# Kinetic Study, Modelling and Optimization of Adsorption Processes for Removal of Crude Oil from Contaminated Water using Chitosan-Rice Husk Ash Composite

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***Authors' contributions***

*This work was carried out in collaboration between all authors. Author GGO performed the laboratory experiment, manage the literature searches and produced the first draft of the manuscript. Author MTI design the study and wrote the protocol. Author MSG and AOA performed the statistical analysis, and managed the analyses of the study. All authors read and approved the final manuscript.*

**Original Research Article**

## ABSTRACT

This study was aimed at developing chitosan-rice husk ash adsorbent for the removal of crude oil from contaminated water. Design Expert software 6.06 was used to design the adsorption experiment. The adsorption was tested for Langmuir, Freundlich and Temkin isotherms 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 increased with time and adsorbate concentration and decreased with adsorbent dosage. Models for the prediction of adsorption capacity for the composite was significant with $R^2$ value of 0.8382 and P-value of 0.0017. Optimum conditions were found to be 0.90 wt/wt chitosan/silica ratio, contact time of 5 min, and oil/water ratio of 0.25 v/v, which gave 20.66 g/g sorption capacity respectively. Adsorption isotherm studies of Langmuir, Freundlich and Temkin

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were carried out for the chitosan-rice husk ash composite. Temkin isotherm best fitted with $R^2$ value of 0.9999. The adsorption capacity of composite from isotherm studies was obtained to be 18.85 g/g adsorbent. The heat of adsorption $b_T$ (kJmol$^{-1}$) obtained from Temkin isotherm study was -48.67 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 the composite with $R^2$ value 0.9999.

## 1. INTRODUCTION

Oil contamination is one of the most serious environmental problems and it is becoming increasingly inevitable. The dependency on crude oil derivatives for energy demand has created a need to transport petroleum from drilling point to industries where it is being processed into fuels and petrochemical products and then to areas needed for use and consumption. Crude oil spill constitutes one of the major sources of contamination in seas, oceans and navigable waters. The enormous and undesirable taste and odour that affects tourism, economy and environment make it rapid 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. Also, the transportation process from petroleum industries sometimes contaminates the environment with crude oil and its products as a result of aging of pipelines, equipment failure, corrosion, accidental operational problems or by sabotage [1-7]. There is a major need to explore the biological means of control especially agricultural waste for sustainability and consideration of economy of operation.

Raw rice husk has been used for oil removal in a laboratory simulated case of about 5g/g adsorbent [8]. Thermally treated rice husk silica has also been used for crude oil sorption [9] with sorption capacity of 15.2 g/g of adsorbent at an optimum temperature of 700°C. Chitosan which occurs naturally in the environment in large quantities and runs second in abundance to cellulose has been used for adsorption purposes. It has an amine functional group which is strongly reactive with metal ions [10]. Acetylated rice husk was used as reported by Nwankwere et al. [11] to carry out crude oil sorption studies with sorption capacity of 10.31 g/g of adsorbent. Researches have shown the uptake of metal cations [12] and crude oil [13] by chitosan. The high porosity of this natural polymer results in novel binding properties for metal and lipids making it buoyant on the surface of the water while rice husk silica which can be easily sourced is not.

The aim of this study is to develop chitosan-rice husk ash adsorbent for removal of crude oil from crude oil contaminated water. Response surface methodology which is one of the powerful tools for developing and improving processes will be employed to study and optimize the effect of factors that affect the adsorption process and to develop a model equation for the prediction of the adsorption capacity. This is in addition to conducting equilibrium and kinetic studies of the process.

## 2. MATERIALS AND METHODS

### 2.1 Adsorbent Preparation

Rice husk was locally sourced from Zaria – Nigeria, thoroughly washed with tap water to remove stones and dirt. It was then dried under the atmospheric condition to avoid thermal shock on the material. The dried rice husk was then soaked in 10 w/w % sulphuric acid and boiled for 1 hour and then allowed to stay for 24 hours in the boiled acid solution to remove excess carbohydrates. The rice husk was then thoroughly washed with distilled water to reduce its pH to 6.6 which was close to neutrality and was then dried atmospherically. The beneficiated and acid pre-treated rice husk was charred in an oven for 2 hours at 200°C. The charred rice husk was transferred to the furnace where it was carbonized at 700°C for 6 hours to avoid phase transformation of silica from amorphous to crystalline surface [11].

Chitosan powder was locally synthesised from shrimp shell by demineralisation (1M HCl treatment for 6 hours 25°C), deproteinization to obtain chitin using 1M NaOH (Sigma Aldrich, 98) treatment for 16 hours at 25°C and finally

deacetylation of chitin to obtain chitosan (25M NaOH treatment for 20 hours at 115°C 1atm). Rice husk ash and chitosan powder were mixed using physical admixture method using different formulation ratios obtained by Design Expert. Other influencing factors like contact time and crude oil-water contamination ratio were also studied.

## 2.2 Batch Adsorption Experiment

Batch biosorption experiments were conducted to investigate the influence of 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 composite was put into a beaker containing the calculated 0.25% v/v oil/water ratio for five minutes and agitating the mixture for 200 r.p.m using a mechanical shaker for each run. The same procedure was repeated for other designed conditions of formulation ratios, 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 oil sorption capacity (OSC) of the sorbents was determined from Equation 1 [11].

$$OSC = \frac{Weight\ Gain}{Original\ Weight} \qquad (1)$$

## 2.3 Optimization of the Adsorption Process

The response (OSC) was fed into the experimental design and generated the model equation for the adsorption process. An optimisation study was also conducted using the Design Expert, this gave the optimum conditions for the process. The results were statistically analysed and presented in the appropriate section.

## 2.4 Isotherm and Kinetic Studies

Studies were conducted for Langmuir, Freundlich and Temkin adsorption isotherm. Pseudo-first-order, Second order, Pseudo-second-order and Elovich kinetic model were also studied.

The amount of oil absorbed into the adsorbent is designated by q in g/g of the adsorbent and given by the formula

$$q = \frac{V}{W}(C_o - C_e) \qquad (2)$$

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

## 3. RESULTS AND DISCUSSION

Table 1 presents the experimental design as well as the response (OSC) for the adsorption of laboratory simulated water contaminated with crude oil.

Table 2 shows the analysis of variance (ANOVA) for linear model and parameters contributing to adsorption. The Model F-value of 8.63 implies the model is significant. The model terms are also significant ($P = 0.0017$). In this case, A and AB are significant model terms.
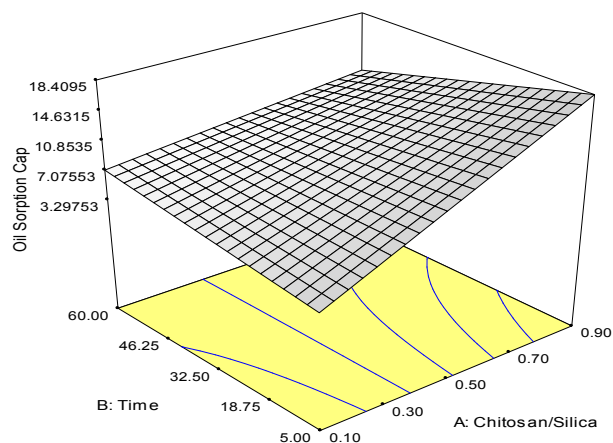


**Fig. 1. Response surface 3D plot of OSC versus contact time and Chitosan/silica**

**Table 1. Results of adsorption of crude oil from water/crude oil mixture using chitosan-silica composite**

| Run | Chitosan/Silicawt/wt % | Time minutes | Oil/Water v/v. % | OSC g/g, % |
|-----|------------------------|--------------|------------------|------------|
| 1 | 0.50 | 32.50 | 0.14 | 8.9920 |
| 2 | 0.10 | 60.00 | 0.14 | 5.5520 |
| 3 | 0.90 | 32.50 | 0.02 | 12.232 |
| 4 | 0.90 | 5.00 | 0.14 | 11.192 |
| 5 | 0.10 | 32.50 | 0.25 | 19.497 |
| 6 | 0.50 | 32.50 | 0.14 | 8.1520 |
| 7 | 0.90 | 60.00 | 0.14 | 8.8320 |
| 8 | 0.50 | 5.00 | 0.25 | 8.4720 |
| 9 | 0.90 | 32.50 | 0.25 | 7.4720 |
| 10 | 0.50 | 32.50 | 0.14 | 6.5920 |
| 11 | 0.50 | 32.50 | 0.14 | 7.9920 |
| 12 | 0.50 | 32.50 | 0.14 | 8.2320 |
| 13 | 0.50 | 60.00 | 0.25 | 21.632 |
| 14 | 0.10 | 5.00 | 0.14 | 7.3920 |
| 15 | 0.50 | 5.00 | 0.02 | 6.5920 |
| 16 | 0.50 | 60.00 | 0.02 | 14.272 |
| 17 | 0.10 | 32.50 | 0.02 | 8.4800 |

**Table 2. ANOVA response for linear model to identify the significant contributing factors**

| Source | Sum of squares | DF | Mean square | F value | Prob>F |
|--------|----------------|----|-----------:|---------|--------|
| Model | 258.25 | 6 | 43.04 | 8.63 | 0.0017* |
| A | 175.67 | 1 | 175.67 | 35.23 | 0.0001* |
| B | 7.22 | 1 | 7.22 | 1.45 | 0.2566 |
| C | 23.23 | 1 | 23.23 | 4.66 | 0.0563 |
| AB | 32.95 | 1 | 32.95 | 6.61 | 0.0279* |
| AC | 12.93 | 1 | 12.93 | 2.59 | 0.1384 |
| BC | 6.25 | 1 | 6.25 | 1.25 | 0.2891 |
| Residual | 49.87 | 10 | 4.99 | | |
| Lack of Fit | 49.74 | 6 | 8.29 | 260.51 | 0.0001 * |
| Pure Error | 0.13 | 4 | 0.032 | | |
| Cor Total | 308.1 | 16 | | | |

*Std. Dev.=1.52; R-Squared=0.8382 * significant variable*

Fig. 1 (3-D plot) presents the response (Oil sorption capacity) with two combined influencing factors while Fig. 2 shows the effect of one factor at a time. It can be interpreted that oil sorption capacity of composite increased with increase in the formulation ratio and oil-water ratio while contact time decreased as sorption increased. This could be attributed to the high adsorption capacity of chitosan present in the composite over rice husk silica. Thus, the more percentage composition of chitosan present in the composite blend, the better the adsorption. This is due to enhanced buoyancy and lipids attracting ability of chitosan.

Final equation in terms of actual influencing factors:

$$OSC = +3.30120 + 14.91781A + 0.042549B - 17.57194C - 0.26091AB + 39.08696AC + 0.39526BC \quad (3)$$

Where, A, B and C are Chitosan/Silica ratio, Contact time and Oil/water ratio respectively. The model equation can be used to predict the adsorption capacity of the process. Optimisation was also conducted for the process using the Design Expert and the results for the optimum conditions were found to be 0.90 wt/wt, 5 min, 0.25 v/v, and 20.66 g/g for chitosan/silica ratio, contact time, oil/water ratio and sorption capacity respectively.

## 3.1 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. Langmuir thus represents the equilibrium distribution of

adsorbate between the solid and liquid phases [14].

The Langmuir isotherm assumes that the ability of a molecule to bind and be adsorbed is independent of whether or not neighbouring sites are occupied. This means, there will be no interactions between adjacent molecules on the surface and immobile adsorption. It also means trans-migration of the adsorbate in the plane of the surface is prevented Equation 4:

$$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{q_m b} \tag{4}$$

Where $C_e$ = equilibrium concentration $q_e$ = the amount of adsorbate adsorbed for unit mass.

The plot of $\frac{C_e}{q_e}$ against $C_e$ will help determine $q_m$ and b, they are related to standard monolayer adsorption capacity and the Langmuir constant, respectively.

A dimensionless separation factor or equilibrium parameter, $R_L$ was proposed by Hall et al. [9] as an essential feature of the Langmuir Isotherm to predict favourability of adsorption which is defined as:

$$R_L = \frac{1}{1+bC_0} \tag{5}$$

$C_o$ = reference fluid-phase concentration of adsorbate (mg/l) b = Langmuir constant (ml/mg)

## 3.2 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
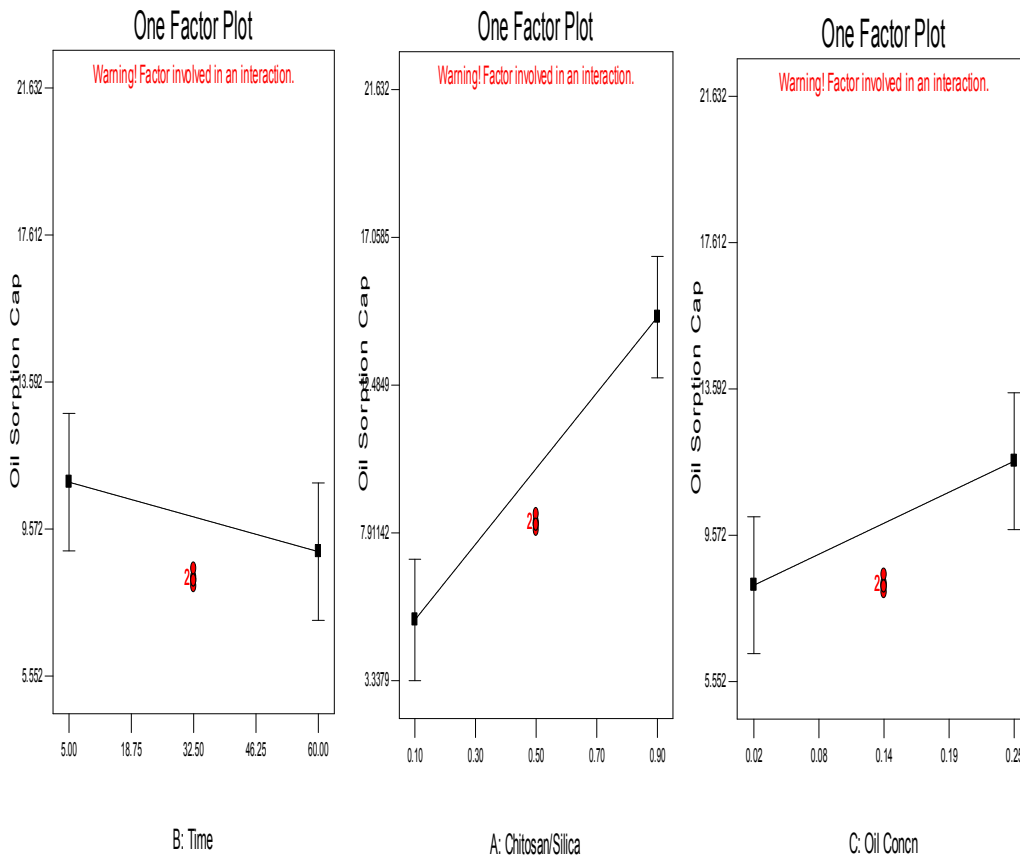


**Fig. 2. Composite adsorption capacity curve against the variables**

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 absorption process is.

## 3.3 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 (a function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [15]. Its equation is given:

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

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 the heat of sorption (J/mol)

The isotherm studies of chitosan-rice husk silica ash composite are shown in the Figure 3, 4 and 5. The kinetic and isotherm parameters are also as presented in Table 3 and 4 respectively.

## 3.4 Pseudo-first-order Kinetics

Lagergren showed that the rate of adsorption of solute on the adsorption is based on the adsorption capacity and follows a pseudo-first-order equation [12,16]. Equation 8 present integrated rate law after application of the initial condition of $q_t$ = 0 at t= 0 from its non-linear form given by Equation 8

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

where, $q_e$ and $q_t$ are the amounts of adsorbate adsorbed g/g at equilibrium time and at any instant of time, t respectively, and $k_1$ min$^{-1}$ is the rate constant of the pseudo first-order adsorption operation.

## 3.5 Second Order-kinetic Model

The second order-kinetic model is shown in Equation 9; it is often used for chemical reaction, in kinetics and chemical reaction engineering, but can also be applied for adsorption processes [17].

$$\frac{1}{c_e} = k_2 t + \frac{1}{c_o} \qquad (9)$$

## 3.6 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:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad (10)$$

Where h = $k_2 q_e^2$

## 3.7 Elovich Model

Elovich model is applicable for chemisorption processes [18]. The equation is valid for adsorption surface that is heterogeneous. Equation 11

$$q_t = \frac{1}{b} In(ab) + \frac{1}{b} In\, t \qquad (11)$$

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 *In* t gives a straight line with a slope of $\frac{1}{b}$ and an intercept of $\frac{1}{b}$In (ab) with correlation coefficients.

The heat of adsorption from Temkin $b_T$ value -48.6715 kJ/mol is very low signifying that it is physisorption. Table 3 presents the adsorption isotherm studies parameters.
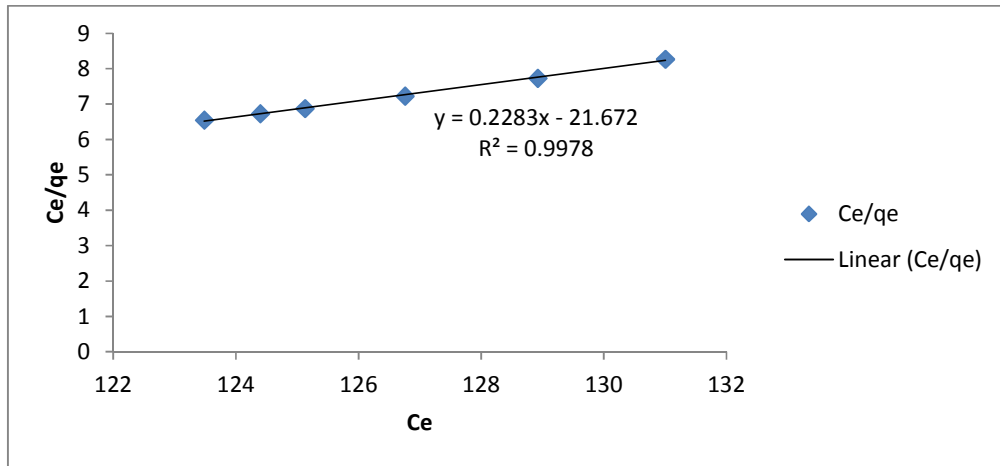
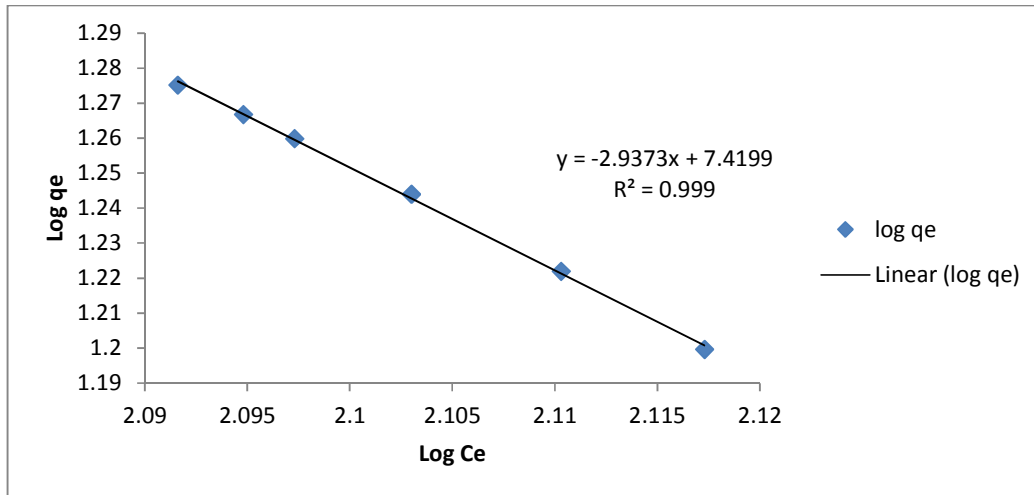**Fig. 3. Composite Langmuir adsorption isotherm plot**



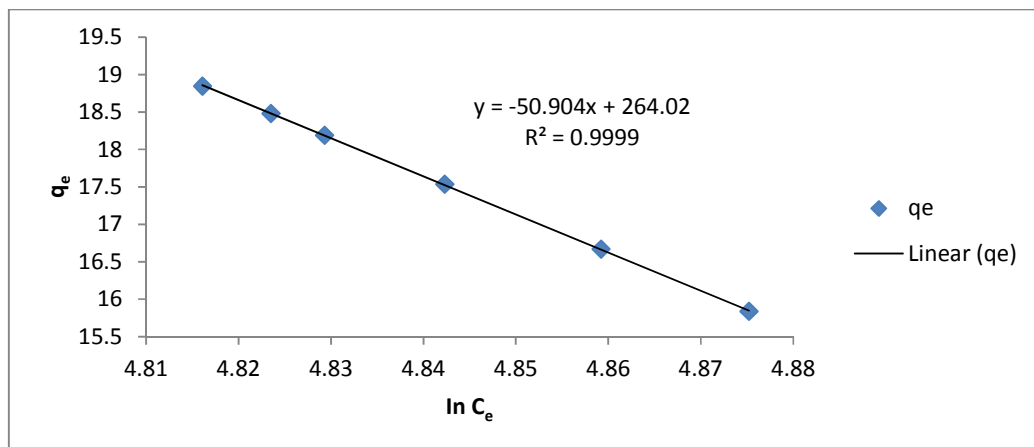**Fig. 4. Composite Freundlich adsorption isotherm**



**Fig. 5. Composite Temkin adsorption isotherm plot**

**Table 3. Composite adsorption isotherm value**

| Isotherm | Parameter | Value |
|----------|-----------|-------|
| Langmuir | b | 0.03895 |
| | $R_L$ | 0.1335 |
| | $R^2$ | 0.9978 |
| Freundlich | $K_f$ | 19.0546 |
| | $1/n$ | -2. 9373 |
| | $R^2$ | 0.999 |
| Temkin | $K_T$ | 0.6885 |
| | $b_T$ | -48.6715 |
| | $R^2$ | 0.9999 |

*Only Temkin isotherm best fits the adsorption with highest $R^2$ value of 0.9999.*
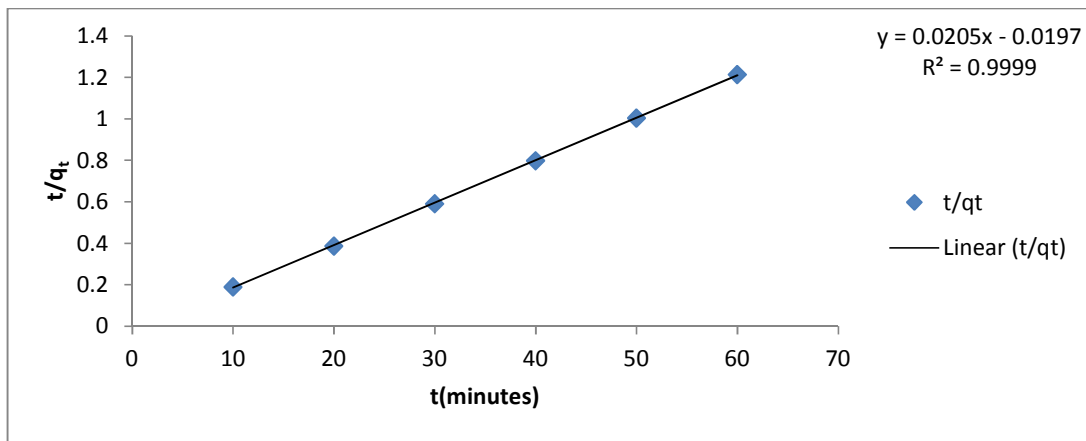*Lagmuir $R_L$ value was 0.1335 (favourable adsorption isotherm studies)*



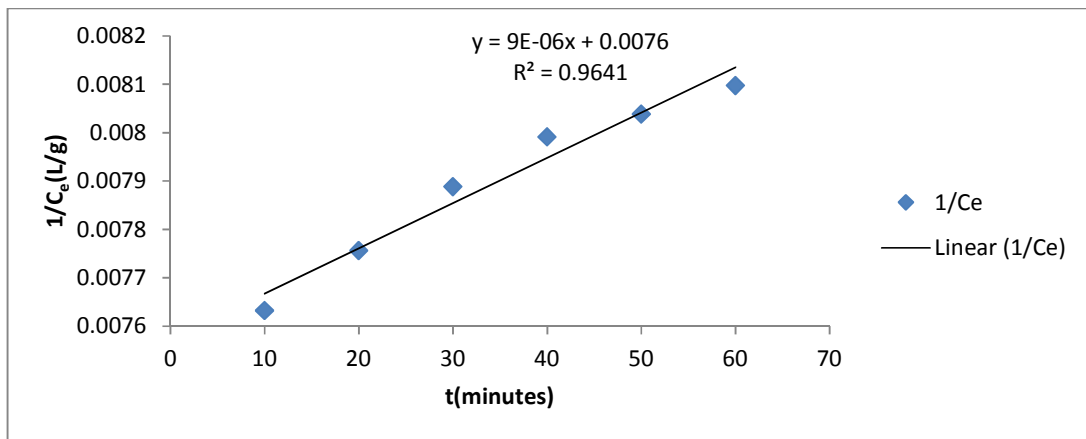**Fig. 6. Composite pseudo-second order kinetic model**



**Fig. 7. Composite second order kinetic model**

**Table 4. Evaluated constants obtained from the tested kinetic model for the composite**

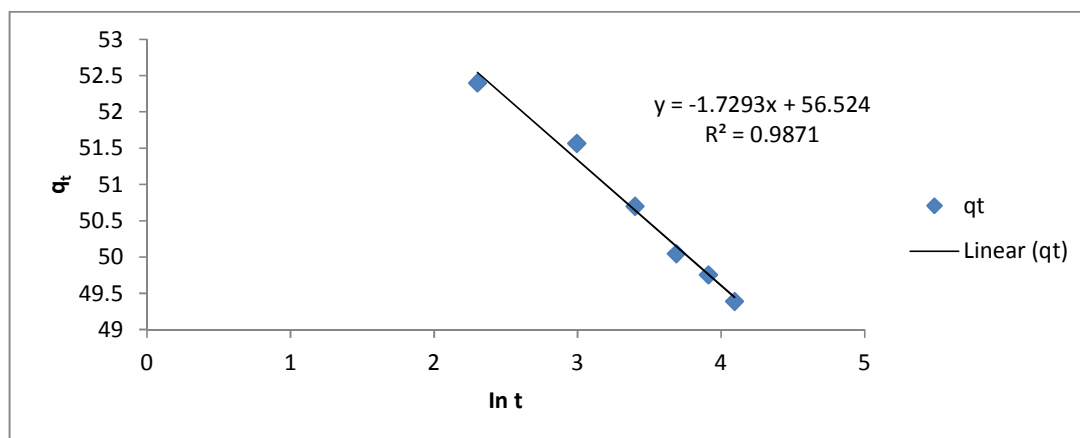| Kinetic model | $R^2$ | Intercept | K | Other constants |
|---------------|-------|-----------|---|-----------------|
| Second order | 0.9641 | 0.0076 | 0.000000009 | $C_o$ = 131.579 |
| Pseudo-second | 0.9999 | 0.0197 | 0.0189 | $q_e$ = 50.7614 |
| Elovich | 0. 9871 | 56.524 | b = -0.5783 | a = 1.1027E-14 |

**Fig. 8. Composite Elovich kinetic model**

## 4. CONCLUSION

An empirical model for the prediction of the adsorption capacity of chitosan-rice husk silica ash was developed using response surface methodology. Analysis of variance indicated that the model was significant with $P = 0.0017$. Also, optimum conditions were found to be 0.90 wt/wt chitosan/silica ratio, contact time of 5 min, and oil/water ratio of 0.25 v/v, this gave 20.66 g/g sorption capacity.

Temkin isotherm best fitted with $R^2$ value of 0.9999. The adsorption capacity from isotherm studies of the adsorbent obtained was 18.85 g/g. Also, the heat of adsorption $b_T$ (-48.67 kJmol$^{-1}$) for the composite obtained from Temkin isotherm studies was low, indicating physisorption of adsorbents to the crude oil. Pseudo-second order kinetic model best fitted for the composite with $R^2$ value 0.9999.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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