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Original Research Article

Kinetic and Thermodynamic Studies of the Treatment of Biseni Crude Oil Polluted Water with Almond Seed Shell Activated Carbon

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ABSTRACT

Crude oil is a toxic environmental pollutant which needs to be removed from domestic water sources. In this work, Almond seed shell activated carbon (ASSAC) was explored for the treatment of crude oil polluted water. The almond seed shell was prepared and carbonized at 400 ℃ for 240 min. From the analysis of the results, the adsorption of crude oil emulsion from Biseni crude oil polluted water onto ASSAC was better represented by Temkin isotherm. The kinetic study shows that the removal of crude oil emulsion from the sample onto ASSAC followed the pseudo second order adsorption model. The thermodynamic parameters for the removal of crude oil from the crude oil polluted water were an enthalpy of 3.27 kJ/mol, entropy of 12.1 J/mol.K and Gibbs free energy of 0.503 J/mol.K. These results shows that ASSAC, has the potential for the removal of crude oil emulsion from crude oil polluted water.

1. INTRODUCTION

Biseni Creek is located in Yenagoa, Bayelsa State, Nigeria. It is a freshwater swamp forest which has been classified as one of the severely oil polluted areas in the Niger Delta part of Nigeria (Kadafa, 2012; Kelle, 2018). Biseni Creek provides huge support of numerous species of aquatic fauna, flora as well as human life (Alkhalssi *et al.*, 2014).

The damages done to this swamp forest vary with the amount crude oil spilled and its toxicity. The plants and animals within this swamp forest are at the verge of extinction (Kafada, 2012; Maulion *et al.*, 2015). Its negative effects on the humans, living in the area also include eyes and mucus membranes, skin irritation, increasing susceptibility to infection and damages to the gastrointestinal track and internal organs when crude oil is taken in (Kukwa *et al.*, 2014; Werth *et al.*, 2019). This undesirable problem has greatly increased to an alarming magnitude with increasing level of the production and transportation of crude oil in the area (Maulion *et al.*, 2015). Some crude oil spill in the past have resulted to some communities been relocated by government agencies, loss of ancestral homes, pollution of the surface and ground water, destruction of fishing zones and depopulation of fishes which is the major occupation of the inhabitants in this creek (Kadafa, 2012). These consequences associated with crude oil polluted water, makes it of extreme concern to the people of this community, the public, the government and industries operating in this creek (Asadu *et al.*, 2021). The people living in Biseni community and environs deserve safe portable water for their livelihood; however, they are now faced with crude oil polluted water and all its associated negative effects.

Presently, crude oil-polluted water treatment is carried out by gravity separation (Elhemmali *et al.*, 2020), coalescence method (Dorota, 2019), membrane separation (Wang *et al.*, 2016), chemical demulsification (Kokal, (2002), electrochemical method (Dorota, 2019),, sedimentation (Luter *et al.*, 2019), biochemical method (Aljuboury *et al.*, 2017), oxidation pond, coagulation, anaerobic contact (Aljuboury *et al.*, 2017), adsorption, or a combination between these methods.

Adsorption-filtration operations using activated carbon is generally used to remove pollutants in water because of its degree of efficiency and affordability (Mokkapati *et al.*, 2019; Ogbodo *et al.*, 2021). Commercial activated carbon is expensive and the cost of regeneration it is also high (Menya *et al.,* 2017). The people in the rural areas finds it difficult to afford it, hence the persistence of lack of safe potable water in these areas. Most researchers have explored activated carbon from agro-based substances for the treatment of crude oil emulsion from water, but these does not include activated carbon from almond seed shell (Menya *et al.,* 2017). Alkhalssi *et al.* (2014), researched on the emulsified crude oil in produced water using corn-cobs adsorbent. They got cutting oil from East Baghdad field, Iraq. In their research, a fixed-bed system was used to study the effectiveness of corncob adsorbent. The initial concentration of the oil was (600 – 1500 ppm, volumetric flow rate of 2 – 5 l/min bed height of 25 – 35 cm and a particle size of 1.05 – 1.6 mm), but the kinetic study and thermodynamic behavior of the adsorption operation were not considered. Also, the optimal conditions of the adsorption were not spelt out. Tontiwachwuthikul *et al.* (2016), investigated the treatment of waste lubricating oil spill using potato peels adsorbent. In their work, adsorption capacity was obtained as 2.15 g/g and the contact time used was 30 minutes. The operation followed a pseudo second order adsorption kinetic, but the optimal conditions, adsorption isotherm and thermodynamics of the adsorption were not considered. Maulion *et al.* (2015), investigated simulated oil using corncobs activated carbon tablets. In their findings, the quality of the corncobs activated carbon had a pH of 7.0, bulk density of 0.26 g/cm^3, average pore size of 45 nm, iodine number of 137 mg/g and a surface area of 1205 m^2/g. The optimum contact time was obtained as 60 minutes for the 3 tablet of activated carbon. Langmuir isotherm model gave the best fit among the isotherms used, while the kinetic and thermodynamic behaviors of the adsorption were not researched in the work. Asadu *et al.* (2021), worked on the removal of crude oil using grafted mango seed shell composite. They used selected operating conditions for the carbonization, activation and adsorption. They did not carry out design of experiment to obtain the optimum conditions at which the carbonization and activation of the grafted mango seed shell and removal of the crude oil was carried out. Ogbodo *et al.* (2021), investigated treatment of simulated crude oil contaminated water agricultural waste (musa-paradisiaca peels) adsorbent. They selected the operating conditions at which they carried out carbonization and activation of musa-paradisica peels. The operating conditions at which adsorption was also carried out was selected. Design of experiment was not carried out to obtain these operating conditions.

Almonds fruits are produced from Almond tree, also known as *Prunus dulcis* and botanically known as *Terminalia catappa*. It is a member family of Rosaceae (order Rosales). *Prunus dulcis* is an economically important tree crop grown primarily in Mediterranean climates. It grows mainly in the tropical regions of Asia, Australia and Africa. It is found in many parts of Southern Nigeria. It is often referred to as 'Ebeleboh' in Edo and Delta States (Asadpour et al, 2019). Beyond the rich sources of various nutrients of tropical

Almond, extracts from it contain several phytochemicals that can work against various ailments (Tontiwachwuthikul et al., 2016). The roots, stems, bark, shoots, leaves and fruit play an integral part in tackling diseases. Presently, the byproducts of almond (Skins and Shell) are used majorly as cattle feed or burned for energy (Asadpour et al., 2019).

Therefore, in this work, almond seed shell activated carbon was explored for the removal of crude oil from crude oil polluted water collected from Biseni community in order to fill these gaps in the field of adsorption-filtration operation.

2. MATERIALS AND METHODS

2.1. Collection and Carbonization of Almond Seed Shell

Almond seed Shell were collected from Crown estate, Okada, Edo State, Nigeria. They were washed thoroughly with tap water, to ensure that every water-soluble material attached to them was removed, and thereafter they were dried under the sun for several hours. The shells were sliced and the nut removed before they were dried again. The char Almond seed shell (800 g) was weighed and fed into the furnace set at 400 ^oC and allowed to remain it for about 240 min before been withdrawn, kept in a desiccator and allowed to cool down. The Almond seed shell carbon (ASSC) was crushed with mortar and pestle, sieved with standard sieve of less than 800 micron and kept in an air tight container. A total mass of 290.79 g was obtained from the carbonization.

2.2. Chemical Activation of the Adsorbent

An impregnation ratio of 1:3 of the carbonized almond seed shell and 0.175 M HCl was used (Gumus and Okpeku, 2015; Olufemi and Otolorin, 2017). This was then fed into the furnace (Nabertherm GmbH) set at 1000 ± 5 ^oC. After 240 min, it was withdrawn from the furnace and allowed to cool in a desiccator. It was washed severally with distilled water while the pH of the filtrate was been monitored with a pH meter (PH-2601) until the pH was 7.0 ± 0.5. The wet Almond seed shell activated carbon was then transferred to a stainless steel plate and fed into an oven set 110 ±5 ^oC in batches. It was withdrawn after 120 min, kept in a desiccator to allow it to cool down to room temperature. A total of 261.87 g of the activated carbon was obtained and it was packed in an air tight corner, ready for use.

2.3. Characterization of Almond Seed Shell Activated Carbon

The surface area of almond seed shell activated carbon was determined using Brunauer Emmett Teller (BET) analysis method. The surface morphology was determined using scanning electronic microscope (SEM). The functional groups present in the almond seed shell activated carbon was determined using the Fourier transform infra-red (FTIR) spectroscopy and the active minerals present in the activated carbon were determined by X-ray diffractometer analysis. The pH of the Almond seed shell activated carbon was determined using previously reported methods (Gumus and Okpeku, 2015; Ekpete *et al.*, 2017). The pore volume and porosity were determined using the method reported by Dagde, (2018). The ash content was determined using the method reported by Gumus and Okpeku, 2015; El-Araby *et al.*, 2017. The moisture content and bulk density were determined using the methods reported by Rafatulla *et al.* (2012). The iodine number was using the method reported by Adie *et al.* (2012) and Olufemi and Otolorin, (2017).

2.4. Isotherm Studies

The batch adsorption experiment was carried out by agitating 1 g of Almond seed shell activated carbon with 25 ml of the crude oil sample having concentrations of 100, 120, 140, 160 and 180 mg/l in a temperature controlled water bath set at 50 ℃ for 40 min. The amount of crude oil adsorbed onto the Almond seed shell activated carbon was calculated using Equation (1).

$$q_e = \frac{(C_o - C_e)V}{X} \quad (1)$$

Where q_e = amount of crude oil removed or adsorbed at equilibrium, C_o (mg/l) and C_e (mg/l) are the initial concentration of the crude oil and concentration of the crude oil in the filtrate at equilibrium, X is the mass (mg) of the adsorbent and solution volume (V) (Adie *et al.*, 2012).

The removal of the crude oil was tested with two parameters models like Langmuir (Hameed and El-Khaiary, 2008), Freundlich (Ghogomu *et al.*, 2016) and Temkin (Yuh-Shan *et al.*, 2009), represented as Equations (2) to (4) respectively, and three parameters models such as Redlich-Peterson (Oseke *et al.*, 2018), Dubinin-Radushkevic (Onwuka *et al.*., 2018) and Toth (Adebayo *et al.,* 2015; Debela, 2016; Iryani *et al.*, 2017) represented as Equations (5) to (7) respectively.

$$\frac{Ce}{q_e} = \frac{1}{b\,a} + \frac{Ce}{a} \tag{2}$$

$$Log\ q_e = \text{Log}\ K_f + \frac{1}{n}\text{Log}\ C_e \tag{3}$$

$$q_e = \frac{RT}{b_T}\ln K_T + \frac{RT}{b_T}\ln C_e \tag{4}$$

$$\frac{C_e}{q_e} = \frac{a_R C_e^{\beta}}{K_R} + \frac{1}{a_R} \tag{5}$$

$$\ln(q_e) = \ln(q_{max}) - \beta E^2 \tag{6}$$

$$\left(\frac{C_e}{q_e}\right)^t = \left(\frac{1}{q_s b_T}\right)^{t^t} + \left(\frac{1}{b_T}\right)^t C_e^t \tag{7}$$

2.5. Kinetic Studies

Kinetic studies was carried out by agitating 1 g of Almond seed shell activated carbon, with 25 ml of 180 mg/l concentration of the crude oil sample at 50 ℃ in a temperature controlled water bath. The sample was withdrawn after 20, 25, 30, 35 and 40 minutes and the solutions were filtered from. The concentrations of filtrates were measured spectrophotometrically by monitoring the concentration at 540 nm, using a visible spectrophotometer. This adsorption at variable contact time was tested using the pseudo first order, pseudo second order models (Bridelli and Crippa, 2008) and the nth order kinetic model as represented with Equations (8) – (10) (Bokanyi, 2012).

$$\text{Log}\ (q_e - q_t) = \text{Log}\ q_e - \frac{K_1\, t}{2.303} \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}\text{t} \tag{9}$$

$$K_n\text{t} = \frac{(q_e - q_t)^{-(n-1)}}{n-1} - \frac{q_e{}^{-(n-1)}}{n-1} \tag{10}$$

Where q_t and q_e are adsorption capacity at time t and adsorption capacity at equilibrium (mg/l), is the mass of adsorbent; k is the rate constant.

The performance level of the kinetic model which best fit the adsorption data was also tested with statistical expressions such as Chi square (X^2), total error of the kinetic model of adsorption (Er^2) and root mean square error (RMSE). They are represented as Equations (11) – (13) respectively (Adie *et al.*, 2012).

$$X^2 = \sum_{i=1}^{n}\frac{(q_{obt} - q_{com})^2}{q_{obt}} \tag{11}$$

$$(\text{E}r^2) = \sum_{i=1}^{n}(q_{obt} - q_{com})^2 \tag{12}$$

$$\text{RMSE} = \frac{1}{n}\sqrt{\sum_{i=1}^{n}(q_{obt} - q_{com})^2} \tag{13}$$

2.6. Thermodynamic Studies

Adsorption experiment was also carried out by agitating 1 g of almond seed shell activated carbon with 25 ml of 104 mg/l concentration of crude oil was fed into the waterbath set at 30, 35, 40, 45 and 50 ℃. The samples were withdrawn after 40 minutes at each of the temperatures. The crude oil was filtered from the ASSAC. The concentrations of the filtrate were measured spectrophotometrically by monitoring the absorbance at 540 nm using a visible spectrophotometer (6700 Vis.). The thermodynamic distribution coefficient of the crude oil adsorbed from the Biseni Creek sample was calculated. These thermodynamic parameters of the adsorption-filtration operation were determined for the various experimental data obtained at various temperatures using the following Gibbs free energy equations:

$$\Delta G° = \Delta H° - \mathrm{T}\Delta S° \quad (14)$$

$$\Delta G° = -RT\ K_d \quad (15)$$

$$\mathrm{In}\ K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (16)$$

Where $K_d = \frac{q_e}{Ce}$, is the distribution coefficient for the adsorption-filtration operation, T (K) is the absolute temperature, while R is gas constant (8.314 J/mol.K). ΔG^o, ΔH^o, and ΔS^o are Gibbs free energy change, enthalpy change and entropy change of the adsorption-filtration operation, respectively (Levenspiel, 2008; Dagde, 2018).

3. RESULTS AND DISCUSSION

3.1. Characterisation of ASSAC

The characteristics of the ASSAC determined in the experiment are surface area, pore size, bulk density, pH, porosity, moisture content, iodine number, ash content and pore volume. The results are presented in TableT 1. The BET surface area of Almond seed shell activated carbon was obtained as 1055.45 m^2/g. This agreed with the report of Maulion *et al.* (2015), though the value is a little less than what they reported in their research. The bulk density of almond seed shell activated carbon was obtained as 0.33 g/cm^3 which is very close to the value reported by Maulion *et al.* (2015). The pH of the almond seed shell activated carbon was obtained as 8.75, a value which agreed with the report of Olufemi and Otolorin (2017). The extent of adsorption using almond seed shell activated carbon was further evaluated by measuring moisture content (20.95%), ash content (8.73%), pore volume (0.62 m^3/g), porosity (21.44%), BET pore size (32.45 A), and iodine value (103.07 mg/g).

Table 1: Characteristics of almond seed shell activated carbon

Property	Value
pH	8.75
Moisture content %	20.95
Porosity %	21.44
Ash content %	8.73
Pore volume (m^3/g)	0.62
Iodine value (mg/g)	103.07
Bulk density (g/cm^3)	0.328
BET surface area (m^2/g)	1055.45
BET pore size (A)	32.45

Figure 1 shows the scanning electronic microscope (SEM) microgram of Almond seed shell activated carbon (ASSAC) before the adsorption operation. It is clear from this image that ASSAC has reasonable layers of pores which will possibility allow adsorbates to be adsorbed in them.

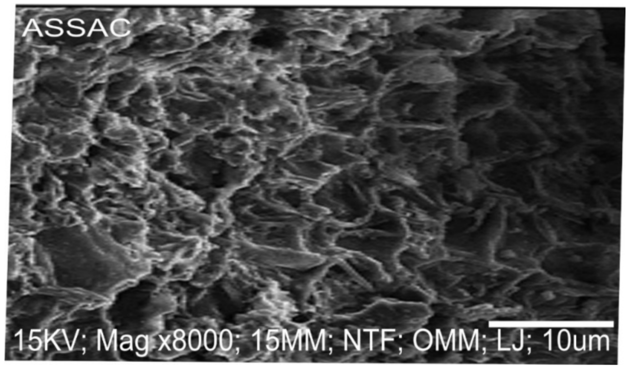

Figure 1: SEM image of ASSAC

Figure 2 shows the Fourier transform infrared spectroscopy (FTIR) spectrum of the Almond seed shell activated carbon. The spectrum show variation of adsorption peaks intensities which corresponds to the existence of different functional groups detected in the adsorbents. The peak at 2927.76 cm^{-1} represents $-CH_2$ of aliphatic compounds. This agrees with the report of Rafatullah *et al.* (2012). The peak at 3445 cm^{-1} represents $-OH$ stretching vibration of phenol group of cellulose and lignin. This trend agrees with the reports of El-Araby *et al.* (2019) and Rafatullah *et al.* (2012). The band 2375.83 cm^{-1} is from carbon dioxide (CO_2) in air, which agrees with the report of El-Araby *et al.* (2019). The band 1877 cm^{-1} is $C = O$, while that at 1631.73 cm^{-1} corresponds to non-ionic carboxyl group ($-COOH-$). The FTIR spectrum shows that certain functional groups OH, CO could be responsible for binding of crude oil from the solution by the adsorbent. The XRD pattern of the ASSAC as presented in Figure 3 shows two broad peaks appeared at 15^{o} and 38^{o} in the crystalline pattern, suggesting that ASSAC are typical of XRD pattern of alpha cellulose.

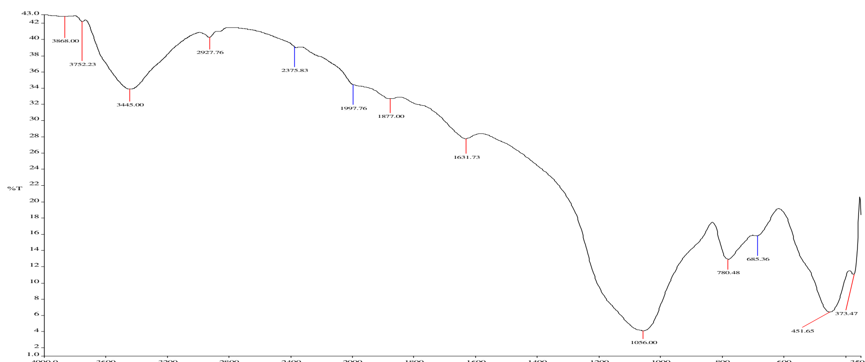

Figure 2: Fourier transform infrared spectrum for almond seed shell

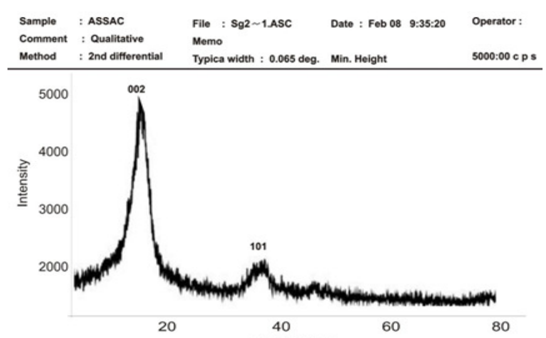

Figure 3: XRD spectrum for almond seed shell

3.2. Isotherm Studies

The Langmuir isotherm model represented by Figure 4 did not give a good fit for the adsorption. This suggests the crude oil uptake did occur on a homogenous surface and can be observed from the high value of the model adsorption capacity presented in Table 2 and confirmed by the negative (-0.3329) adjusted correlation coefficient obtained from the plot as presented in Table 2. The Freundlich isotherm model gave better fit for the adsorption than Langmuir isotherm model as shown in Figure 5. The magnitude of the exponent n, presented in table 2 gives an indication the adsorption process is not favorability. Also, the adjusted correlation coefficient (0.4460) obtained from the plot and presented in Table 2 is far below unity. These suggest the model confirms the adsorption did not occur on a homogenous surface, and it does not involve a multilayer, hence the non-applicability of the model. The Temkin isotherm model gave better fit for the adsorption-filtration operation than Langmuir and Freundlich isotherm models as shown in figure 6 above. This is consistent with the fact that Temkin model considers the heterogeneity of the surface of the adsorbent and take into account the adsorbate-adsorbent interactions. The adjusted correlation coefficient obtained and presented in Table 2 with other parameters from the plot was 0.540. This value may not be up to unity but it is above 0.5 and this trend agrees with the report of Olufemi and Otolorin, (2017) and Oseke *et al.* (2018). Figure 7 shows that Redlich-Peterson isotherm model did not give good fit for the adsorption-filtration operation. This is consistent with the fact that the Redlich-Peterson isotherm combines the features of both Langmuir and Freundlich isotherms. At high concentration, it approaches the Freundlich model and the Langmuir model at low concentration. A negative adjusted correlation coefficient of -0.3329 (Table 2) was obtained, which agrees with the value of adjusted correlation coefficient obtained for Langmuir isotherm.

Table 2: Isotherm models of the treatment of Biseni crude oil polluted water

Model	2 – Parameter			
Langmuir	Q_o= 6136.65	b=0.0003		$Adj\ R^2$= -0.3329
Freundlich	K_f= 1.7162	n=0.9856		$Adj\ R^2$= 0.4660
Temkin	b_T=30.34	A_T= 0.06		$Adj\ R^2$= 0.5400
	3 – Parameter			
Redlich-Peterson	a_R= 6136.48	K_R=11181.62	β=1.0	$Adj\ R^2$= -0.3329
Dubinin-Radushkevic	β= -0.109	q_{max}= 30.94	ε= 55.61	$Adj\ R^2$= 0.4431
Toth	q_s= -61.39	b_T = -57.43	t = 0.5987	$Adj\ R^2$= 0.3328

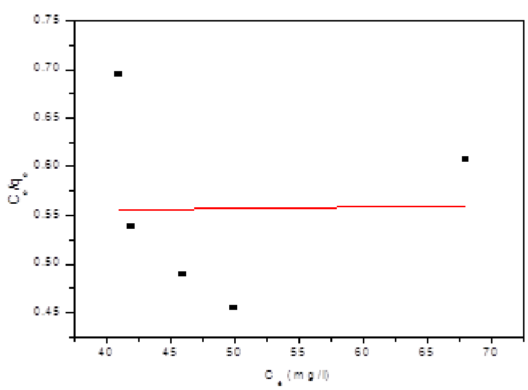

Figure 4: Langmuir isotherm model for crude oil adsorption with ASSAC

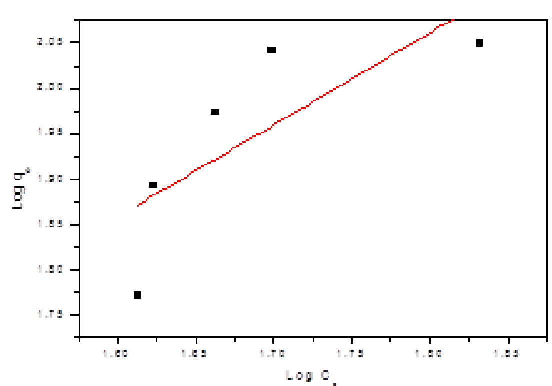

Figure 5: Freundlich isotherm model for crude oil adsorption with ASSAC

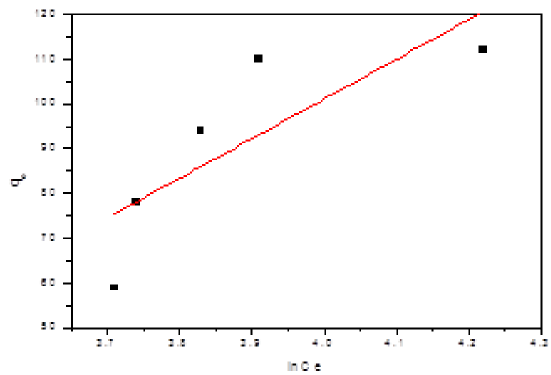

Figure 6: Temkin isotherm model for crude oil adsorption with ASSAC

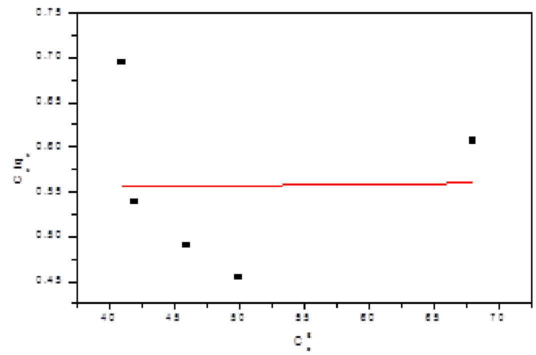

Figure 7: Redlich-Peterson isotherm for crude oil adsorption with ASSAC

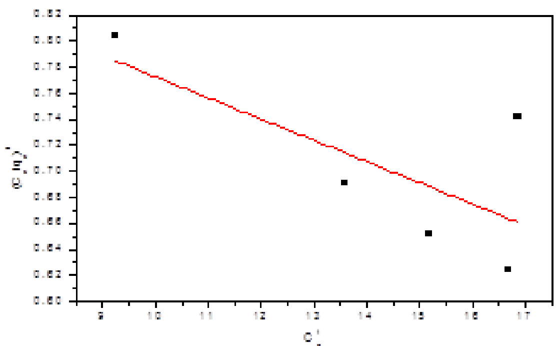

Figure 8: Tóth isotherm model for crude oil adsorption with ASSAC

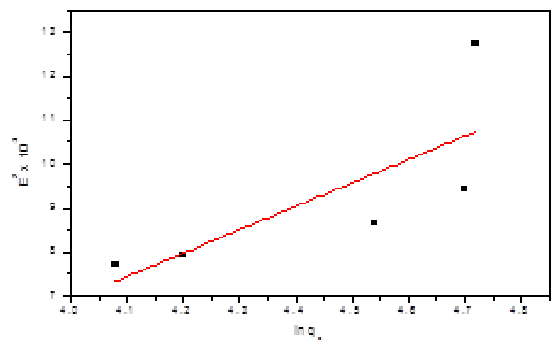

Figure 9: Dubinin-Radushkevic isotherm model for crude oil adsorption with ASSAC

The Toth isotherm model did not give the best fit for the adsorption-filtration operation based on the adjusted correlation coefficient of 0.3328 obtained and presented in Table 2, but gave better fit than Langmuir and Redlich-Peterson isotherm models. This is so because Toth isotherm model assumes adsorbate adsorption on energetically heterogeneous surface and the heterogeneous nature of the adsorbent surface has been confirmed by both Freundlich and Temkin isotherm models. The Dubinin-Radushkevic isotherm model (Figure 9) describe adsorption mechanism with the distribution of Gaussian energy on heterogeneous surfaces perform a below average for the adsorption-filtration operation. The adjusted correlation coefficient of 0.4431 obtained and presented in Table 2 agrees with other models that suggest the adsorption occur on a heterogeneous adsorbent surface.

3.3. Kinetic Studies

The pseudo first order model (Equation 8) prediction was not effective for adsorption-filtration operation of crude oil with ASSAC as represented with Figure 10. The adsorption capacity obtained from the model and presented in Table 3 deviated considerably from the experimental data. The correlation coefficient is not just small but negative, suggesting that it is not applicable for the adsorption. The pseudo-second order kinetic model was tested on the experimental data and Figure 11 shows the curve fitting plot of crude oil adsorption with ASSAC. The parameters obtained from the plot shown in Table 3 confirmed the applicability of pseudo second order equation to the adsorption-filtration operation. The computed adsorption capacity is within the range of the experimental data and the correlation coefficient from the plot is close to 1. This trend agrees with those of previous researchers (Kukwa *et al.*, 2014; Olufemi and Otolurin, 2017; Oseke *et al.,* 2018; Husin *et al.*, 2011; Kelle, 2018; Asadpour *et al.,* 2019). The calculated adsorption capacity was obtained as 1.4174 mg/g and the rate constant as -1.8910 g/mg.min. The nth order kinetic model represented with Figure

12 gave 0.9101 as the order of the adsorption operation, a correlation coefficient of 0.0165 and excessively large adsorption capacity which deviated considerably from the experimental data. These data as presented in Table 3 shows that the nth order kinetic model is not applicable for this adsorption.

Statistical evaluation of the adsorption kinetic of crude oil with ASSAC presented in table 4 was done using some predictive test tools like total error, Chi squared, and Root Mean Square error as defined in equations 11, 12 and 13 respectively. The value of the total error (Er^2) obtained for the nth order model is excessively large, that of pseudo first order model was 11.123 which is not negligible, but a considerably negligible value of 0.048 total error was obtained for the pseudo second order model. The Chi square value obtained for the pseudo second order model was 0.030 and negligibly small compared to 7.45 obtained for pseudo first order model or the excessively high value of 8.63 x 10^{17} obtained for the nth order. The root mean square error (RMSE) obtained for the pseudo first order, pseudo second order and nth order models presented in table 4 shows that the RMSE value obtained for pseudo second order model (0.044) is negligibly small when compared to that of pseudo first order which is 1.49 or nth order which is 2.979 x 10^{34}. These values of pseudo second order model reported show that the error margin of the model in the adsorption of crude oil with ASSAC is marginal and therefore the model gives the best fit for the adsorption process.

Table 3: Kinetic parameters of the treatment of Biseni crude oil polluted water with ASSAC

Model	k (g/mg.min)	q_e (mg/g)	R^2
Pseudo 1st	-0.007	0.000	-0.3333
Pseudo 2nd	-1.8910	1.4174	0.9621
nth	1.725 x 10^{17}	1.7256 x 10^{17}	0.0165

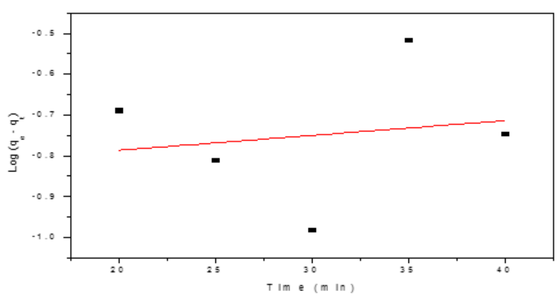

Figure 10: Pseudo-first order model for crude oil adsorption with ASSAC

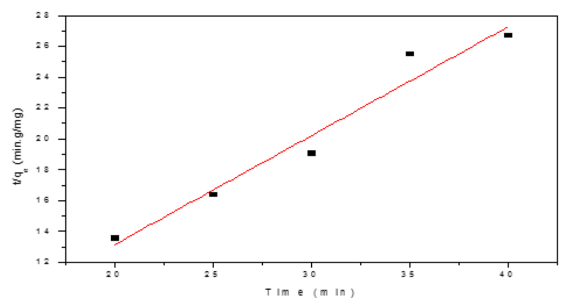

Figure 11: Pseudo-second order model for crude oil adsorption with ASSAC

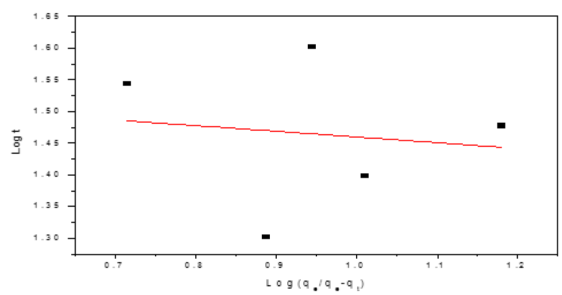

Figure 12: nth order model for crude oil adsorption with ASSAC

Table 4: Level of performance of the kinetic model on crude oil with ASSAC

Model	Total error (Er^2)	Chi square (X^2)	RMSE
Pseudo 1st order	11.123	7.45	1.49
Pseudo 2nd order	0.048	0.030	0.044
nth order	1.4895 x 10^{35}	8.63 x 10^{17}	2.9791 x 10^{34}

3.4. Thermodynamic Studies

The plot of ln K_d versus 1/T for crude oil adsorption is shown in Figure 13 almond seed shell activated carbon (ASSAC) using Equation (16). The values of ΔH° and ΔS° of the adsorption of crude oil with ASSAC was evaluated from Equation (16) and the value of $\Delta G°$ was obtained using Equation (15). These values are presented in Table 5. The standard enthalpy change was obtained as 3.27 kJ/mol and the value shows that standard enthalpy change ($\Delta H°$) for the adsorption of crude oil from Biseni polluted water onto ASSAC is positive and less than 84 kJ/mol, indicating that the adsorption operation is physical and endothermic. The standard entropy change of the adsorption was obtained as 12.1 J/mol.K and this value show increased disorderliness at the solid−solution interface. The change in Gibbs free energy was obtained as 0.503 kJ/mol. The standard change in Gibbs free energy ($\Delta G°$) value shows that the adsorption operation is spontaneous and little separation work is done.

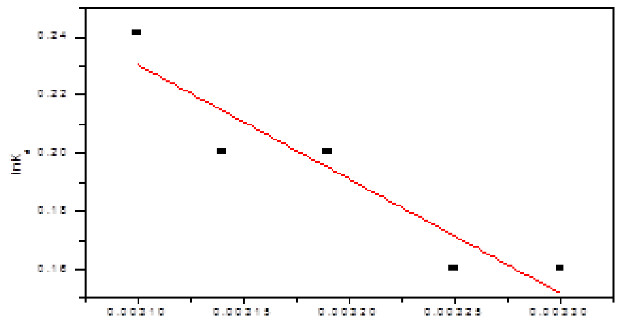

Figure 13: Thermodynamic data of crude oil adsorption with ASSAC

Table 5: Thermodynamic parameters of ASSAC in Biseni polluted water

ΔG (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o(J/mol.K)
0.503	3.27	12.1

4. CONCLUSION

The quality or characteristics of the almond seed shell activated carbon obtained show that it can effectively serve as good substitute to commercial activated carbons. Temkin adsorption model provided a good fit for the adsorption of crude oil from Biseni polluted water onto almond seed shell activated carbon. The kinetic study show that the adsorption of crude oil from Biseni polluted water onto almond seed shell activated carbons obeys the pseudo-second order model with good adsorption capacity. The level of significance of the analysis of variance show that the error margin of the separation for crude oil from Biseni polluted water was marginal. The values of $\Delta H°$, $\Delta S°$ and $\Delta G°$ obtained show that the adsorption-filtration operation of crude oil from Biseni polluted water onto almond seed shell activated carbon is an endothermic process and the enthalpy value is within the range of physical adsorption operation. These results from the characterization, activation, adsorption, kinetic and thermodynamic studies reveal that activated carbons from almond seed shell has the potential to adsorb crude oil from Biseni polluted water and can serve as a reliable substitute for commercial activated carbon.

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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