Adsorption of Crude Oil onto Chitosan: Isotherms, Modelling and Kinetic Studies

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Abstract : *This work was conducted to develop chitosan adsorbent for the removal of crude oil from contaminated water. Chitosan, a biodegradable and environmentally friendly adsorbent was used to remove crude oil from contaminated water in this study. It was prepared from Prawns shells waste sourced from the Atlantic Ocean, River Nun entrance in Bayelsa state. The chitosan was characterized using FTIR, XRD and AAS and proximate analysis and were used to remove crude oil spill from simulated crude oil contaminated water using batch adsorption. The chitosan yield was 20.33%. The degree of deacetylation using C/N ratio and FTIR peaks were 85.70% and 86.27% respectively. Design Expert software 6.06 was used to design the adsorption experiment. The adsorption was tested for Langmuir, Freundlich and Temkin isotherm and the kinetic studies also carried out. The effect of influencing parameters such as contact time, adsorbate concentration, adsorbent dosage and formulation ratio were studied. It was generally shown that adsorption process increases with time and adsorbate concentration and decreases with adsorbent dosage. Model for the prediction of adsorption capacity was significant with R^2 value of 0.8488 and P-value of 0.0001. Adsorption isotherm studies of Langmuir, Freundlich and Temkin were carried out. Temkin isotherm best fitted for all with R^2 value 0.9999. The adsorption capacity of chitosan from isotherm studies was obtained to 18.34 g/g adsorbent. The heat of adsorption b (kJ/mol) obtained from Temkin isotherm study was of low value of -52.55 kJ/mol indicating physisorption of adsorbents to the crude oil. Kinetic studies indicated that the pseudo-second order model suitably described the removal of crude oil by chitosan with R^2 value 0.9995.*
Keywords:Chitosan, Adsorption, Batch studies, Adsorption isotherms, Adsorption kinetics,

I. INTRODUCTION

Oil pollution among many others is one of the most serious environmental problems in oil exploration regions and its becoming increasingly inevitable. The crude oil and its derivatives on high demand for energy has created a need for its transportation from drilling point to industries where it's been processed into fuels and petrochemical products and then to areas needed for use and consumption. The enormous and undesirable taste andodour that affects tourism, economy and environment makes it necessary to be removed quickly. So, water sources protection must be one of the essential concerns in our life and necessary actions should be done to remove these pollutants because the balance of the ecosystem depends on water purity. [1, 22-27]

Crude oil tends to form insoluble layers with water as a result of its hydrophobicity, which can be easily separated from seawater by gravity and skimming. Much more difficulties are experienced when there is oil-water emulsion due to mixing in turbulent cases. Report has shown that spraying of expanded graphite and chalk, in-situ burning of oil with wicks, use of chemical dispersant, mechanical skimming, gelling, sinking and absorbing, disposing of oil with detergent, application of mechanical floating barriers, booms or skims, use of polymeric foams and other sorbents, and enhanced biodegradation are some methods used in remediation of such contamination [2]. These materials, over time are limited in regenerability, biodegradability, efficiency, usage and economy.

Bio-sorption, a biological method of environmental control using biomass for adsorption separation process can be an alternative to conventional adsorbents for removal of crude oil spill from water surface. Natural biopolymers are industrially attractive because of their capability to float and adsorb liquid to their pore spaces. Biopolymers are used for this bio-adsorption process because they are cheap resources and are widely available engineering materials that can be converted to useful materials from there raw state [3].

Raw rice husk has been used for oil removal in a laboratory simulated case of about 5g/g adsorbent [4]. Thermally treated rice husk silica has also been used for crude oil sorption [5] with sorption capacity of 15.2g/g of adsorbent at optimum temperature of 7000C.

Chitosan occur naturally in the environment in large quantities and run second in abundance to cellulose, has been used for adsorption purposes. It has an amine functional group which is strongly reactive

with metal ions for crude oil adsorption [6]. Acetylated rice husk was used according to Nwankwere *et al*. [7] to carry out crude oil sorption studies with sorption capacity of 10.31g/g of adsorbent. Researches have also shown the uptake of metal cations.

Many researchers have published a lot of works showing the effectiveness of numerous agricultural products for oil clean-up process such as wood [9], straws [9-10], sugarcane bagasse [11], and corn cobs [12].

In this present research work, the effect of contact time, chitosan dosage and oil water ratio have been investigated under simulated contamination with Design Expert Software to obtain a model equation for adsorption and optimization of the process.

II. MATERIALS AND METHODS

2.1 Adsorbent preparation

Common estuarine prawn shells as locally called (Hastatusspp) were sourced as waste from fishermen at River Nun, Atlantic Ocean of Bayelsa state, Nigeria. The shells obtained were washed thoroughly with distilled water and dried in an oven to constant weight at a temperature of 35^0C for an hour. The dried shells were size- reduced to 75μm. The demineralization of the biomass involved treating the shells with 1M HCl (1:10 w/v) at ambient temperature (approximately 28^0C) for 6 hours after which it was washed in the acid until no bubbles were seen and no colour change was observed followed by thorough with distilled water to completely remove all traces of hydrochloric acid. Deproteinization was done to remove protein and sugar in the sample thus isolating the crude chitin attached to the demineralized samples by treating it with 1 M Sodium hydroxide solution at solute to solvent ratio of 1:10 (w/v) for 16 hours in 250 ml conical flasks at ambient temperature (28 ℃). Washing with distilled water to pH of 7.3 removed all traces of sodium hydroxide. Chitin from this step were treated in 25 M of Sodium hydroxide (NaOH) solution of 1:10 (w/v) for 20 hours at a temperature of 115℃ and atmospheric pressure using a Bunsen burner in order to further leach out the undissolved proteins and remove the acetyl groups from the chitin.
The extracted chitosan samples were washed thoroughly with distilled water to pH of 7.4, filtered and then dried to constant weight using an oven at 35℃ for an hour.

2.2 Batch adsorption experiment

Batch biosorption experiments were conducted to investigate the influence of physiochemical parameters such as contact time, oil-water initial concentration ratio and adsorbent dosage crude oil adsorption using Design Expert 6.06. For adsorption process, 0.25 grams of chitosan was put into a beaker containing the calculated 0.25% v/v oil/water ratio for five minutes. It was agitated under these designed conditions keeping the pH at 2.0 (acidic) [3] of the medium and agitating the mixture for 200 r.p.m using mechanical shaker for each runs. The same procedure was repeated for several designed conditions of chitosan dosages, time and adsorbate concentration. The mixture was poured into a sieve and allowed to drain to get the new weight of the added adsorbent. The best adsorbent and adsorbate concentration which happen to be the optimized dosage was used to carry out these tests at different time intervals which followed the same adsorption process.
The oil sorption capacity (OSC) of the sorbents was determined by Equation 1 [12].
The OSC of the sorbents were obtained with the formula.

$$OSC = \frac{WeightGain}{OriginalWeight} \qquad (1)$$

III. RESULTS AND DISCUSSION

3.1 Characteristics of adsorbent
The AAS elemental composition is as given in Table 1.

Table 1: Elemental analysis of materials

Materials	Ca mg/g	Fe mg/g	Nitrogen %	Carbon %
Shrimps	18.7427	0.9413	11.9	20.54
Chitosan	1.3339	1.7200	2.81	15.14

Carbon and Nitrogen percentage of chitosan as shown Table 1 are 15.14% and 2.81% respectively. Isa *et al*. [14] reported similar Carbon and Nitrogen value of 13.32% and 2.29% respectively where chitosan was produced mussel shell. The differences may be due to the extent or degree of deacetylation and specie of shrimps. The demineralization of chitosan in terms of calcium removal was effective of about 92.88%.
The FT-IR KBr of Prawn shell chitin and chitosan are as shown in Figure 1, 2 and 3 respectively.

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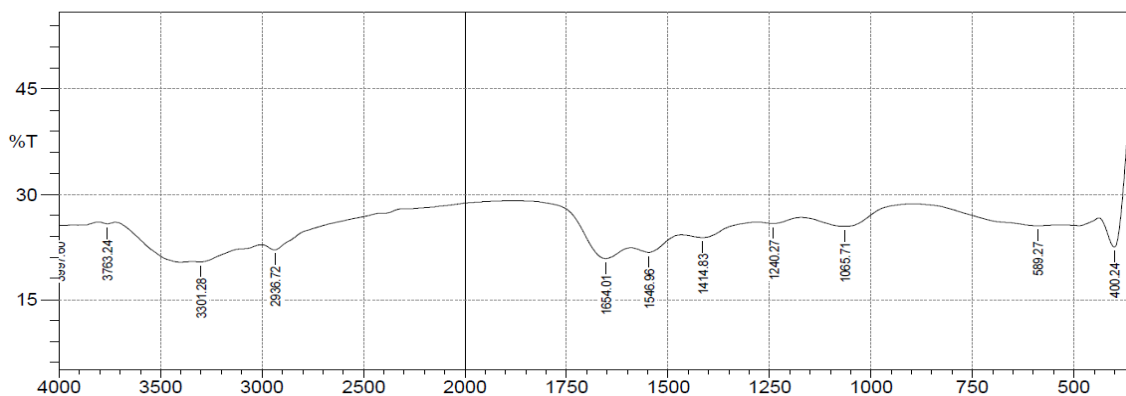
Figure 1: FT-IR spectroscopy analysis of shrimp shells

The wide band in Figure 4.3a at 1654.01 cm^{-1} corresponded C=O stretching vibrations of primary, secondary and tertiary amides group. Likewise, the band observed at 1546.96 cm^{-1} corresponded to N-H bend of the secondary amide group.
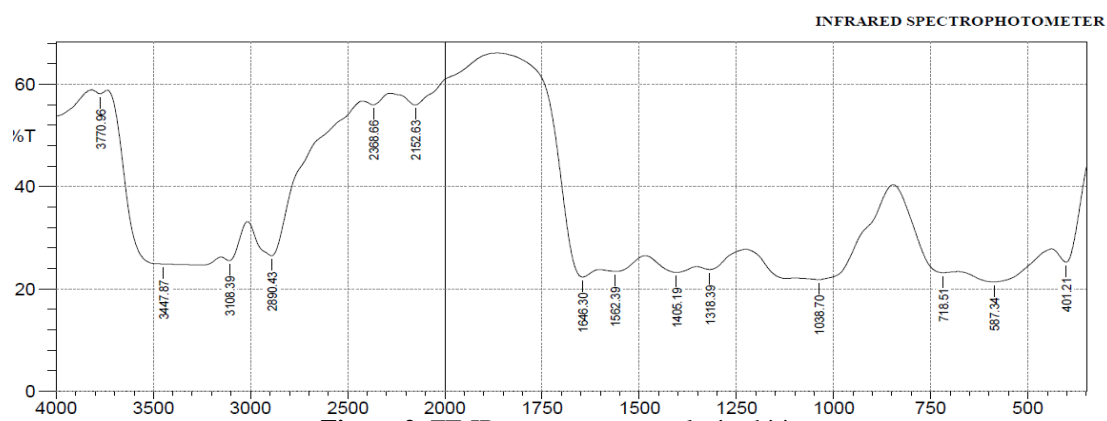
Figure 2: FT-IR spectroscopy analysis chitin

The wide band at 3447.76 cm^{-1} corresponded to N-H stretching vibrations of primary and secondary amides group reduced to 2890.43 cm^{-1} showing deproteinization of nitrogenous group. Likewise, the band observed at 1646.30 cm^{-1} corresponded to C-O stretch of amide II and III. Band length 1045.19 cm^{-1} correspond to a symmetrical deformation of the CH$_3$-group [15] .The band at 1318.39 cm^{-1} is as a result of stretching of amide III component of protein.
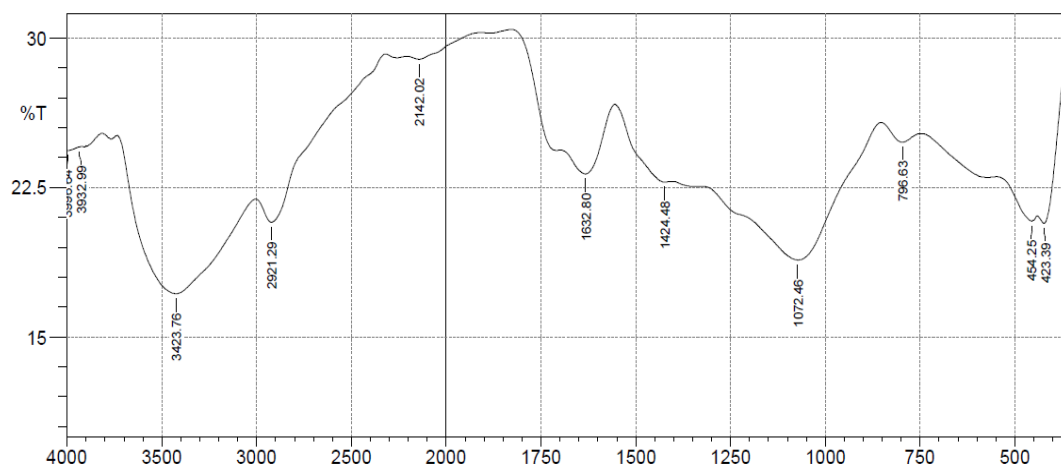
Figure 3: FTIR spectroscopy analysis Chitosan

The wide band of –NH$_2$ at 3423.76 cm^{-1} corresponded to N-H stretching vibrations of free amino groups. Likewise, the band observed at 2921.29 cm^{-1} corresponded to CH stretching vibrations. The band at 1072.46 cm^{-1} is as a result of stretching of primary hydroxyl groups of tertiary O-H stretching. The band at 1632.80 cm^{-1} corresponded C=O stretch of the carbonyl group, a structural feature of chitosan and the occurrence of deacetylation. This functional group attracts anionic ions such as OH−to bind and bridge. Due to this reason, oil has more affinity to adsorb on the surface of chitosan flakes. Electrostatic forces of attraction are present between this positive charge on chitosan surface and the negative charge of fatty acids in oils. Also, chitosan a positively charged biopolymer could adsorb residue oil and destabilize the negatively charged colloids of residue oil by charge neutralization mechanism The adsorption properties of chitosan are mainly because of its positive charge however, the adsorption process could also be the result of other forces that might exist between molecules, such as hydrogen bonding or Vander Waals forces [16].

The XRD pattern of the produced chitosan is as shown in Figure 4 which exhibited sharp diffraction peaks at 2θ = 10º, 20º and 28º . Bangyekan [17] reported that these are the two typical identity and characteristic peak of semi-crystalline chitosan. Similar results were reported by Isa et al. [18] .
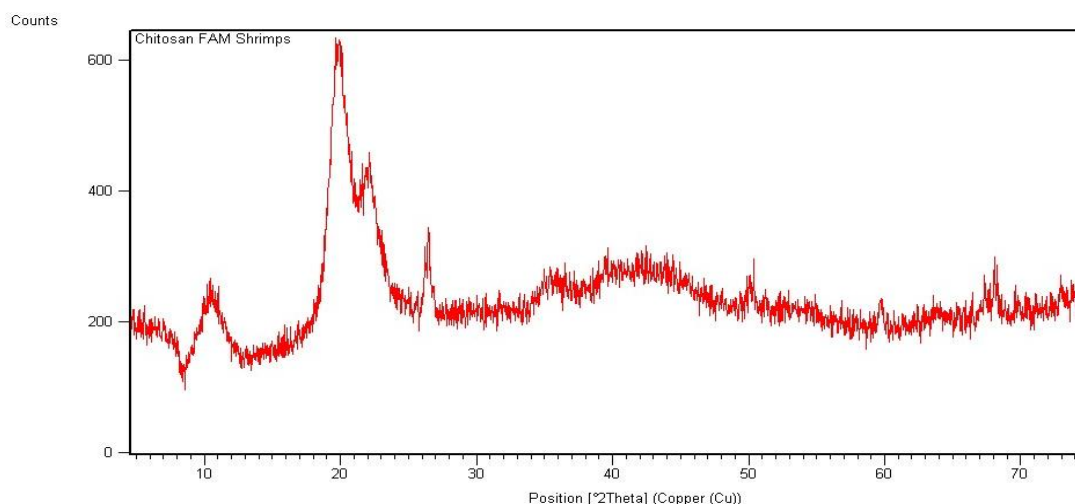

Figure 4: XRD Pattern of Chitosan Extracted From Shrimp Shells

The SEM Micrograph of produced chitosan in Plate 1 has smooth close-fitting surface morphology with minimum residues. Isa et al. [18] gave similar report of chitosan produced chitosan showing prominent sheath-like layers; this could probably be as result of deacetylation of the chitin which removes some bonding agents and exposing more sheaths in the chitosan. Figure 5 (a) and (b) showed the chitosan fibre length and area distribution.
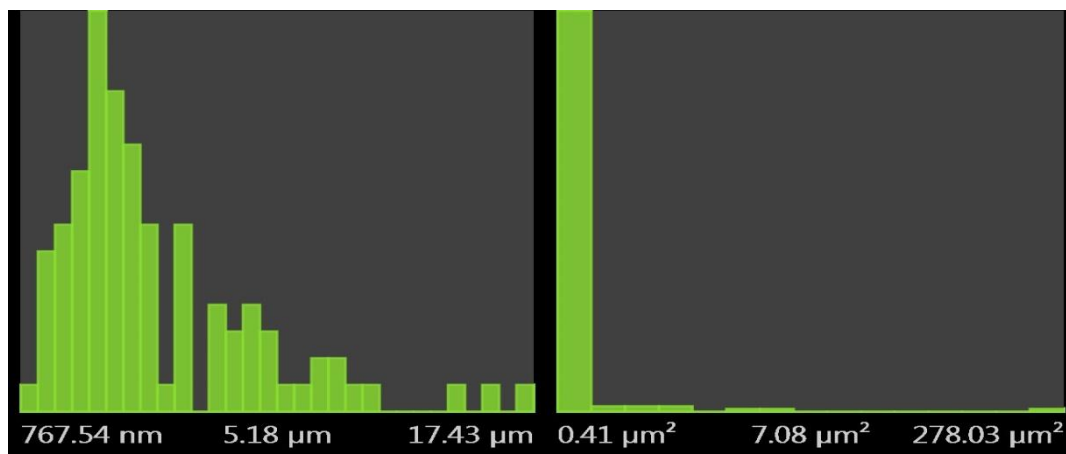

Plate 1: SEM image of Chitosan

Figure 5(a): Chitosan Fibre length histogram (b) Chitosan fibre surface area distribution

3.2 Effects of influencing parameters

The adsorption capacities were calculated for each batch experimental runs as given by Design Expert 6.06 software and presented in Table 2.

Table 2: Chitosan Adsorption Experimental Runs

Run	Chitosan Dosage (g)	Contact Time(mins)	Oil/Water %v/v	Oil Sorption Capacity g/g
1	1.13	32.50	0.14	9.31
2	1.13	32.50	0.14	9.29
3	1.13	32.50	0.14	9.31
4	2.00	5.00	0.02	1.425
5	1.13	78.75	0.14	9.32
6	1.13	32.50	0.14	9.31
7	0.25	60.00	0.02	11.4
8	1.13	32.50	0.14	9.3
9	1.13	32.50	0.33	9.32
10	2.00	5.00	0.25	6.715
11	1.13	32.50	0.14	9.31
12	0.25	5.00	0.25	23.08
13	2.60	32.50	0.14	4.2
14	1.13	32.50	0.06	4.54
15	0.25	5.00	0.02	11.4
16	2.00	60.00	0.25	8.175
17	1.13	13.75	0.14	9.13
18	0.25	60.00	0.25	23.9
19	2.00	60.00	0.02	1.425
20	0.35	32.50	0.14	13.17

Table 3: ANOVA response for square root 2FI model to identify the significant contributing factors.

Source	Sum of Squares	DF	Mean Square	F Value	Prob>F
Model	13.48	3	4.49	29.94	0.0001*
A	9.29	1	9.29	61.91	0.0001*
B	0.012	1	0.012	0.080	0.7809
C	4.18	1	4.18	27.84	0.0001*
Residual	2.40	16	0.15	1.160E+005	0.0001*
Lack of Fit	2.40	11	0.22		
Pure Error	9.408E-	5	1.882E-006		
Cor Total	006	19			
	15.88				

Standard Deviation: 0.39; R-Squared : 0.8488 *significant variable

The ANOVA Table 3 indicated that the model was significant due to the P-value of 0.0001. Significant model terms were A and C due to their P-value of 0.0001. This implies that the models will fit experimental data.
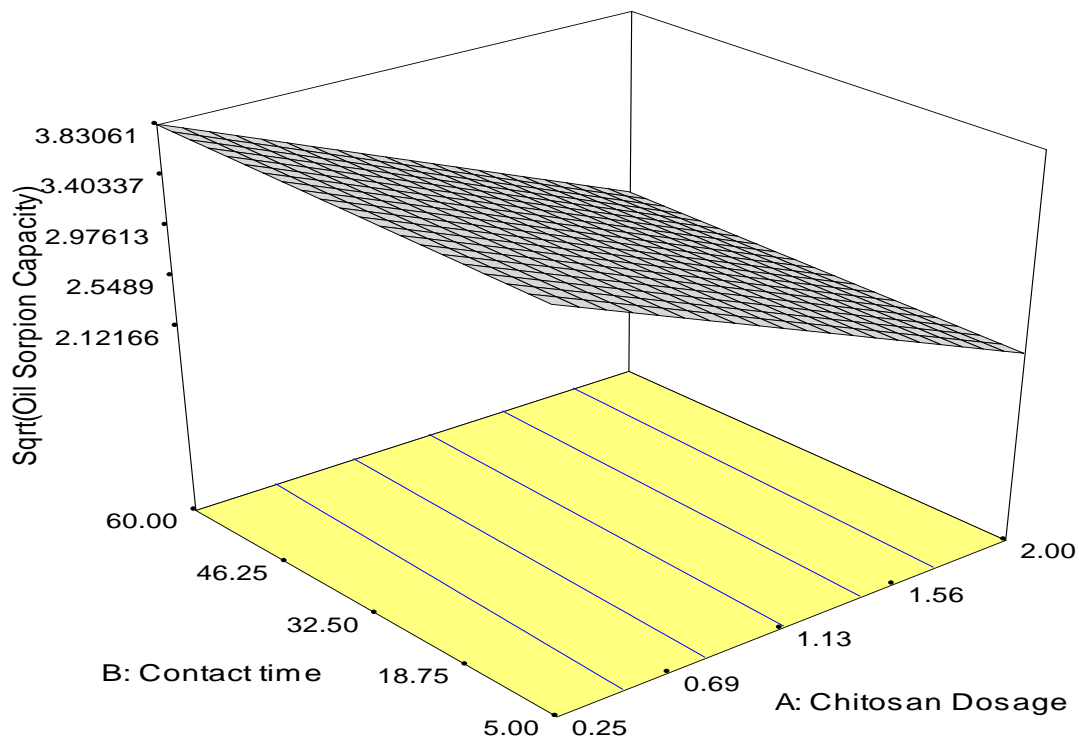
Figure 6: Response surface 3D plot of OSC versus Contact time and Chitosan dosage
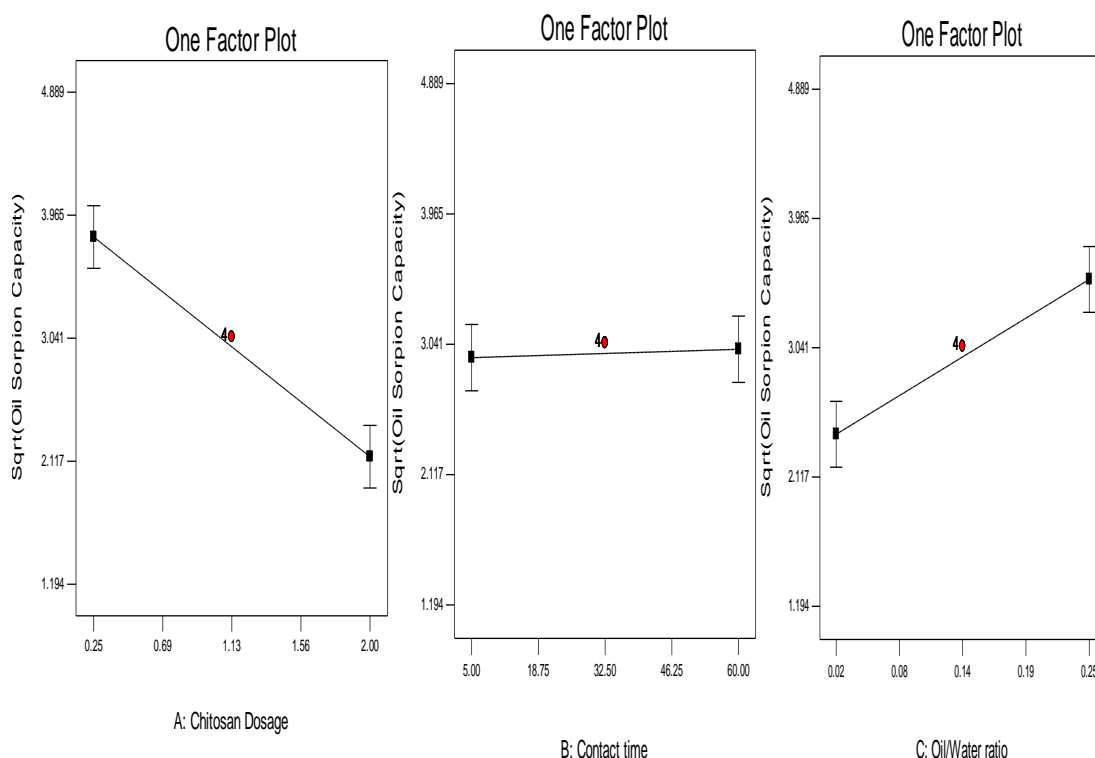

Figure 7: Effect of influencing parameters

The 3D-Figure 6 and 7 shows the response (Oil sorption capacity) with two combined influencing factors and single variable respectively. It can be deduced that oil sorption capacity of chitosan increased with increase in contact time and oil water ratio while it decreased with amount of adsorbent concentration (dosage). The decrease in adsorption capacity by increasing the adsorbent amount is basically due to the sites remaining

unsaturated during the adsorption process. It thus follows that if adsorbent dosage is increased by keeping the adsorbate concentration constant, the amount of adsorbate taken up per unit dosage of adsorbent showed a decrease due to availability of less amount of oil per unit mass of the adsorbent. [6] Reported adsorption capacity of chitosan also to decrease with increase in adsorbent dosage because smaller quantities of oil present to be adsorbed per unit mass of adsorbent dosage.

The proposed model equation is given as:

$$OSC = (+35222 - 0.94265 * A + 1.07855E - 003 * B + 4.80985 * C)^2 \qquad (2)$$

Where A= Chitosan dosage, B= Contact time and C=Oil/water concentration

The model was optimised for chitosan adsorption giving 0.25, 60.0, 0.25, 4.384 and 0.863 as Chitosan dosage, Contact time, Oil/Water ratio, Sqrt(OSC) and Desirability respectively.

3.3 Isotherm and kinetic studies
Theory
The amount of oil adsorbed into the adsorbent is designated by q in g/g of the adsorbent and given by the formula $q = \frac{V}{W}(C_o - C_e)$ $\qquad (3)$
Where C_o and C_e (g/mL) are the concentration of oil at initial and equilibrium respectively, W is the weight of the adsorbent used in grams and V is the volume of the solution in litres

Langmuir adsorption isotherm
Langmuir is the simplest type of theoretical isotherms. Langmuir adsorption isotherm describes quantitatively the formation of a monolayer of adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of adsorbate between the solid and liquid phases [19].
The Langmuir isotherm assume that the ability of molecule to bind and adsorbed is independent of whether or not neighbouring sites are occupied. This mean, there will be no interactions between adjacent molecules on the surface and immobile adsorption. Also mean, trans-migration of the adsorbate in the plane of the surface is prevented. Equation 4:
$$\frac{C_e}{q_e} = \frac{1}{q_m}Ce + \frac{1}{q_m b} \qquad (4)$$
Where Ce= equilibrium concentration qe= the amount of adsorbate adsorbed for unit mass
The plot of $\frac{C_e}{q_e}$ against Ce will help determine q_m and b are related to standard monolayer adsorption capacity and the Langmuir constant, respectively.
A dimensionless separation factor or equilibrium parameter, R_L was proposed by [20], as an essential feature of the Langmuir Isotherm to predict favourability of adsorption which is defined as:
$$R_L = \frac{1}{1+bC_0} \qquad (5)$$
Co= reference fluid-phase concentration of adsorbate (mg/l) (initial adsorbate concentration)
b= Langmuir constant (ml/mg)

Freundlich adsorption isotherm
Freundlich isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface. It represents an initial surface adsorption followed by a condensation effect resulting from strong adsorbate-adsorbate interaction. Freundlich isotherm curves in the opposite way of Langmuir isotherm and is exponential in form. The heat of adsorption, in many instances, decreases in magnitude with increasing extent of adsorption. This decline in heat is logarithmic implying that the adsorption sites are distributed exponentially with respect to adsorption energy. This isotherm does not indicate an adsorption limit when coverage is sufficient to fill a monolayer. It is given by Equation 6.
$$\log q_{e} = \frac{1}{n}\log C_e + \log K_f \qquad (6)$$
K_f = Freundlich constant related to maximum adsorption capacity (mg/g). It is a Temperature-dependent constant.
n= Freundlich constant related to surface heterogeneity (dimensionless). It gives an indication of how favourable the adsorption processes.

Temkin adsorption isotherm
Temkin isotherm contains a factor that explicitly takes into the account of adsorbent –adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of

adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [21]. Its equation is given as:

$$q_e = \frac{RT}{b_T} \ln Ce + \frac{RT}{b_T} \ln K_T \qquad (7)$$

Where A_T =Temkin isotherm equilibrium binding constant (L/g)
b_T = Temkin isotherm constant R= universal gas constant (8.314J/mol/K)
T= Temperature at 298K. B = Constant related to heat of sorption (J/mol)
The isotherm studies of chitosan are shown in the Figure. The kinetic and isotherm parameters are also as presented in Table 4 and 5 respectively.
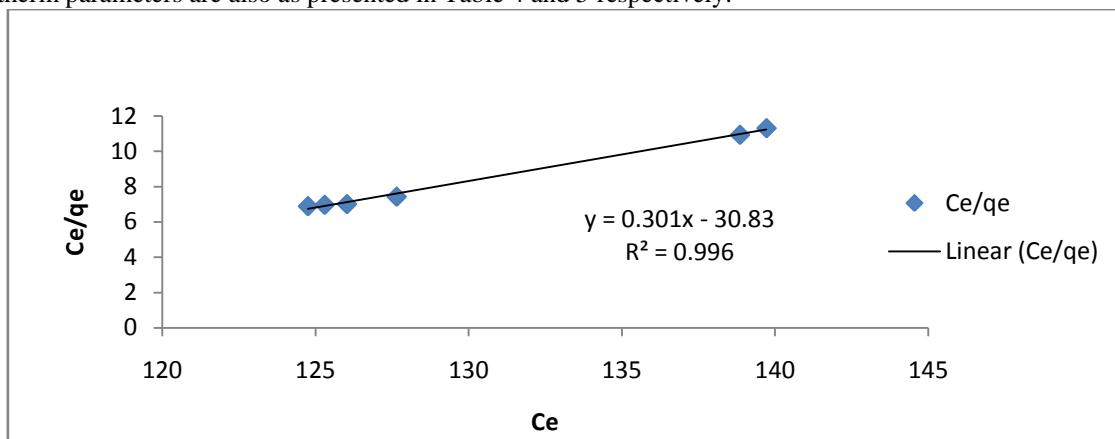

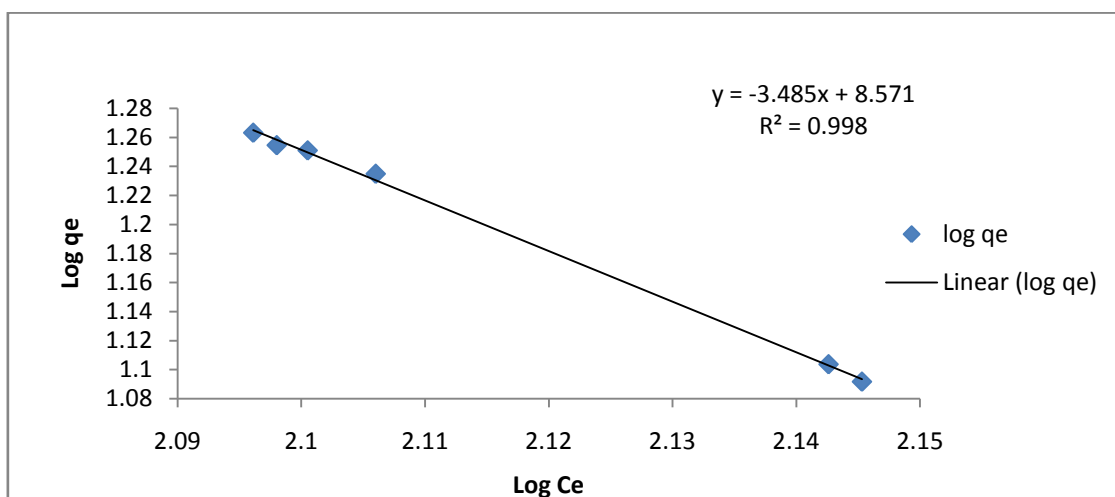
Figure 8: Chitosan Langmuir isotherm plot

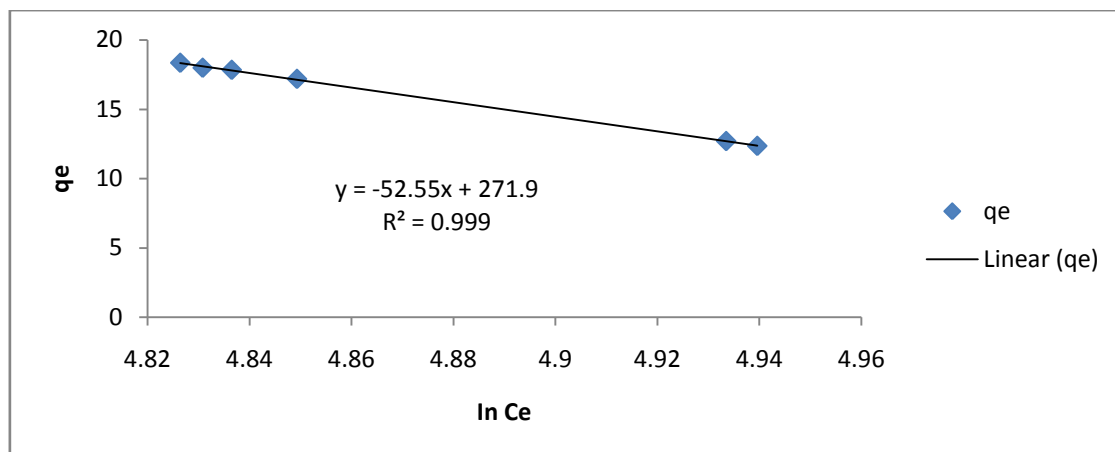**Figure 9:** Chitosan Freundlich isotherm plot

Figure 10: Chitosan Temkin isotherm plot

Temkin isotherm best fit the adsorption with R-squared value of 0.9995 and R_L value of 0.05376 with R-squared value of 0.9964 (favourable adsorption isotherm studies). The heat of adsorption from Temkin$b_T$value -47.146 J/mol is very low signifying that it is physisosorption. Table 4 presents the isotherm parameter calculated value.

Table 4: Chitosan adsorption isotherm value

Isotherm	Parameter	Value
Langmuir	b	0.0983
	R_L	0.05376
	R^2	0.9964
Freundlich	K_f	19.055
	1/n	-3.4856
	R^2	0.9987
	K_T	0.6835
	b_T	-47.146
	R^2	0.9985

Pseudo-first-order kinetics

The linear form of pseudo-first-order equation is given by Equation 8

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{8}$$

Where, qe and qt are the amounts of adsorbate adsorbed g/g at equilibrium time and at any instant of time, t respectively, and k_1l $min^{-1}$is the rate constant of the pseudo first-order adsorption operation.

Second order-kinetic model

The second order-kinetic model is shown in Equation 13; it is often used for chemical reaction In kinetics and chemical reaction engineering, but can also be applied for adsorption processes.

$$\frac{1}{C_e} = k_2 t + \frac{1}{C_o} \tag{9}$$

Pseudo-second-order kinetics

Pseudo-first-order kinetics differs from a true first order equation in two ways: (i) the parameter $k_1(q_e - q_t)$ does not represent the number of available sites, and (ii) the parameter log (qe) is an adjustable parameter and often found not to be equal to the intercept of the plot of log $(q_e - q_t))$ versus t, whereas in a true first order log q_e should be equal to the intercept. In such cases, applicability of the second order kinetics should be tested with the rate equation given by Equation 10

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{10}$$

Elovich model

Elovich model is applicable for chemisorption processes. The equation is often used valid for adsorption surface that is heterogeneous. Equation 11

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t \tag{11}$$

Where a is the initial adsorption rate (mg/gmin) and b is related to the extent of surface coverage and the activation energy for chemisorption (g/mg). A plot of q_t against $\ln t$gives a straight line with a slope of $\frac{1}{b}$ and an intercept of $\frac{1}{b}\ln(ab)$ with correlation coefficients.

Figure 11-13 present second order,pseudo-second order and Elovich kinetic models for chitosan respectively. The kinetic data best fit into pseudo-first order kinetic model with highest R^2 value of 0.9995.Data generated are presented in Table 5
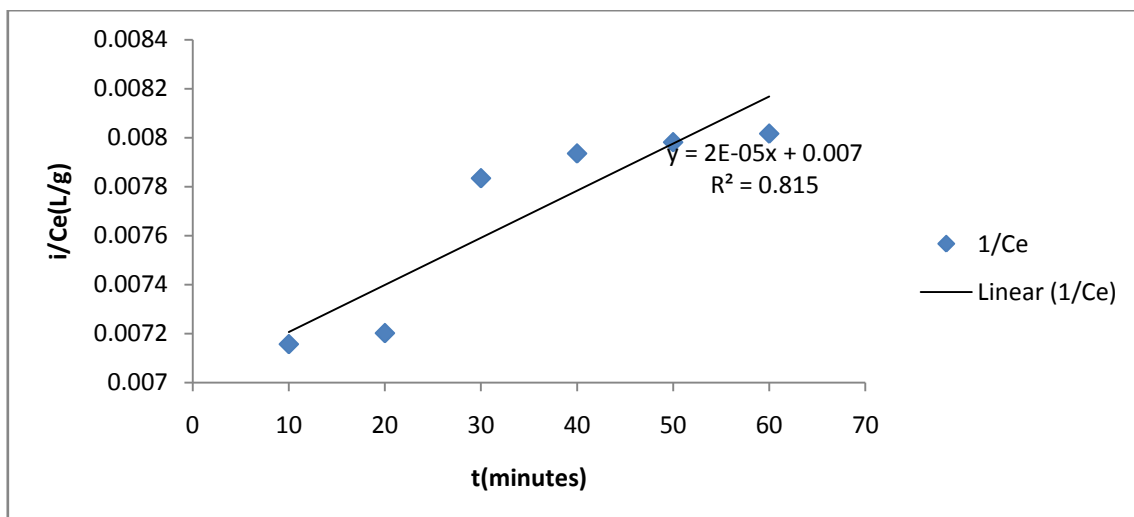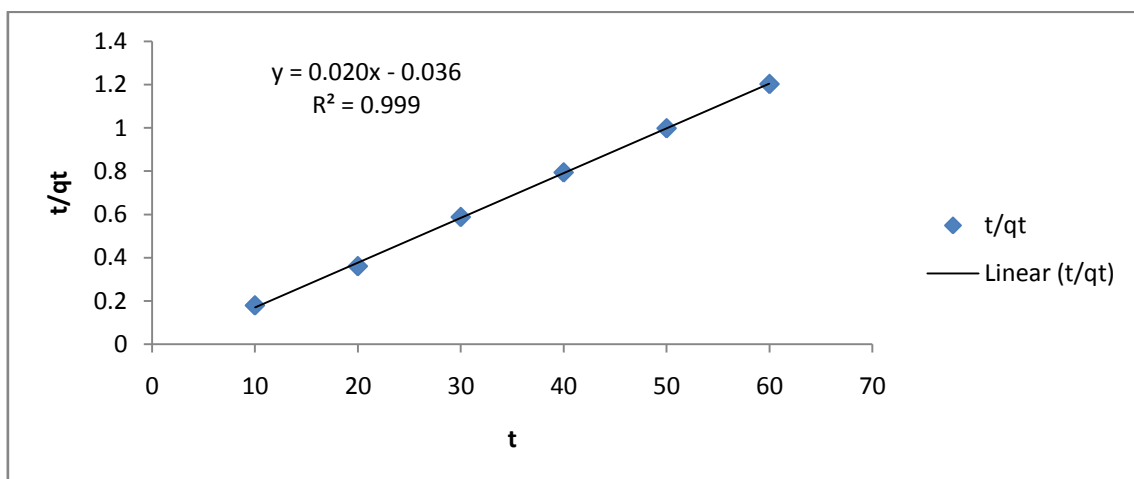
Figure 11: Chitosan Second order kinetic model.

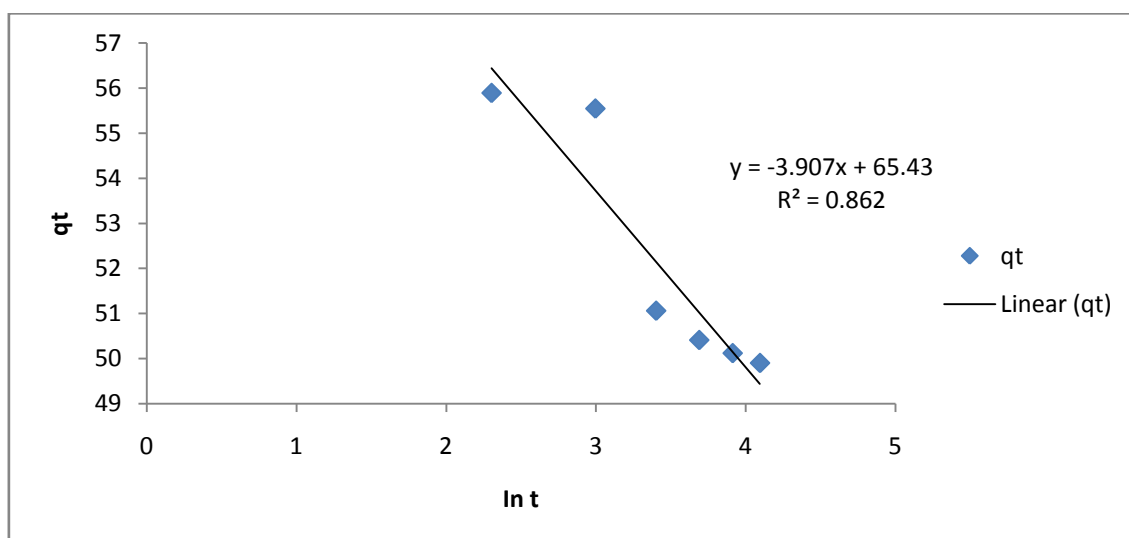**Figure 412:** Chitosan Pseudo-second order kinetic model

Figure 13: Chitosan Elovich kinetic model

Table 5: Evaluated constants obtained from the tested kinetic model for chitosan

Kinetic model	R^2	Intercept	K	Other constants
Second order	0.8157	0.0071	0.00002	C_o=142.8572
Pseudo-second order	0.9995	0.0369	0.065778	q_e=27.1003
Elovich	0. 8623	65.436	b=-0.256	a=5.3243E-08

IV. CONCLUSION

Chitosan prepared from prawn shell waste was suitable for oil removal from oil water solution. Equilibrium data are well fitted with the Temkin isotherm. The maximum adsorption capacity is obtained as 18.34 g g^{-1}.

The rate kinetics of oil adsorption on chitosan is better explained by pseudo-second order with R^2 value 0.9995. Models for the prediction of adsorption capacity of chitosan was successfully developed by application of response surface methodology of Design Expert Software with R^2 value of 0.8488, and the model was significant with P-value of 0.0001. The heat of adsorption b ($kJmol^{-1}$) obtained from Temkin isotherm studies was low, indicating physisorption of adsorbents to the crude oil.

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