0.62 for the modified and unmodified sorbents respectively. The Langmuir isotherm gave average regression coefficients that were less than 0.95, but the values of dimensionless parameter, RL increased with the increase in temperature showing that the sorption was more favored at low temperature. The average regression coefficient with the Freundlich isotherm was 0.999 for the modified sample and 0.973 for the unmodified sorbent, hence, the Freundlich isotherm perfectly predicted the isotherm of the modified sorbent. The Temkin model also predicted the sorption isotherm with average R^2 value of 0.96 for both the modified and unmodified sorbent, and the isotherm parameter bT with average values of 0.19 and 1.12 kcal/mol for the modified and unmodified sorbent showed that the sorption with the modified sorbent was purely by physical adsorption. The entropy and enthalpy changes were negative showing that the process was exothermic, and the degree of oil molecular mobility was higher in the solution than in the sorbent. The statistical analysis with Box-Behnken design of experiment showed that functional relationship between the sorption capacity, and time, temperature and oil concentration fitted into quadratic model with R^2 , adjusted R^2 , and predicted R^2 values of 0.992, 0.987 and 0.976, respectively. However, the effect of sorption time on the sorption capacity was not significant at 0.05 level. The optimum parameters for the modified sorbent were estimated at 24 mins, 30.6°C, 0.05 g/mL and 8.6 g/g for time, temperature, initial oil concentration and sorption capacity respectively, while that of the unmodified sorbent were 25 mins, 30°C, 0.04, and 2.5 g/g, respectively.

Index Terms- Sorption, Crude oil, Husks, Kinetics, Thermodynamics, Optimization

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1 INTRODUCTION

Oil spillage constitutes major environmental hazards and challenges, overwhelming nations in search of effective remediation processes [1]. The use of biomass as oil sorbent has attracted wide research interest in connection to its simplicity, affordability, and environmental friendliness. Understanding the kinetics of oil sorption is essential in applying the laboratory data to practical oil cleanups. Basically, the pseudo first and second order kinetics are the two kinetics models that were studied for oil sorption. However, the pseudo second order model dominates in consistency with the experimental data of sorption experiment using variety of sorbents such as hydrophobic Kabok fiber in oil sorption [2], esterified coconut coir [3], banana pseudostem fiber [4], Borasus aethiopicum coir [5], magnetite adsorbent [6]. Nevertheless, the comparison has often been limited to the two models, which fall under the film diffusion controlled-sorption with little said about intraparticle diffusion controlled-sorption kinetics. The first task here was to explore the full kinetics of the sorption of oil molecules using modified bambara nut husks with a view of generating design data fit for effective decontamination of oil-infested water.

Furthermore, adsorption isotherms are required to fully appreciate the nature of sorption distribution within the pores or on the surface of the sorbent, and although several models have been developed to describe isothermal relationships, no single model is generally a descriptive of sorption process [7]. One of the most common isotherm models is the Freundlich model, which states that at a constant temperature, the amount of adsorbate bound per unit weight of adsorbent is a logarithmic function of the residual concentration in the fluid phase at equilibrium [7]. Apart from the simplicity of the Freundlich model, it describes the adsorption process on surface adsorption sites which are energetically heterogeneous, a condition commonly found in adsorption system [8]. However, one

limitation of Freundlich model is that it does not describe a limit in adsorption capacity, which means that the amount of adsorbed may be infinite as solute concentration increases [4]. Another model that sometimes fits isothermal sorption is the Langmuir model, which is based on the assumption that maximum sorption corresponds to a saturated monolayer of solute molecules on the adsorbent site, meaning that monolayer adsorption occurs on a homogeneous surface where there is no interaction between the adsorbed molecules on the neighboring sites [3]. Although some research works indicated that Langmuir isotherm was more favorable than Freundlich isotherm, the assumption that sorption takes place on energetically uniform sites is seldom in practical oil sorption [7]. In view of the drawbacks with the two common models, this study deems it essential to know the exact model that favors the sorption of crude oil using modified bambara nut shells. Moreover, the possibility of having a different model such as the Temkin that takes into account the interactions between the sorbent and the oil molecules for a practical description of bambara nut shell-crude oil system was also explored [9].

Another concern that this work addressed was the thermodynamic parameters associated with the sorption of crude oil with bambara nut shells. The absolute value of the enthalpy changes would tell if the sorption is physically or chemically adsorbed, and the sign would tell whether the system is exothermic or endothermic, while the signs of the Gibb's free energy change and entropy changes would indicate of the spontaneity and the favorability of the system, respectively [2]. Wang et al. [2] reported on the sorption of oil in water using superhydrophobic Kapok fiber that the Gibb's free energy change was negative and the absolute values decrease with increase in temperature, meaning that the degree of spontaneity decreases with increase in temperature. Also, Lv et al. [8] reported on the oil using hydrophobic jute fiber that the Gibb's free energy change was negative and the absolute values varied

between 2.48 to 0.97 kJ/mol as the temperature varies between 293 to 323 K. Moreover, both researches indicated that the enthalpy change was negative and the value was less than 40 kJ/mol, meaning that the sorption was dominated by van der Waal's force. The reports also indicated that the entropy changes were negative, which imply that the oil molecules in the sorbents were more orderly and the movement was more restricted. However, Quek et al. [10] studied on the sorption of oil using Kapok fiber and report something different altogether. Although the Gibb's energy change was reported to be negative, the absolute values increased with the increase in temperature, meaning that the degree of spontaneity increased with the increase in temperature. They equally reported positive values for enthalpy and entropy changes, which mean that the process was endothermic and increased degree of disorderliness. Therefore, the discrepancies in reports about the thermodynamics of oil sorption prompted the determination of the exact parameters for oil/bambara nut shell sorption system.

Finally, this work looked into the optimization and statistical analysis of the sorption of oil with bambara nut shell using Box Behnken design of Response Surface Methodology (RSM). The analysis was carried out using Design Expert (6.0.6).

2 MATERIALS AND METHOD

2.1 Materials

Husks of Bambara nut (*Vigna subterranea*) were packed from a commercial nuts mill at Enugu in Nigeria. The husks were screened for gravels and sands; thereafter, they were washed with distilled water before spraying under the sun to dry for 2 days. The sun-dried husks were grinded in a mortar and about 20 g was sieved out using 250 μ m mesh. The powder was sealed in an airtight plastic bottle, labeled 'A'.

2.2 Modification of the biomass

In order to increase the hydrophobicity of the biomass, the acetylation method as described by Behnood et al. [11] was applied with little modification. This same method was applied by Asapour et al. [12] as they modified corn silk for oil sorption. In this method, 30 g of the Bambara powder, 'A' was mixed thoroughly with 0.7 g of N-bromosuccinimide (NBS) in a 500 mL conical flask. Approximately 300 mL of acetic anhydride was added into the flask and the mixture was further homogenized. The flask was connected to a reflux condenser with an electric heating mantle as the heat source. The acetic anhydride served as the solvent why the NBS was the catalyst. After refluxing for 3hrs, the residual husks were allowed to settle and decanted off the solvent. Ethanol and acetone were successively added to the biomass to remove any entrained liquid and by-products. The acetylated husks were dried in oven at 65°C for 24hours. After cooling, the treated husks were collected in another airtight container labeled 'B'.

2.3 The batch sorption experiment

The Sorption experiment was performed with beakers containing the oil-water mixture and the sorbent immersed in a water bath. After each run, the mixture was filtered with net of 250 μ m mesh size. This method of filtration ensures that the sorbent particles do not mix with the adsorbate [8]. The oil-water mixture remaining at the end of each experiment was separated with equal volume of N-hexane in a separating funnel, and the absorbance of the remaining oil was measured in a UV-Vis spectrophotometer at a wavelength of 410nm [13]. The corresponding oil concentration was determined from a standard graph of oil concentration in N-hexane plotted against the absorbance. The regression coefficient of the standard was 0.9919 (Figure 1), meaning that the absorbance and the concentration were highly correlated.

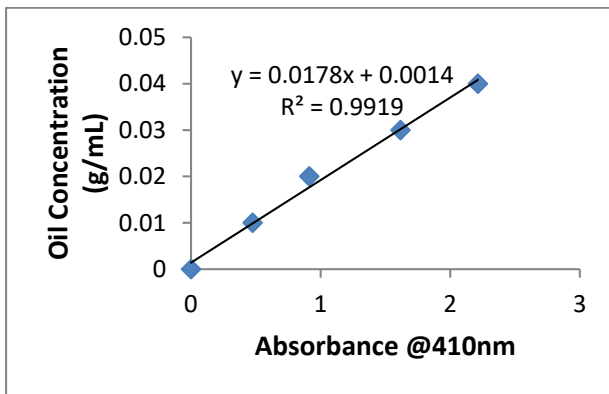


Fig 1: The standard of oil concentration against the absorbance

3.0 RESULTS AND DISCUSSION

3.1 The Kinetics Study

The experiment was conducted by varying time at different temperatures. The oil-water mixture was prepared by mixing 1g of oil per 40mL of water in different beakers. For each of the kinetics experiment, 0.1g of the sorbent was weighed into a beaker containing the oil-water mixture and the mixture was stirred while the beaker was immersed in a water bath at a given temperature. The experiment was carried out for 5, 10, 15, 20, and 25 minutes at different temperatures because the equilibrium sorption at the different temperatures was achieved before 25minutes. At each run, the residual oil concentration was calculated as described above and the data generated was modeled with the kinetics model in Equations 1-3 for pseudo first order, pseudo second order and Weber-Morris models respectively.

$$\log_{10}(q_e - q_t) = \log_{10} q_e - \frac{k_1 t}{2.303} \quad (1)$$

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

$$q_t = K t^{1/2} + l \quad (3)$$

Where

q_e = The equilibrium adsorption capacity

K_1, K_2, K and l are constants

3.2 The Kinetics Parameters

The kinetics parameters shown in Table1 indicate that the kinetics did not fit perfectly into the pseudo first order

kinetics looking at the regression coefficients. The sorption with the unmodified biomass, 'A', was more fitted into the pseudo first order model than the modified biomass, 'B', and the fitness into the pseudo first order model was not a function of temperature. It can be deduced that the rate constant decreased with the increase in temperature and the equilibrium sorption capacity equally decreased with the increase in temperature. The calculated equilibrium capacity from the pseudo first order model was not in agreement with the observed equilibrium capacity, meaning that the kinetics data could not correlate with the pseudo first order model. Husin et al. [4] also reported that the kinetics of oil sorption using banana pseudostem fiber did not fit into pseudo first order kinetics, but Arinze-Nwosu et al. [5] reported that the kinetics of oil sorption using modified *Borassus aethiopum* coir fitted into pseudo first order while the untreated coir fitted into pseudo second order model.

Taking a close look at the kinetics parameters for the pseudo second order model in Table 2, it can be observed that regression coefficients were close to 1.0, the average was 0.990, which means that only 0.98% of the data could not be explained by the model. Moreover, the calculated equilibrium adsorption capacities were in close agreement with the observed equilibrium adsorption capacities. The kinetics constant for the modified biomass were less than the values for the unmodified biomass, but the modified biomass had higher equilibrium sorption capacity than the unmodified biomass. This means that though the modified bambara nut shell could adsorb higher oil at equilibrium, the rate of sorption was higher with unmodified biomass. Lv et al. [8] reported that the sorption kinetics of jute fiber fitted more with the pseudo second order kinetics model.

Weber-Morris model in Table 3, which is based on intraparticle diffusion predicted the kinetics of the sorption with average R^2 values of 0.902 and 0.960 for the modified and unmodified biomass respectively. Although the R^2 values were reasonably close to 1.0, the intercept "I",

deviated from the origin with average values of 2.58 and 0.62 for the modified and unmodified biomass respectively.

Sorbent	Tem (K)	K (g/g.min)	qeCal (g/g)	qeObs (g/g)	R2
B	303	0.092	5.851	5.391	0.998
	323	0.043	5.705	5.039	0.983
	343	0.040	4.863	4.099	0.988
A	303	0.219	2.167	1.870	0.989
	323	0.207	1.733	1.585	0.995
	343	0.176	1.664	1.515	0.988
Sorbent	Tem (K)	K (g/g.min)	qeCal (g/g)	qeObs (g/g)	R2
B	303	0.333	8.510	5.391	0.887
	323	0.100	2.820	5.039	0.874
	343	0.072	2.576	4.099	0.788
	343	0.072	2.576	4.099	0.788
A	303	0.100	0.955	1.870	0.889
	323	0.093	0.065	1.585	0.931
	343	0.059	0.555	1.515	0.999

The deviation from origin correlated with the difference between the R2 values and 1.0, which explains that the sorption was controlled by both intraparticle and surface diffusions. It can be observed that the modified biomass gave higher intercepts than the unmodified biomass, meaning that the modification enhances surface controlled sorption [5].

TABLE 1: PSEUDO FIRST ORDER MODEL PARAMETERS

TABLE 2: PSEUDO SECOND ORDER MODEL PARAMETERS

TABLE 3: WEBER-MORRIS MODEL PARAMETERS

Sorbent	T (K)	K ^{0.5} (min)	L (g/g)	qeObs (g/g)	R2
B	303	0.540	3.40	5.391	0.882
	323	0.531	2.30	5.039	0.940
	343	0.430	2.04	4.099	0.883
A	303	0.414	0.840	1.870	0.943
	323	0.373	0.247	1.585	0.969
	343	0.144	0.763	1.515	0.969

3.3 The Sorption Isotherm

The sorption isotherms were studied using the Langmuir, Freundlich and Temkin models. The sorption experiment was carried out by investigating the effect of initial oil concentrations on the equilibrium sorption capacity at different temperatures. Different concentrations of crude oil in water (0.01, 0.025, 0.035 and 0.05g/mL) were prepared, and 30mL of each of the mixtures was transferred into different beakers. The sorption of the oil was monitored with 0.1 g of the sorbent in water bath at 30, 50 or 70°C. The

equilibrium sorption capacity was calculated and the data generated was modeled into Langmuir, Freundlich and Temkin isotherms as shown in Equations 4-6, respectively.

$$\frac{C_e}{q_e} = \frac{1}{b \times q_m} + \frac{C_e}{q_m} \quad (4)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

$$q_e = B \ln A_T + B \ln C_e \quad (6)$$

$$B = \frac{RT}{b_T} \quad (7)$$

Where

q_m = Langmuir monolayer constant

b =constant

K_f = Freundlich constant

n =Freundlich index

A_T , b_T =Temkin constants

R = 8.314J/mol.K

T = Temperature (K)

3.4 The Langmuir isotherm

The parameters for the Langmuir isotherm for both the modified sorbent 'B', and the unmodified sorbent 'A' are shown in Table 4. The maximum monolayer sorption capacity, q_m was calculated from the slope of Equation 4, while the constant, b was calculated from the intercept. The regression coefficients, R^2 , were high but there were some significant deviations from 1.0, meaning that there was some surface heterogeneity. Besides, Proctor & Toro-Vazquez [7] states that the Langmuir assumption that sorption takes place on energetically uniform sites is seldom achieved in practice. Langmuir provides a dimensionless quantity RL that is used to test the favorability of sorption. RL is defined according to Equation 8, and the average value are given in Table 4. The average values of RL were less than 1.0, meaning that the sorption was favorable [4]. However, the values of RL increased with the increase in temperature, which shows that the sorption was less favorable at higher temperatures. Moreover, the RL values for the modified sorbent were less

than the values for the unmodified sorbent, but the maximum monolayer sorption capacities for the modified were higher than the unmodified sorbents.

$$R_L = \frac{1}{1+bC_0} \quad (8)$$

TABLE 4: THE LANGMUIR ISOTHERM PARAMETERS

Sorbent	Tem (K)	Qm (g/g)	b (mL/g)	RL (Average)	R2
B	303	23.753	40.723	0.487	0.952
	323	22.727	18.304	0.666	0.992
	343	17.544	17.606	0.674	0.917
A	303	2.500	105.263	0.284	0.998
	323	2.324	51.314	0.434	0.957
	343	2.294	45.966	0.459	0.896

3.5 The Freundlich isotherm

Table 5 contains the parameters of the Freundlich isotherm, which were obtained from Equation 5. The regression coefficients were high enough to affirm that the Freundlich isotherm predicted the sorption. The slope ($1/n$) indicates the intensity and the surface heterogeneity of the sorption with values closer to zero showing more surface heterogeneity. The values of the slope increased with the

increase in temperature, supporting that sorption intensity decreased with the increase in temperature. Husin et al. [4] and Siregar et al. [6] also reported that Freundlich isotherm was favored for oil sorption using biomass and clay respectively.

TABLE 5: THE FEUNDLICH ISOTHERM PARAMETERS

Sorbent	Temp (K)	Kf	1/n	R2
B	303	133.486	0.718	0.999
	323	146.368	0.826	0.998
	343	166.204	0.836	0.999
A	303	8.549	0.426	0.989
	323	9.171	0.538	0.981
	343	9.512	0.564	0.948

unmodified sorbent where between 1 and 20kcal/mol, meaning that the sorption with the unmodified sorbent was a combination of both physical and chemical sorption. Furthermore, the bT values have positive sign meaning that the sorption was exothermic. This collaborates with the fact that the sorption capacity deceased with the increase in temperature.

TABLE 6: THE TEMKIN ISOTHERM PARAMETERS

Sorbent	Temp (K)	AT (ml/g)	bT (J/mol)	bT (Kcal/mol)	R2
B	303	529.18	802.27	0.192	0.956
	323	370.769	800.719	0.191	0.970
	343	358.264	842.522	0.201	0.948
A	303	994.180	4517.020	1.080	0.998
	323	472.244	4778.342	1.142	0.959
	343	422.373	4816.715	1.151	0.912

3.6 The Temkin Isotherm

The parameters for the Temkin isotherm is shown in Table 6, and the values were obtained following Equations 6 and 7. The regression coefficients were high enough to admit that the Temkin isotherm predicted the sorption, which means that there were interactions between the oil molecules and the sorbent, and the energy of sorption was a function of the surface coverage [9]. The constant 'AT' is related to the sorption binding energy while bT is related to the energy of sorption. The values of bT were converted to kcal/mol, and the results indicates that the sorption with the modified sorbent 'B' were all physical because the bT values were less than 1kcal/mol [14]. The bT values for the

3.7 The thermodynamics of the sorption

The thermodynamics study was carried out by varying the sorption temperature at constant initial oil concentration and time. Studies were carried out at different initial oil concentration and the thermodynamics parameters were estimated using the Van't Hoff's equation given in Equations 9 to 11 [2]. The entropy and the enthalpy changes were obtained from the intercept and the slope of Equation 10, respectively.

$$\Delta G^{\circ} = -RT \ln K_d \quad (9)$$

$$\ln K_d = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (10)$$

$$K_d = C_s / C_e \quad (11)$$

Where

R = The universal gas constant (8.314J/mol.K)

T = The absolute temperature (K)

ΔG° = The standard Gibb's free energy change (J/mol)

ΔH° = The standard enthalpy change (J/mol)

ΔS° = The standard entropy change (J/mol.K)

K_d = The equilibrium constant

C_s = The equilibrium oil concentration in the sorbent (g/mL)

C_e = The equilibrium oil concentration in the mixture (g/mL)

3.8 The thermodynamics parameters at different initial oil concentrations

Table 7 shows the thermodynamics parameters at different initial oil concentrations. It can be seen that the enthalpy changes were negative, which means that the sorption was exothermic. In other words, heat was not actually needed to achieve high sorption capacities. This correlates with the Temkin isotherm parameter, bT , which was positive, suggesting that the sorption releases heat to the surrounding. Secondly, the absolute values of the enthalpy changes were less than 40KJ/mol, which is within the range of physisorption [2]. It can equally be observed that the absolute values of the enthalpy changes decreased with the increase in oil concentration, meaning that high oil concentration translated to high sorption capacity as less heat was evolved. The absolute values of the standard enthalpy changes is plotted against the initial oil concentration as shown in Figure 2. It can be seen that the modified sorbent had less enthalpy change than the unmodified sorbent, which means that the sorption with the modified sorbent evolved less heat, giving higher sorption capacity than the unmodified sorbent.

The entropy changes were equally negative, meaning that the degree of disorderliness in the sorbent was less than the degree of disorderliness in the mixture. The absolute values of the entropy changes equally decreased with the increase in oil concentration. Lv et al. [8] reported that the standard

entropy changes for the sorption of oil on hydrophobic jute fiber was negative and the standard enthalpy change which was less than 40kJ/mol suggested that the sorption held by Van der Waal forces.

TABLE 7: THE THERMODYNAMICS PARAMETERS

Sorbent	Initial Oil Conc(g/mL)	$-\Delta H^\circ$ (kJ/mol)	$-\Delta S^\circ$ (J/mol.K)	R ²
B	0.010	12.926	36.436	0.852
	0.025	10.134	29.296	0.947
	0.035	8.782	26.139	0.965
	0.050	7.551	22.880	0.899
A	0.010	16.912	54.601	0.882
	0.025	15.324	54.616	0.899
	0.035	7.683	31.344	0.780
	0.050	8.717	37.496	0.904

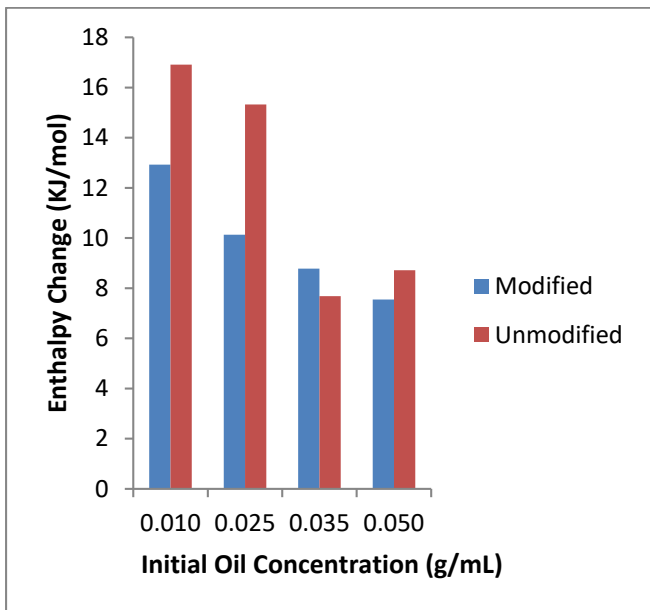


Figure 2: The Standard enthalpy changes

3.9 The optimization and statistical analysis

Box-Behnken design of Response Surface Methodology (RSM) was applied and 34 experimental runs were generated. The design comprised three numeric factors (time (A), temperature (B), initial oil concentration (C)), and one categorical factor (the sorbent type, modified and unmodified sorbents (D)). The analysis was carried out with Design Expert and the Analysis of Variance (ANOVA) table is shown in Table 7. The analysis was based on quadratic model and the R^2 , adjusted R^2 and Predicted R^2 were reasonably close to 1.0, hence the model was adequate. The p-values of temperature (B) and initial oil concentration (C) were less than the 0.01, meaning that even at a significance level of 0.01, the variations in sorption capacity as a result of the changes in temperature and initial oil concentration were statistically significant. However, the p-value for time was higher than 0.05, meaning that at 0.05 level, time was not a significant factor. In other words, the effect of time on the sorption capacity was not statistically significant. This agrees with the report by [15] that sorption of oil takes place quickly so that after a short period, the maximum sorption capacity would have attended. From Table 6, it can be seen that the interactive

terms were not statistically significant, explaining that the effect of one factor on the sorption capacity was not influenced by the level of other parameters. It can also be seen that the p-value for the categorical factor (D) was less than 0.01, which means that differences in sorption capacities from the modified and unmodified sorbents were statistically significant; the modification actually improved the sorption capacity of the biomass.

Table 8: The ANOVA Table

						Squared
Source	Sum of Squares	DF	Mean Square	F-Value	Prob > F	
Model	210.9863	13	16.22971	192.1479	< 0.0001	<p>3.10 The model equations and 3D graphs</p> $q = 0.996 + 0.038 \times A - 0.056 \times B + 267.7 \times C - 1550 \times C^2 \quad (12)$ <p>The quadratic model equations of sorption capacity as a function of time (A), temp (B) and oil conc(C) are shown in Equations 12 and 13 for the modified and unmodified sorbent respectively. The equations contain only the significant terms as the non significant terms were truncated. The 3D graphs are shown in Figures 3-5 for the modified sorbent only. The 3D plot of Figure 3 shows that when the oil concentration was kept constant, the sorption capacity was controlled by variations in temperature, as the plot tilted along the temperature axis with high sorption capacity at low temperature, thus confirming that time was not a significant factor. Equally, Figure 4 shows that when temperature was constant, the sorption capacity was controlled by variations in oil concentration, as the effect of time was insignificant. Figure 5 shows that when time was kept constant, the sorption capacity was influenced by both temperature and oil concentration, but the effect of oil concentration was higher than the effect of temperature.</p> $q = -0.02739 + 0.039 \times A - 0.04 \times B + 143.3 \times C - 1550 \times C^2 \quad (13)$
A	0.275625	1	0.275625	3.263197	0.0859	
B	2.25	1	2.25	26.63835	< 0.0001	
C	48.65063	1	48.65063	575.9876	< 0.0001	
D	130.8497	1	130.8497	1549.164	< 0.0001	
A2	0.003368	1	0.003368	0.03988	0.8437	
B2	0.312053	1	0.312053	3.694474	0.0690	
C2	3.237053	1	3.237053	38.32432	< 0.0001	
AB	0.03125	1	0.03125	0.369977	0.5499	
AC	0.005	1	0.005	0.059196	0.8102	
AD	0.000625	1	0.000625	0.0074	0.9323	
BC	0.28125	1	0.28125	3.329793	0.0830	
BD	0.4225	1	0.4225	5.002089	0.0369	
CD	24.75063	1	24.75063	293.0292	< 0.0001	
Residual	1.689294	20	0.084465			
Std. Dev.	0.290628		R-Squared	0.992057		
Mean	3.379412		Adj R-Squared	0.986894		
C.V.	8.599962		Pred R-	0.975599		

DESIGN-EXPERT Plot

Response 1
X = A: Time
Y = B: Temp

Actual Factors
C: Conc = 0.03
D: D = Modified

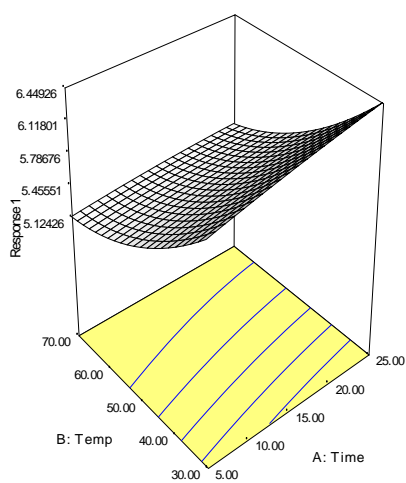


Fig 3: 3D plot for time, temp and sorption capacity using modified sorbent

DESIGN-EXPERT Plot

Response 1
X = B: Temp
Y = C: Conc

Actual Factors
A: Time = 15.00
D: D = Modified

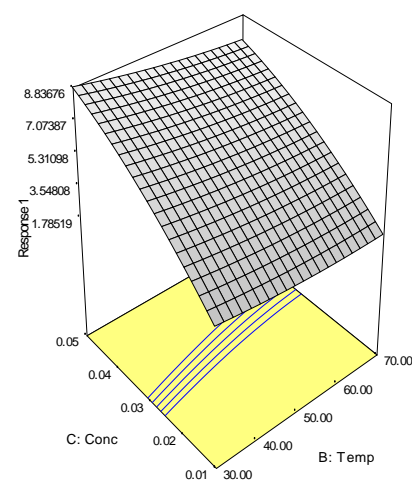


Fig 5: 3D plot for temp, oil conc and sorption capacity using modified sorbent

DESIGN-EXPERT Plot

Response 1
X = A: Time
Y = C: Conc

Actual Factors
B: Temp = 50.00
D: D = Modified

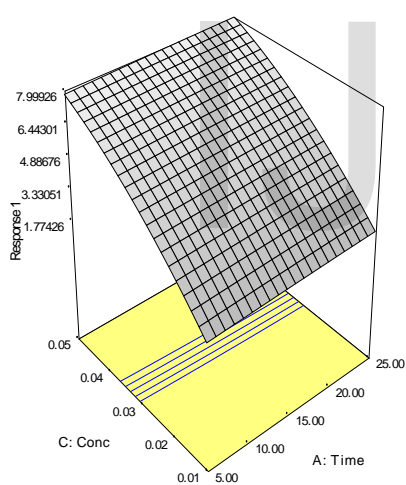


Fig 4: 3D plot for time, oil conc and sorption capacity using modified sorbent

3.11 The numerical optimum solution

Table 9 shows the numerical optimum solution that was obtained using Design Expert. The theoretical sorption capacities were verified and the actual values were reasonably close to the theoretical values. Therefore, the optimum parameters for the modified sorbent were 8.6g/g, 24minutes, 30.6°C, 0.05g/mL and that of the unmodified sorbent were 2.5g/g, 25minutes, 30°C, 0.04g/mL for sorption capacity, time, temperature and oil concentration, respectively. Oseke et al. [16] reported optimum values of 5minutes, 0.25v/v, and 20.66g/g for time, oil:water ratio, and sorption capacity at room temperature, respectively, using chitosan-rice husk ash composite as sorbent on crude oil. Alameri, et al. [17] reported optimum parameters of 32.5g/g, 70minuts, 45°C for sorption capacity, time and temperature, respectively, using peat-derived biochar as sorbent on crude oil. Therefore, the optimum parameters actually depend on the type of sorbent.

TABLE 9: THE NUMERICAL OPTIMUM SOLUTION

Time	Temp	Conc	D	q (g/g)	Actual q (g/g)
24.03	30.61	0.05	Modified	8.9	8.6
25.00	30.00	0.04	Unmodified	2.4	2.5

4 CONCLUSION

The kinetics of the oil sorption using bambara nut husks fitted more with pseudo second order kinetics than pseudo first order kinetics, and the calculated equilibrium sorption capacities with the pseudo second order kinetics agreed closely with the observed equilibrium sorption capacities. The Weber-Morris or intraparticle diffusion theorem also fitted with the kinetics with high regression coefficients, but the intercept of the model deviated from zero with the modified sorbent giving higher intercept than the unmodified sorbent, meaning that the sorbent modification enhanced surface sorption.

The regression coefficients obtained from the Langmuir isotherm was not close to 1.0, but the values of the dimensionless parameter k_L revealed that the sorption was less favorable at high temperature. Freundlich isotherm predicted the sorption with high regression coefficients, and the values of the Freundlich parameters indicated that the sorption intensity decreased with the increase in temperature, and the surface heterogeneity was more in the unmodified sorbent. Temkin isotherm also predicted the sorption process with high regression coefficient, and the values of the parameters suggested that the sorption with the modified sorbent was pure physical.

The thermodynamic analysis shows that the standard enthalpy changes were negative, and the absolute values decreased with the increase in initial oil concentration, supporting that high oil concentration was more favorable

with respect to sorption capacity. The standard entropy changes were negative, which means that the mobility of the oil molecules in the sorbent was less than the mobility in the mixture.

The statistical analysis showed that quadratic model predicted the relationship between the sorption capacity and time, temperature and initial oil concentration with high coefficient of determination. Moreover, the effects of temperature and oil concentration on the sorption capacity were statistically significant, while the effects of time and the interactive terms were not significant. Furthermore, statistical analysis showed that the differences between the sorption capacities obtained from the modified and the unmodified sorbents were statistically significant, meaning that the modification of the sorbent was effective.

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