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Kinetic, Isotherm and Thermodynamics Studies of the Adsorption of Crude Oil from Surface Water Using Esterified Rice Husk and Saw Dust

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ABSTRACT: *The adsorption of crude oil from surface water was carried out using esterified rice husk and saw dust adsorbents respectively. 2.0g of carbonized rise husk and saw dust respectively were esterified by treating them differently with 0.4g of fatty acid (stearic acid) in 200 ml of n-hexane containing two drops of concentrated* H_2SO_4 *as catalyst, and the mixture further refluxed in a dean stark apparatus at 65°C for 4 hrs. The kinetic, isotherm and thermodynamic studies of the crude oil adsorption were investigated at varied time intervals of 20 to 100 minutes, temperature ranges of 30°C, 40°C, 60°C, 80°C and 100°C, and varied pH of 2, 4, 6, 8 and 10 for both adsorbents respectively. The pseudo-first-order, pseudo-second-order, Elovich and Weber Morris kinetic models were used for the kinetic studies. The* R^2 *values for all the models used were above 0.93 for both adsorbents respectively showing a good data fit except for rice husk adsorbent* ($R^2 = 0.867$) *for Weber Morris model. The Langmuir, Freundlich, Temkin and Dubinin–RadushKevich (R-D) Isotherm models were used to study the adsorption behaviors. The experimental data did not fit into Freundlich and Temkin isotherms for both adsorbents. The experimental data fitted best into Langmuir Isotherm for both adsorbents with* R^2 *values of 0.997 and 0.957 for saw dust and rice husk respectively. The values of* ΔG° *for both saw dust and rice husk were negative showing that adsorption processes were spontaneous and feasible at temperature ranging from 30 to 100°C. The standard enthalpy changes* ΔH° *for both saw dust and rice husk were positive and less than 80 KJ/mol respectively, implying that the process was endothermic and was more of physisorption. This also means that the sorption was a surface phenomenon. Also the* ΔS° *values were positive for both adsorbents respectively, indicating system disorderliness, which further implies the feasibility process.*

Keywords: *Kinetics, Thermodynamics, Isotherm, Crude oil, Adsorption*

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I. INTRODUCTION

In recent years, one of the environment distresses in the petroleum industry is spilled oil on sea water (Robabeh et al., 2015). Also in recent decades, water pollution of seas and oceans is a growing concern for the contributions of several countries in the destruction of biodiversity and the rest of the Earth too (Reza et al., 2014). One of the major sources of pollution in seas and oceans is oil spill that may be due to releases of crude oil or its derivative products such as gasoline, diesel or lubricant oil from tankers, ships, offshore platforms, or heavier fuels used by large ships such as bunker fuel (Reza et al., 2014).

The methods commonly used to remove oil involve oil booms, dispersants, skimmers, sorbents etc. The main limitations of some of these techniques are their high cost and inefficient trace level adsorption (Wardle-Smith, 1983). Also most of the dispersants are often inflammable and cause health hazards to the operators and potential damage to fowl, fish and marine mammals. They can also lead to fowling of shorelines and contamination of drinking water sources (NRC, 1989; Shashwat et al., 2006).

Removal of oil by sorption has been observed to be one of the most effective techniques for complete removal of spilled oil under ambient conditions (Shashwat et al., 2006). Various organic wastes have been used as adsorbents (Lin et al., 2010). During the last years of searching for new materials for the preparation of adsorbents, greater attention is paid to the utilization of renewable resources such as agricultural wastes or wastes from food processing industry (Sathasivam and Haris, 2010; Nduka et al., 2008). Plant-processing wastes can be used directly for purification of sea water from oil spills, or after some thermal retreatment, increasing their adsorption capacity several times (Angelova et al., 2011).

The work aimed at the kinetic, thermodynamic and isotherm studies of the adsorption of crude oil from surface water using esterified rice husk and saw dust as adsorbents.

II. MATERIALS AND METHOD

2.1 Materials

The materials used for this work include rice husk, saw dust, crude oil, distilled water, phosphoric acid (H_3PO_4), potassium hydroxide (KOH), sulphuric acid (H_2SO_4), hydrochloric acid (HCl), stearic acid, sieving net, n-hexane.

The rice husk and saw dust were washed with water to remove unwanted materials and oven dried at 110°C for 2hrs.The dried rice husk and saw dust were further carbonized in a muffle furnace at 600°C for 8 hours respectively. After the carbonization, the samples were cooled and stored in a dry transparent container for further use (Angelova et al., 2011).

2.2 Methods

Characterization of the samples was carried out using proximate analysis and scanning electron microscopy (SEM).

Modification of the carbonized samples by esterification

2.0g of carbonized rice husk and sawdust were treated differently with 0.4g of fatty acid (stearic acid) in 200ml of n-hexane containing two drops of concentrated H_2SO_4 as catalyst. The mixture was refluxed in dean stark apparatus at 65± 2°C for 4 hrs. After reaction, the esterified acid-grafted sawdust and rice husk were washed severally with n-hexane. The fatty grafted sawdust and rice husk were dried in an oven at 110°C for 12 hours respectively (Banerjee et al., 2006). They were then stored in dry tightly closed bottles respectively.

Batch adsorption experiment

The isotherm study was carried out in batch experiments. Five sets of constant initial concentration of 20 g/L of crude oil-water mixture were prepared. Onto the floating crude oil, different weights of adsorbents of 0.2g, 0.4g, 0.6g, 0.8g and 1.0g were added and filtered after 60mins at ambient temperature and constant pH of 7 with a sieving net, they were air dried overnight and weighed. This process was repeated for the two adsorbents by increasing their concentration progressively from 10 g/L to 50 g/L. The experiments were also carried out at varied time intervals of 20 minutes to 100 minutes; at varied temperatures of 30°C, 40°C, 60°C, 80°C and 100°C, and varied pH of 2, 4, 6, 8 and 10.

2.3 KINETICS STUDY

2.3.1 Pseudo First order kinetics

The linear form of the Lagergren or pseudo first order kinetics equation is given in Equation 2.1 (Lagergren, 1898).

$$\mathrm{Log}\,(q_e - q_t) = \log q_e - \left(\frac{k_1 t}{2.303}\right) \tag{2.1}$$

Where q_e= equilibrium adsorption capacity (mg/g)
q_t = instantaneous adsorption capacity (mg/g)
k_1= pseudo first order adsorption constant (min^{-1})

B. Pseudo Second Order kinetics

The linear form of the Pseudo second order kinetics is shown in Equation 2.2. This model is based on the assumption that chemisorption is the rate determining step (Ho &McKay, 1998).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2.2}$$

Where k_2 = the pseudo second order adsorption constant (g/mg min)

The calculated adsorption capacity qe_{cal} is obtained from the slope of the plot of $\frac{t}{q_t}$ against t while k_2 is obtained from the intercept

2.3.2 Elovich Kinetic Model

Another kinetics model that was applied is the Elovich equation (Low, 1960). This model was originally developed for adsorption of gases on solid surfaces but it also provides a good model for solid-liquid or solid –solid adsorption (Folasegun & Kovo, 2014). The linear form of the equation is given in Equation 2.3.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad (2.3)$$

Where α is the initial sorption rate constant (mg/g min) and β (g/mg) is related to the extent of surface coverage and the activated energy for chemisorption.

2.3.3 Weber Morris Kinetics Model

Another kinetics model that is often used in adsorption study is the Weber Morris model (Das & Mondal, 2011). This model provides indices of the intra-particle diffusion rate (k_d) and boundary layer effect (l).The larger the l, the greater the contribution of surface sorption in the rate determining step. The model is given in Equation 2.4.

$$q_t = k_d t^{1/2} + l \quad (2.4)$$

Where k_d= intra-particle diffusion rate constant (mg/g min ^{½})
l= the boundary layer effect (mg/g)

2.4 ADSORPTION ISOTHERMS

2.4.1 Langmuir Isotherm

This isotherm was based on the assumption took place in monolayer surface coverage. The linear form of the Langmuir isotherm is given in Equation 2.5.

$$\frac{c_e}{q_e} = \frac{1}{q_l k_l} + \frac{c_e}{q_l} \quad (2.5)$$

Where
q_l = Monolayer adsorption capacity (mg/g)
k_l = Langmuir adsorption constant (L/mg)

Langmuir isotherm provides a dimensionless quantity known as separation factor RL that reflects the nature of the adsorption process. Adsorption process can be irreversible (RL = 0), favorable (0 < RL < 1), linear (RL = 1) or unfavorable (RL > 1) (Folasegun & Kovo, 2014; Anirudan & Radhakrishnan, 2008). The equation for calculating RL is given in Equation 2.6.

$$R_l = \frac{1}{[1+K_l C_o]} \quad (2.6)$$

Where C_o is the initial concentration of the adsorbate (g/l)

2.4.2 Freundlich Isotherm

Another adsorption isotherm that is often used to model the adsorption of heavy metals is the Freundlich isotherm. The linear form of this isotherm is given in Equation 2.7.

$$\log q_e = \log k_f + {}^{1}\!/_{n} \log C_e \quad (2.7)$$

Where
K_f = Freundlich adsorption constant (mg/g) $(L/mg)^{1/n}$
n = adsorption index, reflecting the intensity of the adsorption. If n lies between 1 and 10, it indicates a favorable adsorption (Freundlich, 1906).

2.4.3 Temkin Isotherm

This Isotherm takes into account the interaction between adsorbents and metal ions, and is based on the assumption that the free energy of sorption is a function of the surface coverage. The linear form of this isotherm is as shown in Equation 2.8 (Anirudan & Radhakrishnan, 2008).

$$q_e = B \ln A + B \ln C_e \quad (2.8)$$

Where

$$B = RT/b_T \quad (2.9)$$

B is related to the heat of adsorption. A is the equilibrium binding constant (mg/L), b_T $(\frac{J.g}{L.mol})$ is adsorption constant, R is the universal gas constant (8.314J/mol. K), T is the absolute temperature of the adsorption process.

2.4.4 Dubinin-Radushkevich (R-D) Isotherm

Another isotherm that is applied in metal ion adsorption is the R-D isotherm. The linear form of this isotherm is given in Equation

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (2.10)$$

Where
β is a coefficient related to the mean free energy of adsorption per mol of the metal ion (mol^2/J^2),
q_m is the theoretical saturation capacity (mg/g) and Ɛ is the polanyi potential expressed as:

$$\varepsilon = \mathrm{RT}\ln(1 + {}^{1}/_{\mathrm{C_e}}) \qquad (2.11)$$

$\mathrm{C_e}$ is the equilibrium concentration (mg/L)

2.5 THERMODYNAMICS OF THE ADSORPTION PROCESS

The thermodynamic parameters that would be applied to the system are the standard Gibb′s free energy change (ΔG°), the standard enthalpy change (ΔH°) and the standard entropy change (ΔS°). The standard Gibb′s free energy change would indicate if the process is spontaneous ($\Delta G^\circ < 0$), if the process is non-spontaneous ($\Delta G^\circ > 0$) or if the process is at equilibrium ($\Delta G^\circ = 0$). The standard enthalpy change would indicate if the process is endothermic ($\Delta H^\circ > 0$) or exothermic ($\Delta H^\circ < 0$). Moreover, the absolute value of the standard enthalpy change would indicate if the process is chemisorptions ($80 < \Delta H^\circ < 200$kJ/mol) or physiosorption ($\Delta H^\circ < 80$ kJ/mol) (Folasegun & Kovo, 2014). The standard entropy change would indicate the degree of disorderliness of the process. The process is possible ($\Delta S^\circ > 0$) or not possible ($\Delta S^\circ < 0$). Equations 2.11 - 2.13 are used to calculate the thermodynamic parameters (Liu & Liu, 2008).

$$\Delta G^\circ = \mathrm{RTlnK} \qquad (2.12)$$

$$\mathrm{lnK} = \frac{\Delta G^\circ}{\mathrm{RT}} = \frac{-\Delta H^\circ}{\mathrm{RT}} + \frac{\Delta S^\circ}{\mathrm{R}} \qquad (2.13)$$

Using Equation 2.13, a plot of lnK against the inverse of temperature would produce a straight line where the standard enthalpy change would be calculated from the slope and the standard entropy change would be calculated from the intercept.

III. RESULTS AND DISCUSSION

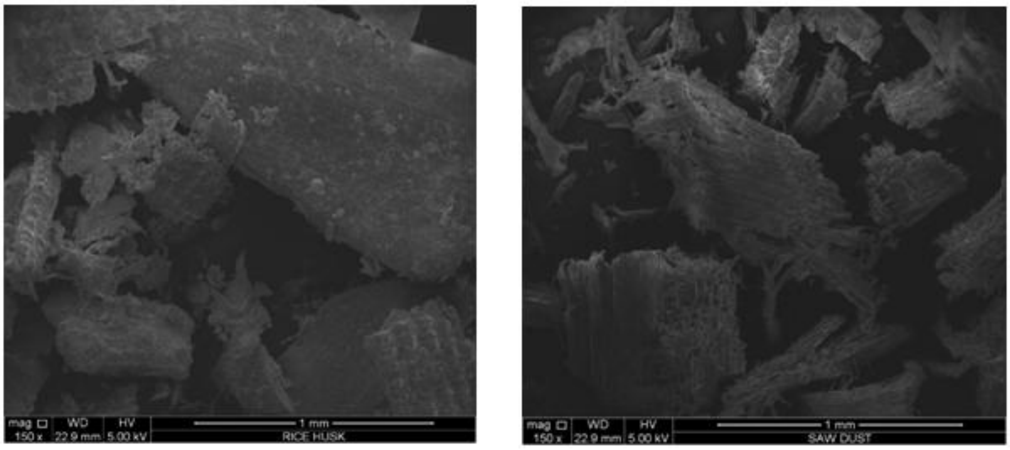
3.1 Characterization Studies

Table 3.1: Proximate analysis of rice husk and saw dust

Parameters/ Adsorbents	Rice husk, RH			Saw dust, SD		
	Raw	carbonized	Esterified	Raw	Carbonized	Esterified
Fixed carbon (%)	10	50.3	70.38	9.9	53.37	56.6
Ash content (%)	6	4.83	3.52	2.2	4.83	2.97
Surface area (cm^2/g)	769	801	820.1	778	900.34	935
Bulk density (g/cm^2)	0.43	0.87	0.44	0.41	0.52	0.52
Iodine number (mg/g)	588	714	733.42	573	727.16	739
Moisture content (%)	7	1.82	2.75	37	2.41	2.46
Volatile content	50.9	43	31	77	38	38

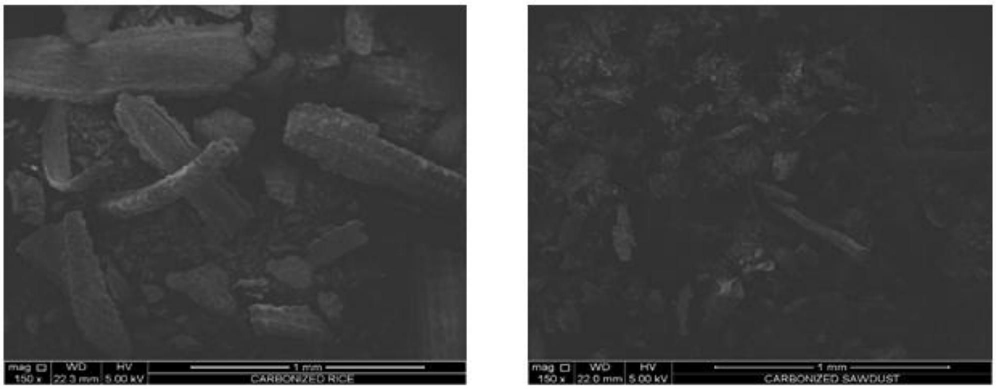
3.1.1 Scanning Electron Microscopy (SEM) Analysis

The surface morphologies of the raw biomass (saw dusts and rice husk), carbonized biomass (saw dust and rice husk) and stearic acid modified biomass (saw dust and rice husk) are presented in Figures 3.1 to 3.3 Figures 3.2 and 3.3 respectively showed that carbonization and further modification of the biomass (saw dust and rice husk) with stearic acid were able to remove the volatile content and opened the pores thereby increasing the adsorption surface area.



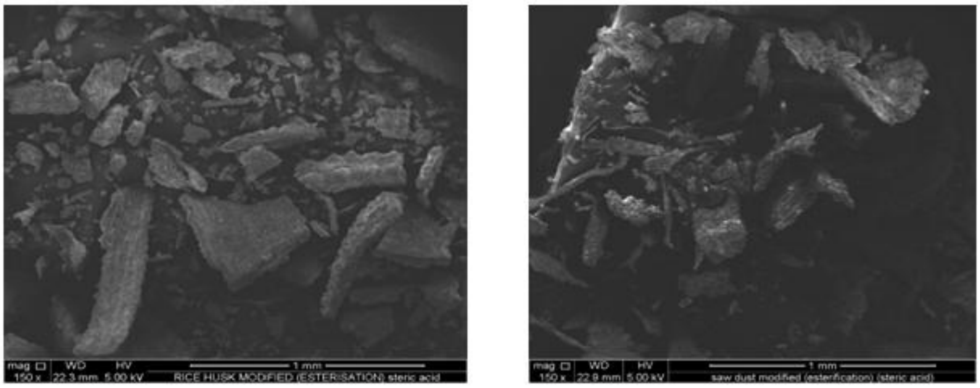
(a) Rice husk **(b) Saw dust**

Figure 3.1: Raw rice husk and saw dust



(a) Rice husk **(b) Saw dust**

Figure 3.2: Carbonized rice husk and saw dust



(a) Rice husk **(b) Saw dust**

Figure 3.3: Stearic acid modified rice husk and saw dust

3.2 KINETICS STUDIES

3.2.1 Pseudo- First-order kinetics

The parameters of the pseudo first order kinetics for the sorption of crude oil using saw dust and rice husk activated carbons are shown in Table 3.2. The experimental data for both adsorbents fitted into the pseudo first order model as the coefficient of determination R^2 values were approximately 0.946 and 0.998 respectively. The observed adsorption capacity for saw dust was 5.05 g/g while the calculated adsorption capacity was 3.64 g/g which means that the observed adsorption capacity was 27.9% higher than the calculated. The observed adsorption capacity of rice husk was also higher than the calculated value. The observed value was 2.55 g/g while the calculated value was 1.9 g/g which mean that the observed value was 22% higher than the calculated value. Comparing the R^2 values for the two adsorbents; 0.946 for sawdust and 0.998 for rice husk for pseudo-first-order kinetics respectively, it can be inferred that the experimental data gave good fitness for the kinetics model. Equilibrium was almost attained at the same time; after 80 minutes. The adsorption capacity of saw dust was however higher than that of rice husk. The first order kinetics constants for the two adsorbents were 0.05$min^{-1}$and 0.03min^{-1} for rice husk and saw dust respectively.

Table 3.2: The Pseudo First and Second Order Kinetics Parameters

Saw dust					Rice Husk			
	qe (obs) (g/g)	qe (cal) (g/g)	R^2	K (min^1)	qe (obs) (g/g)	qe (cal) (g/g)	R^2	K (min^1)
1st Order	5.05	3.64	0.946	0.03	2.55	1.90	0.998	0.05
2nd Order	5.05	6.09	0.990	0.01	2.55	2.86	0.997	0.03

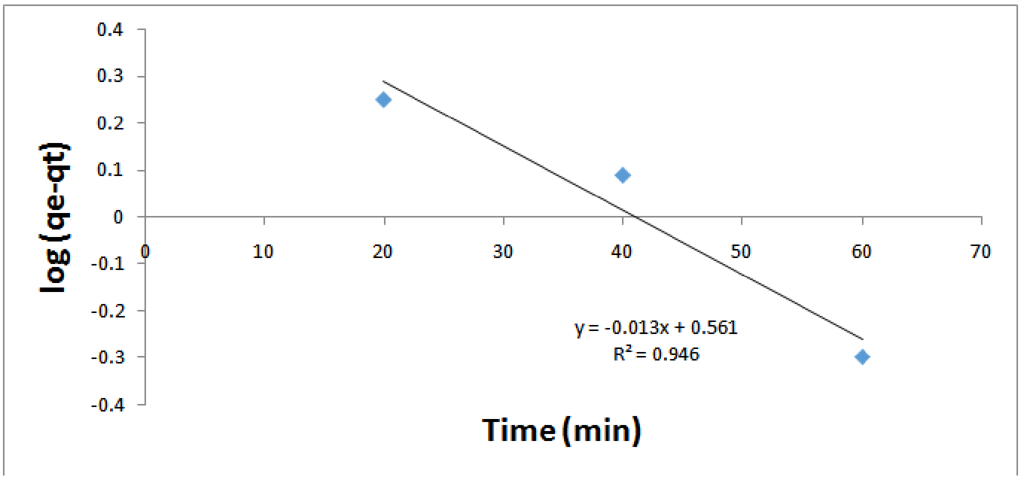


Fig.3.4: The first order kinetics model for saw dust.

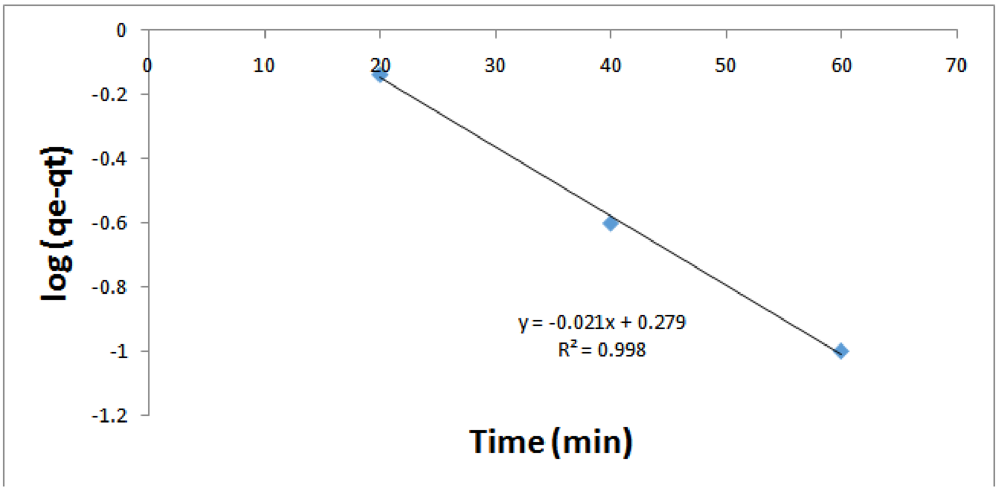


Fig.3.5: The first order kinetics rice husk

3.2.2 Pseudo-Second-Order kinetics

The pseudo-second-order kinetics parameters are also shown in Table 3.2. The experimental data for both rice husk and saw dust equally provided good fit for the pseudo second order kinetics model with coefficient of determination R^2 values of 0.990 and 0.997 for saw dust and rice husk respectively. The calculated and observed equilibrium capacities were closer in second order kinetics than in first order. The calculated equilibrium capacity for saw dust was 20% higher than the observed value, while the calculated value for rice husk was 11% higher than the observed value. The second order kinetics constant for saw dust was 0.01min^{-1} while that of rice husk was 0.03min^{-1}.

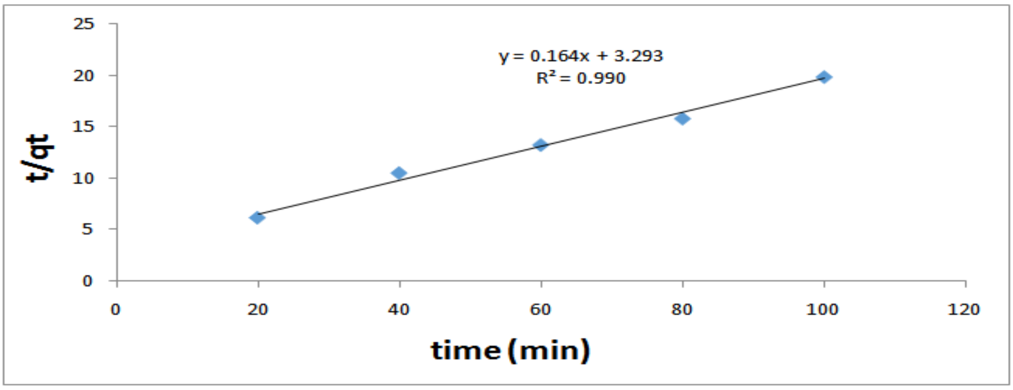


Fig.3.6: the pseudo second order kinetics for saw dust

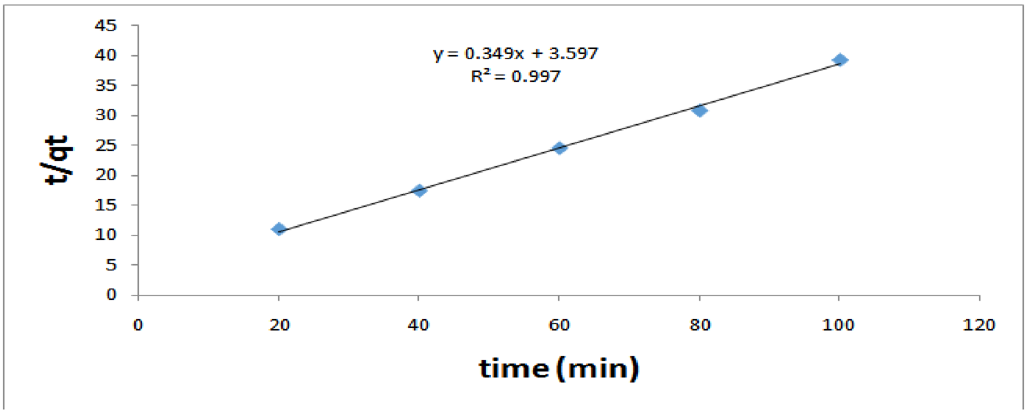


Fig.3.7: The pseudo second order kinetics for rice husk

3.2.3 ELOVICH KINETICS MODEL

The experimental data was also modeled with Elovich kinetics equation given in equation 2.3. The plot of the adsorption capacity (q_t) against the logarithm of time (t) gave straight lines for both adsorptions with saw dust and rice husk respectively. The Elovich parameters α and β were calculated from the intercept and slope respectively. The Elovich model provided a good fit into the experimental data as the coefficient of determination R^2values were approximately 1.0. The Elovich parameters are shown in Table 3.3.

Table 3.3: Elovich Kinetics parameters

	α (g/g.min)	β (g/g)	R^2
Saw dust	0.83	0.82	0.959
Rice Husk	1.27	2.11	0.934

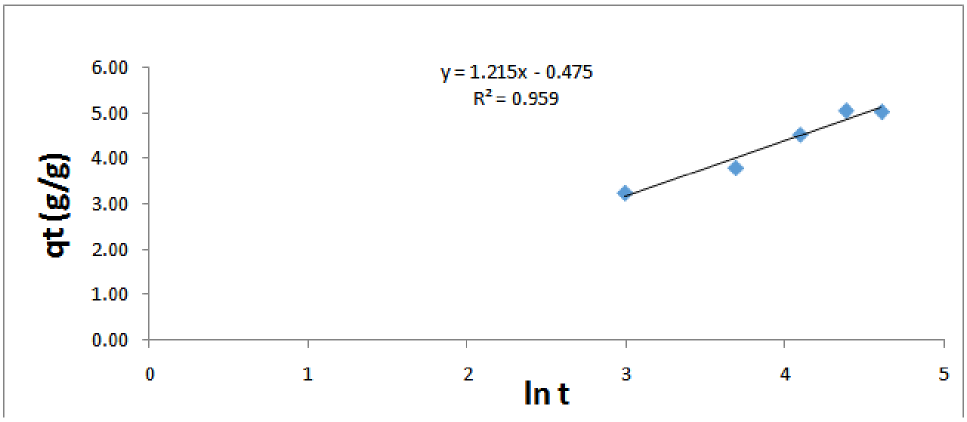


Fig.3.8: Elovich Kinetics model for saw dust

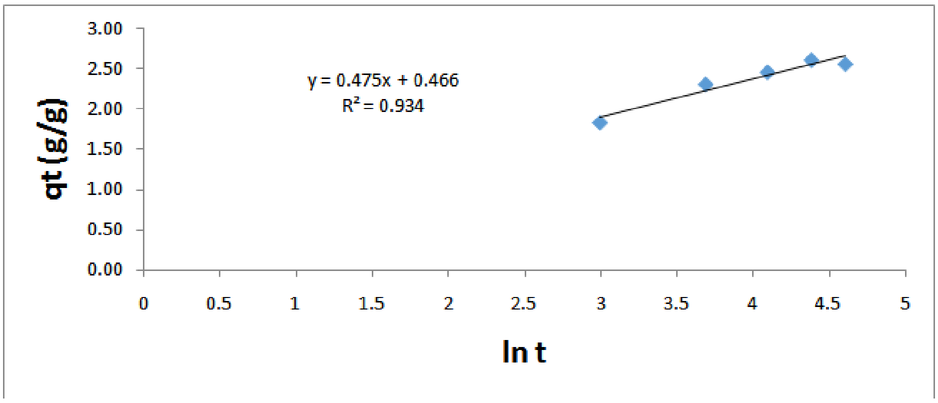


Fig. 3.9: Elovich Kinetics model for rice husk

3.2.4 WEBER MORRIS KINETICS MODEL

Following Equation 2.4, the adsorption capacity was plotted against the square root of time in order to investigate the fitness of the experimental data into Webber Morris Kinetics Model. The intra-particle diffusion rate constant k_d (mg/gmin$^{1/2}$), was obtained as the slope of the plots while the boundary layer effect l (mg/g) was obtained as the intercept of the plots. The adsorption with saw dust provided a good fit with the model as the coefficient of determination was approximately 1.0 while that of rice husk was not close to 1.0. The Webber Morris kinetics parameters for both saw dust and rice husk are shown in Table 3.4.

Table 3.4: Webber Morris Kinetics parameters

	K_d (g/gmin$^{1/2}$)	L (g/g)	R^2
Saw dust	0.354	1.671	0.958
Rice Husk	0.133	0.342	0.867

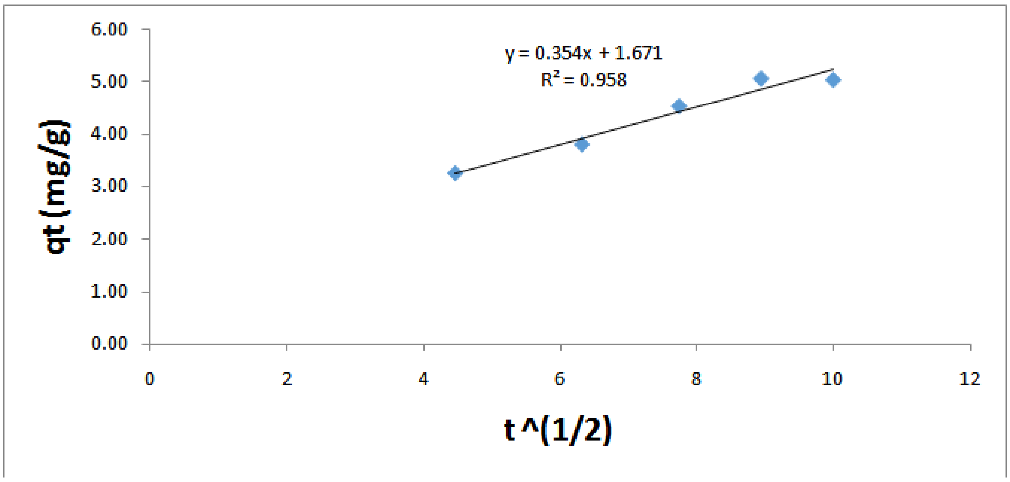


Fig.3.10: Weber Morris Model for saw dust

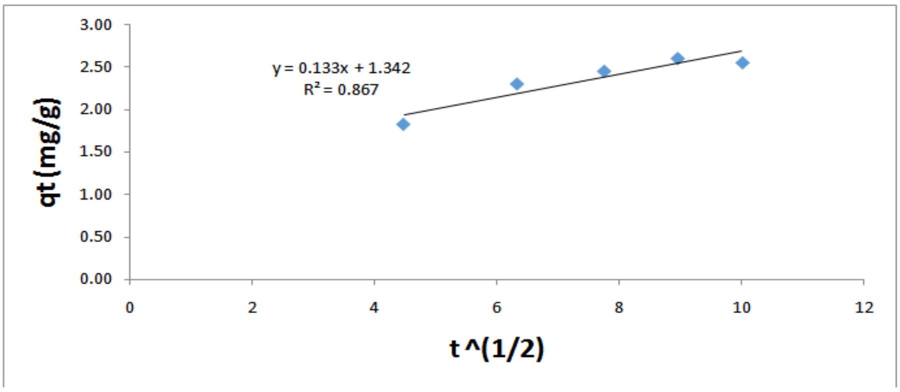


Fig. 3.11: Weber Morris model for rice husk

3.3 ADSORPTION ISOTHERM

The experimental data was modeled into adsorption isotherms given in Equations 2.5 – 2.11. The Isotherm parameters for Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (R-D) are given in Table 3.5. The coefficient of determination R^2 values for Langmuir isotherm of both saw dust and rice husk were close to 1.0. The experimental data can be said to be fitted into Langmuir isotherm. The monolayer adsorption capacity ql for saw dust and rice husk were 5.525 and 2.739 respectively. These values lie between the equilibrium adsorption capacities at the initial concentration between 10-60g/L.

The experimental data did not fit into Freundlich and Temkin isotherms. The coefficients of determination R^2 values were not close to 1.0. For this reason the parameters of the Freundlich and Temkin isotherms cannot be applied to the adsorption using saw dust and rice husk. The parameters were however provided in Table 3.5.

The experimental data for saw dust fitted into R-D isotherm as the coefficient of determination was close to 1.0. The value of the monolayer adsorption capacity q_m agreed closely with that of the Langmuir isotherm. The R^2 value for rice husk was however not close to 1.0 but the calculated monolayer adsorption capacity was close to that of Langmuir isotherm. The R-D parameter for saw dust can be adopted.

Table 3.5: Adsorption Isotherm parameters

Isotherm	Parameter	Saw dust	Rice husk
Langmuir	Kl(L/g)	-6.038	0.496
	ql(g/g)	5.525	2.739
	R^2	0.997	0.957
Freundlich	n	10.87	-33.33
	Kf(g/g)(g/L)^{1}/^{n}	4.24	2.77
	R^2	0.32	0.05
Temkin	bT(J.g/L.mol)	6166	31489
	A(g/L)	49455	7.5E-16
	R^2	0.246	0.052
Dubinin-Radushkevich	B(mol^2/J^2)	4.0E-07	-5.0E-07
	qm(g/g)	5.88	2.45
	R^2	0.765	0.221

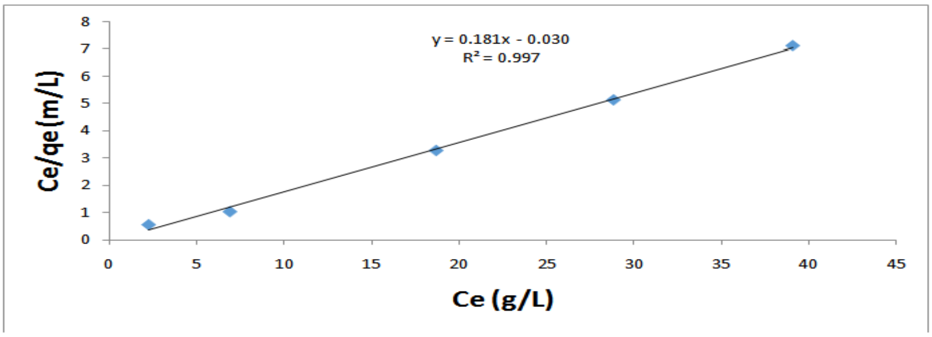


Fig.3.12: The Langmuir Isotherm plot for saw dust

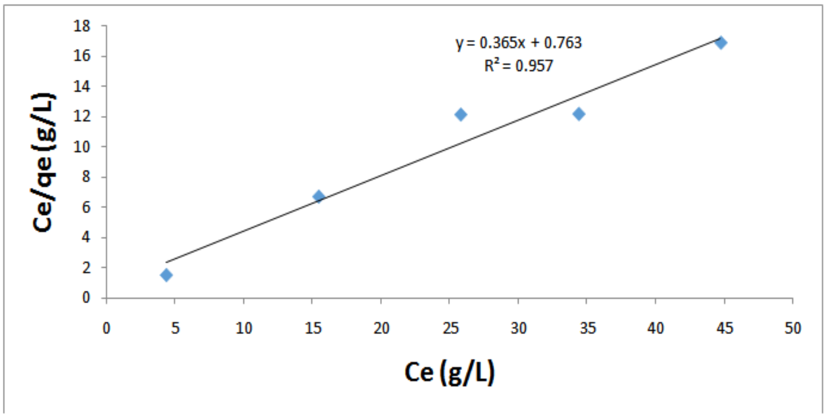


Fig.3.13: The Langmuir Isotherm plot for rice husk

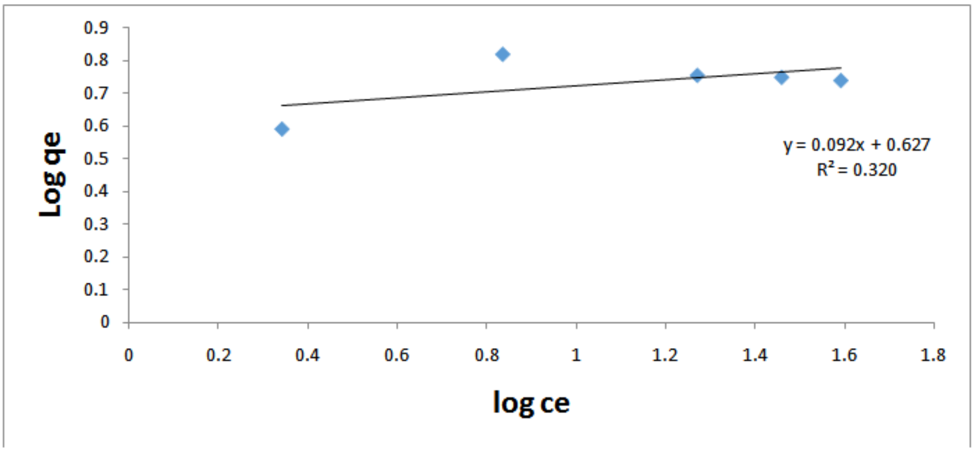


Fig.3.14: Freundlich Isotherm for saw dust

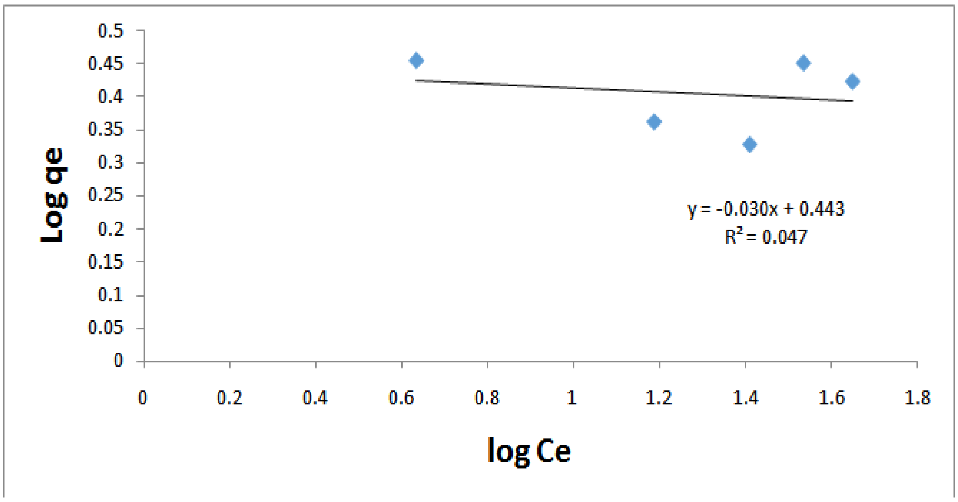


Fig.3.15: Freundlich Isotherm for rice husk

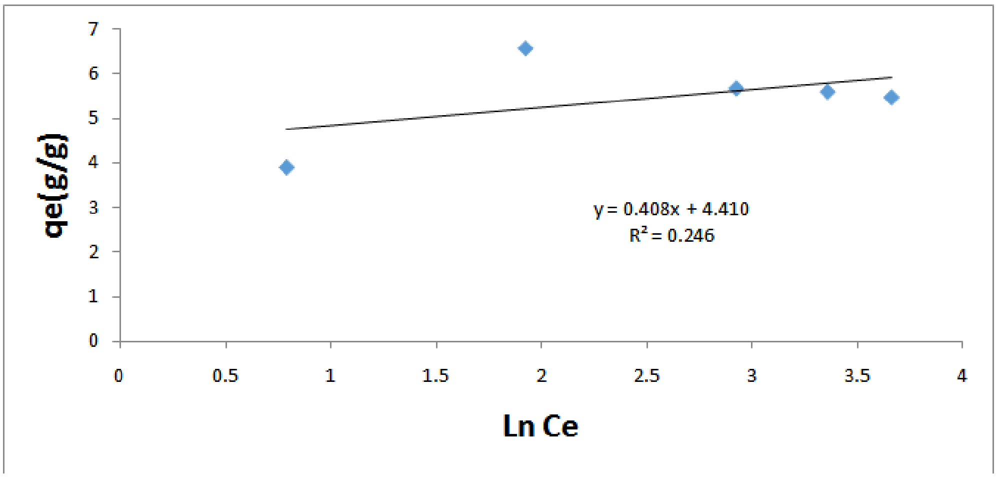


Fig. 3.16: Temkin Isotherm for saw dust

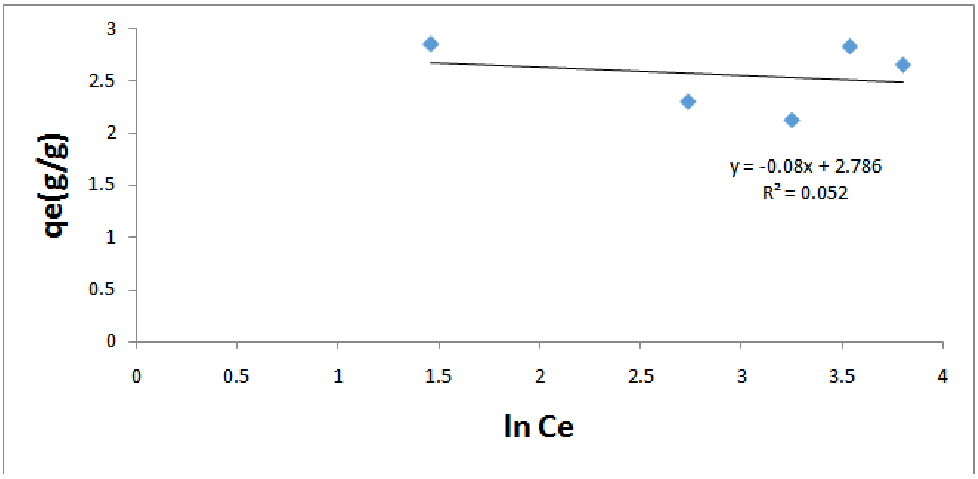


Fig. 3.17: Temkin Isotherm for Rice Husk

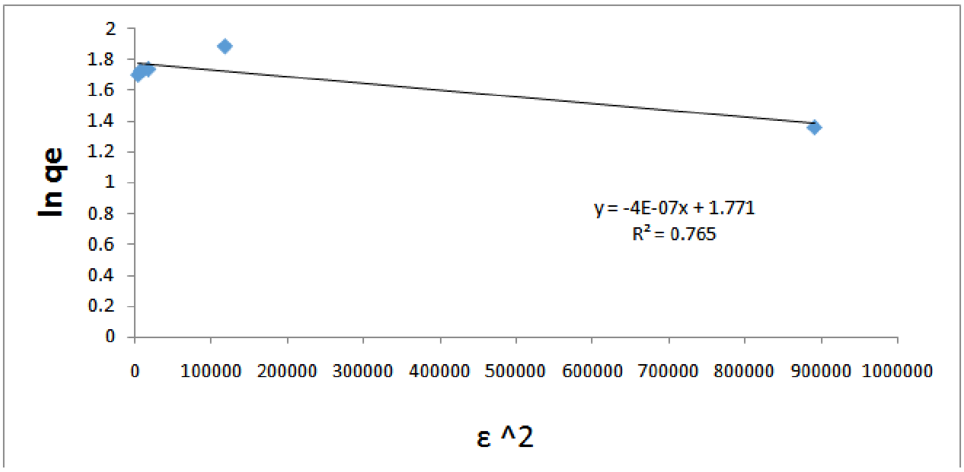


Fig.3.18: R-D Isotherm for saw dust

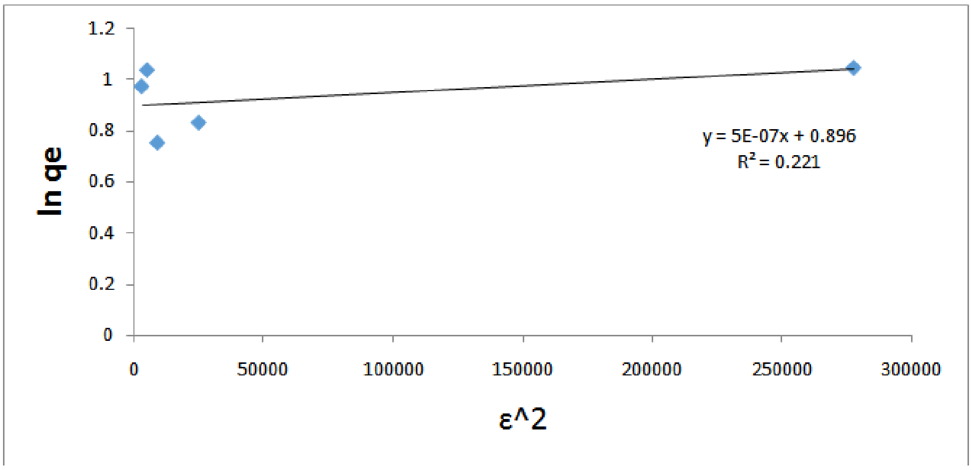


Fig.3.19: R-D Isotherm for Rice Husk

3.4 THERMODYNAMICS

The thermodynamic studies were carried out following Equations 2.11 – 2.13. The natural logarithm of the equilibrium constant k was plotted against the inverse of the absolute temperature as shown in Figures 3.20 and 3.21. The standard Gibb's free energy change ΔG˚ was calculated using Equation 2.12. The values of ΔG˚ for both saw dust and rice husk were negative showing that the adsorption processes were spontaneous and feasible at temperatures ranging from 30 to 100˚C.

The standard enthalpy changes ΔH˚ were calculated from the slope of the plot. The values of the ΔH˚ were all positive showing that the process was endothermic. The values of the ΔH˚ for both saw dust and rice husk were less than 80 KJ/mol showing that the adsorption processes were more of physiosorption. In other words the sorption of oil using saw dust and rice husk activated carbons were physical processes and could be reversed. This also means that the sorption was a surface phenomenon.

The standard entropy changes ΔS˚ for both saw dust and rice husk were obtained from the intercept of the plots. The values of the ΔS˚ were all positive showing increasing disorderliness of the system, in other words the processes were possible. The thermodynamic parameters could be adopted as the coefficient of determination R^2 values were close to 1.0.

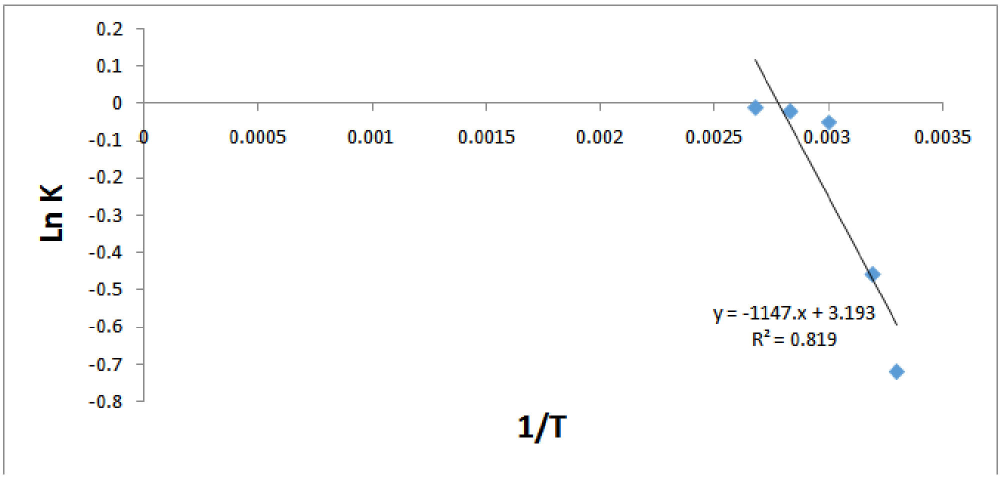


Fig 3.20: Thermodynamics plot for saw dust

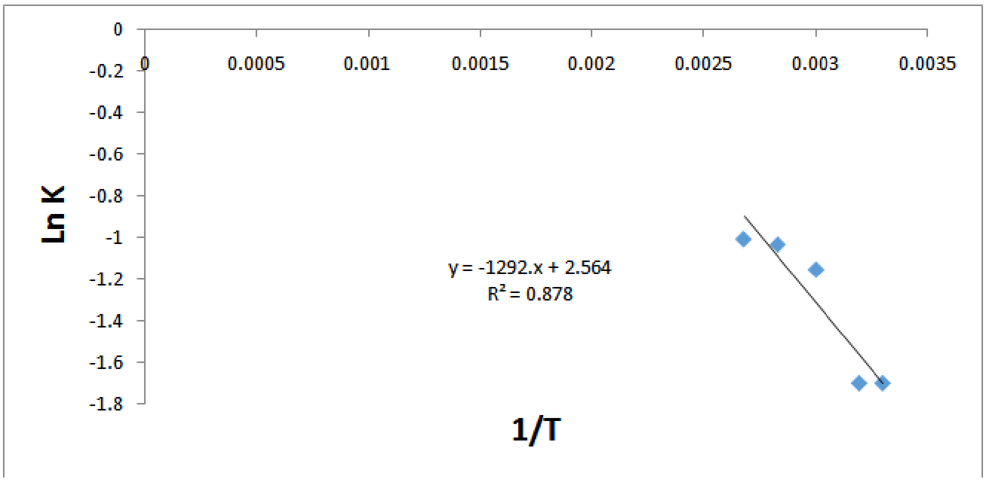


Fig 3.21: Thermodynamics plot for rice husk

Table 3.6; the Thermodynamics parameters

	Saw Dust			Rice Husk		
T (K)	ΔG˚(kJ/mol)	ΔH˚(kJ/mol)	ΔS˚(kJ/mol.K)	ΔG˚(kJ/mol)	ΔH˚(kJ/mol)	ΔS˚(kJ/mol
303	-1812.56	9.54	0.026	-4272.24	10.74	0.021
313	-1191.41			-4413.24		
333	-138.457			-3191.26		
353	-58.6988			-3031.74		
373	-31.0115			-3123.9		

IV. CONCLUSION

Esterified rice husks and saw dusts were explored as adsorbents for crude oil removal from surface water. The experimental data for both adsorbents fitted into the pseudo first order model as the coefficient of determination R^2 values were approximately 0.946 and 0.998 respectively. The experimental data for both rice husk and saw dust equally provided good fit for the pseudo second order kinetics model with coefficient of determination R^2 values of 0.990 and 0.997 for saw dust and rice husk respectively. The data for both adsorbents showed good fit for the Elovich model while saw dust showed a better fit than rice husk in the Webber Morris model. The experiment fitted into Langmuir isotherm but didn't fit into Freudlich and Temkin isotherm for both adsorbents. The values of the ΔH° for both saw dust and rice husk were less than 80KJ/mol showing that the adsorption processes were more of physiosorption. In other words the sorption of oil using saw dust and rice husk activated carbons were physical processes and could be reversed. This also means that the sorption was a surface phenomenon. In general, saw dust showed better adsorption efficiency of crude oil from surface than rice husk in this study conditions.

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