

Original Research Article

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

ABSTRACT

The research was conducted to develop 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 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. Models for the prediction of adsorption capacity was significant with R^2 value of 0.9384 and ANOVA model result of $P>F$ value of <0.0001 . Adsorption isotherm studies of Langmuir, Freundlich and Temkin were carried out for the rice husk silica. Temkin isotherm best fitted with R^2 value of 0.9995. The adsorption capacity of rice husk ash from isotherm studies was obtained to be 18.85 g/g adsorbent. The heat of adsorption b (kJmol⁻¹) obtained from Temkin isotherm study was -50.9 kJ/mol indicating physisorption of adsorbents to the crude oil. For the kinetic studies, the pseudo-second order model suitably described the removal of crude oil by composite with R^2 value 0.9999.

Keywords: rice husk ash; Adsorption; Batch studies, Adsorption isotherms; Adsorption kinetics, Design Expert.

1.0 Introduction

Oil contamination is one of the most serious environmental problems and its becoming increasingly inevitable. This as a result of continuous reliance of modern society on the use of petroleum hydrocarbons for its energy needs. This has created a need to transport petroleum from drilling point to industries where it's been processed into fuels and petrochemical products and then to areas needed for use and consumption. During transportation process, oil and its derivatives sometimes pollute the water bodies and land with fluid wastes, which require urgent removal. Also, petroleum industries sometimes contaminate 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].

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 [2]. Thermally treated rice husk silica has also been used for crude oil sorption [3] 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 [4]. Acetylated rice husk was used according by Nwankwere *et al.* [5] to carry out crude oil sorption studies with sorption capacity of 10.31g/g of adsorbent. Researches have shown the uptake of metal cations [6] and crude oil [7] by chitosan.

This present work set to understudy the application of Design package for simulated contamination of water with crude oil under adsorption influencing factors with their equilibrium and kinetic studies as well. A model equation was also developed to predict adsorption process without carrying out the experiment.

2.0 Materials and methods

2.1 Adsorbent preparation

Prepared rice husk ash and chitosan powdered were composited using physical admixture method using different formulation ratios as designed by Design Expert 6.06 software. Other influencing factors like contact time and crude oil-water contamination ratio were also considered in the experimental design.

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

55 composite was put into a beaker containing the calculated 0.25% v/v oil/water ratio for five
 56 minutes and agitating the mixture for 200 r.p.m for each runs. The same procedure was
 57 repeated for several designed conditions of composite formulated ratios, time and adsorbate
 58 concentration. The mixture was poured into a sieve and allowed to drain to get the new
 59 weight of the added adsorbent. The best adsorbent and adsorbate concentration which happen
 60 to be the optimized dosage was used to carry out these tests at different time intervals which
 61 followed the same adsorption process.

62 The oil sorption capacity (OSC) of the sorbents was determined by Equation 1 [5].

63 The OSC of the sorbents were obtained with the formula.

$$64 \quad OSC = \frac{\text{Weight Gain}}{\text{Original Weight}} \quad (1)$$

65

66 Table 1 presents the adsorption response as the process parameters contributing to adsorption
 67 of simulated crude oil contaminated water were investigated.

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69 Table 1: Composite adsorption experimental results

Run	Chitosan/Silica wt/wt %	Time Minutes	Oil/Water v/v. %	OSC %g/g
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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

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71 Table 2: ANOVA response for linear model to identify the significant contributing factors

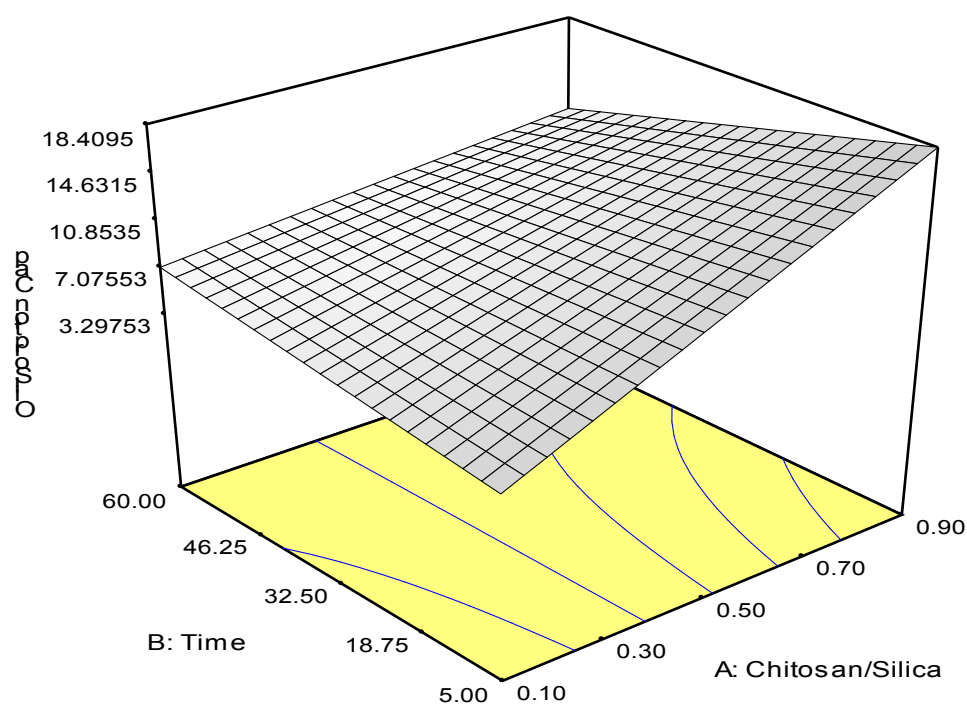
Source	Sum of Squares	DF	Mean Square	F Value	Prob>F
Model	258.25	6	43.04	8.63	0.0017*
A	175.67	1	175.67	35.23	0.0001*
B	7.22	1	7.22	1.45	0.2566
C	23.23	1	23.23	4.66	0.0563
AB	32.95	1	32.95	6.61	0.0279*
AC	12.93	1	12.93	2.59	0.1384
BC	6.25	1	6.25	1.25	0.2891
Residual	49.87	10	4.99		
Lack of Fit	49.74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

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

73 Table 2 shows the statistical ANOVA response for linear model and parameters contributing
74 to adsorption.

75 The Model F-value of 8.63 implies the model is significant. Values of "Prob > F" less than
76 0.0500 i.e 0.0017 indicate model terms are significant. In this case A and AB are significant
77 model terms.

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80 Figure 1: Response surface 3D plot of OSC versus Contact time and Chitosan/Silica.

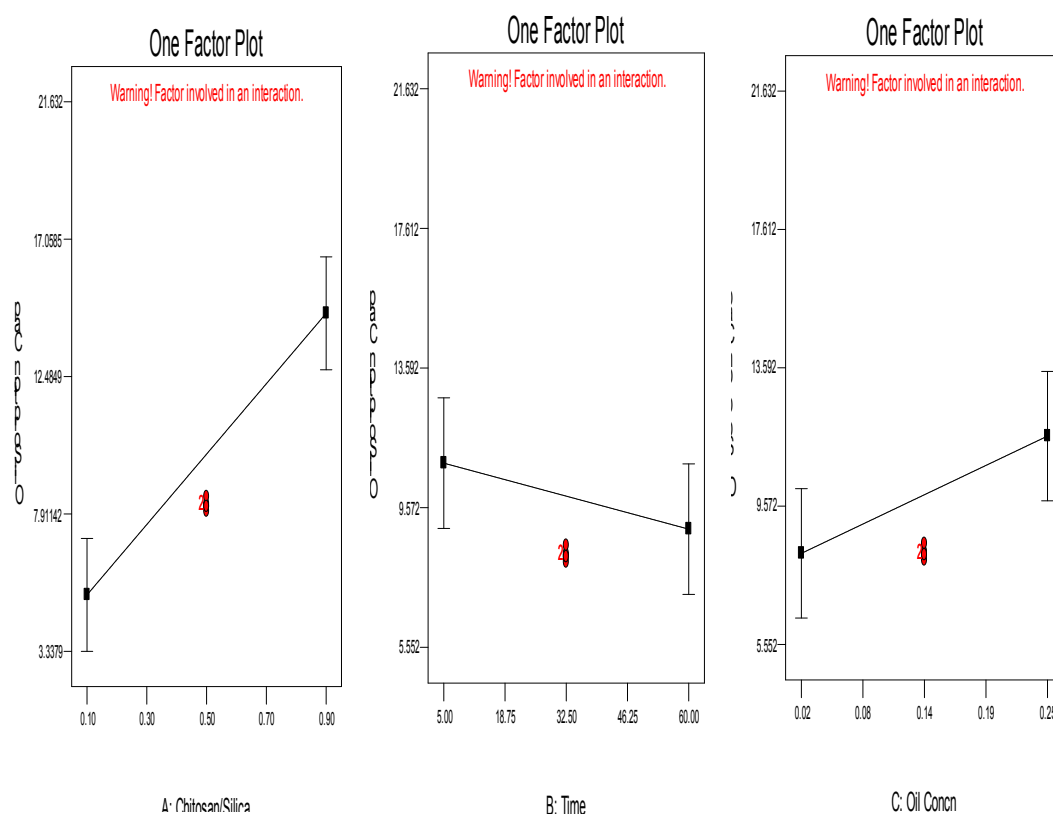


Figure 2: Composite adsorption capacity curve against the variables

From the 3Ds Figure and single variable Figure 1 and Figure 2, 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 presents in the composite blend, the better the performance.

Final equation in terms of actual influencing factors:

$$OSC = +3.30120 + 14.91781A + 0.042549B - 17.57194C - 0.25091AB + 39.08696AC + 0.39526BC \quad (2)$$

where A,B and C are Chitosan/Silica ratio, Contact time and Oil/water ratio respectively.

Thus with the model equation, one could likely mimick and predict adsorption without carrying it out laboratorily and will still arrive at a good result inputing in the factors contributing to adsorption.

The model was optimized and the result of optimisation design summary are given as 0.90, 5.00, 0.25, 20.6611 and 0.940 for formulation ratio, contact time, adsorbate concetration and sorption capacity and desirability respectively.

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 $q = \frac{V}{W}(C_o - C_e)$ (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 [9].

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:

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

It is linearly re-written as:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b} \quad (5)$$

Plotting $\frac{C_e}{q_e}$ against C_e

Where C_e = equilibrium concentration in solution q_e = the amount of adsorbate adsorbed for unit mass of adsorbent

q 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 Hall *et al* [9] as an essential feature of the Langmuir Isotherm to predict favourability of adsorption which is defined as:

$$R_L = \frac{1}{1+bC_0} \quad (6)$$

C_0 = 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 7.

$$q_e = K_f C_e^{1/n} \quad (7)$$

The linearized equation is given by:

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (8)$$

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 [8]. Its equation is given:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \quad (9)$$

The linearized equation is given by:

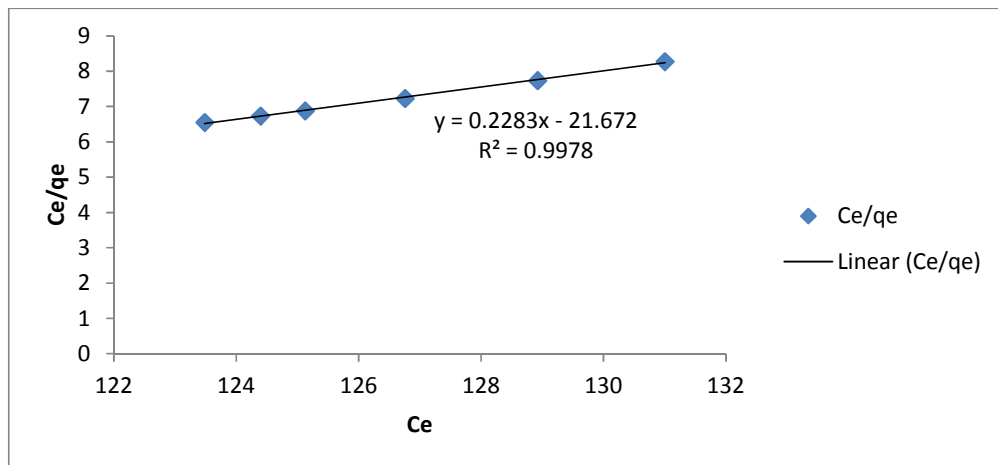
$$q_e = \frac{RT}{b_T} \ln C_e + \frac{RT}{b_T} \ln K_T \quad (10)$$

Where A_T = Temkin isotherm equilibrium binding constant (L/g)

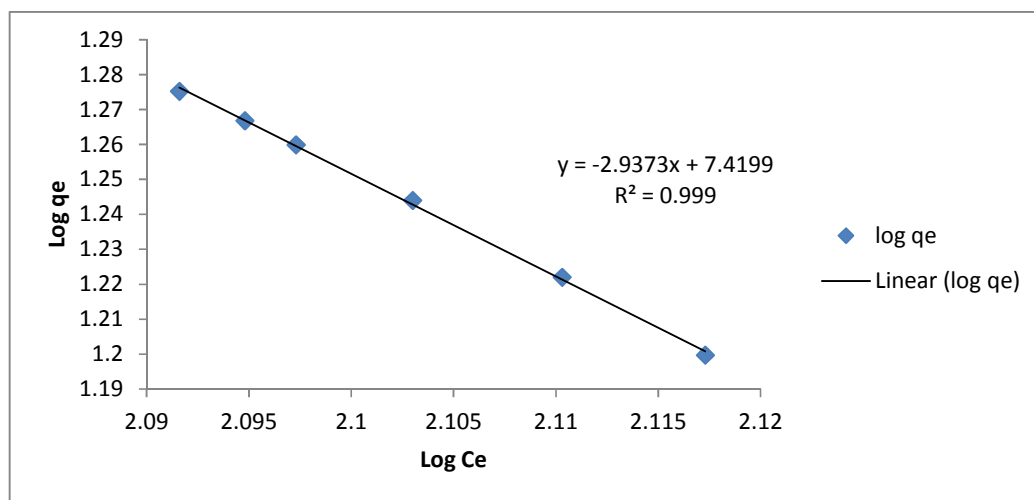
b_T = Temkin isotherm constant R = universal gas constant (8.314J/mol/K)

T = Temperature at 298K. B = Constant related to heat of sorption (J/mol)

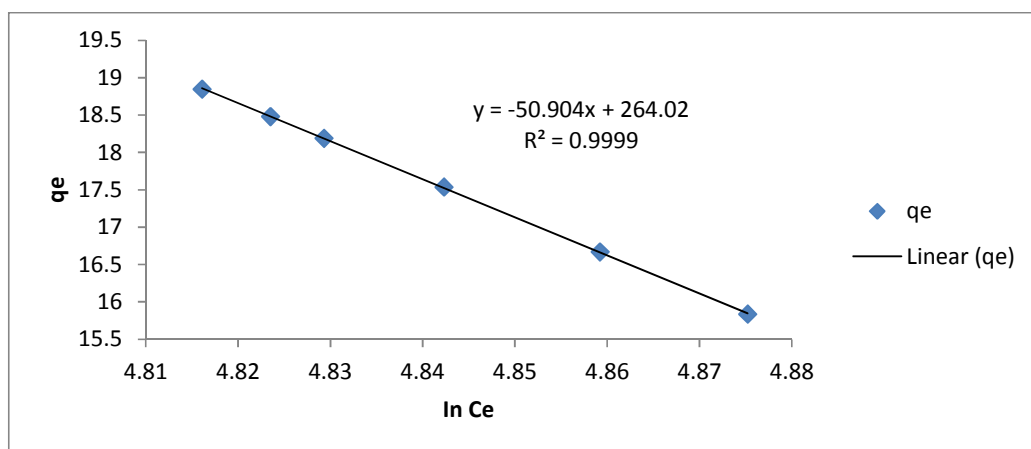
157 The isotherm studies of chitosan-rice husk silica ash composite are shown in the Figure 3, 4
 158 and 5. The kinetic and isotherm parameters are also as presented in Table 3 and 4
 159 respectively.



160
 161 Figure 3: Composite Langmuir adsorption isotherm plot
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163
 164 Figure 4: Composite Freundlich adsorption isotherm
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Figure

Figure 5: Composite Temkin adsorption isotherm plot

The heat of adsorption from Temkin b_T value -48.6715 J/mol is very low signifying that it is physisorption

Table 3 presents the adsorption isotherm studies parameters.

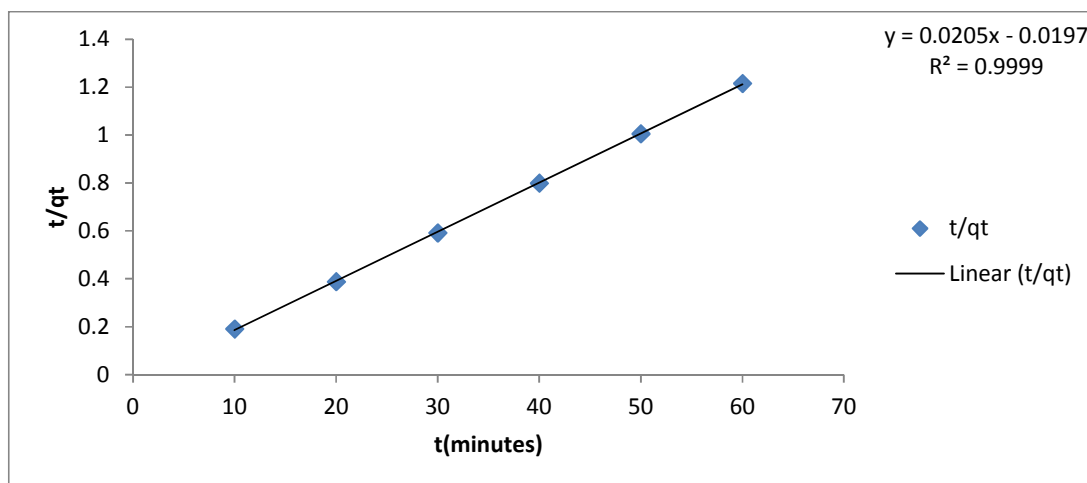
Table3: Composite adsorption isotherm value

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

173 Only Temkin isotherm best fit the adsorption with highest R^2 value of 0.9999.

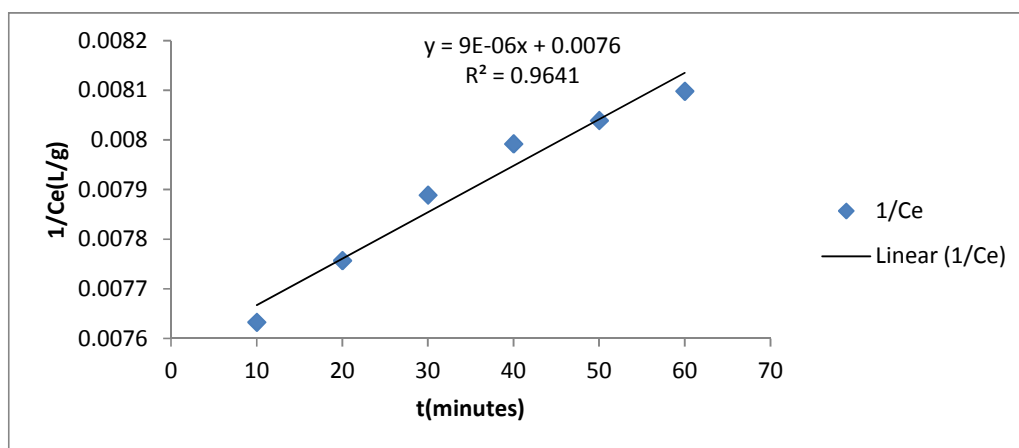
174 Lagmuir R_L value was 0.1335 (favourable adsorption isotherm studies)

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177 Figure6: Composite pseudo-second order kinetic model



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179 Figure 7: Composite second order kinetic model

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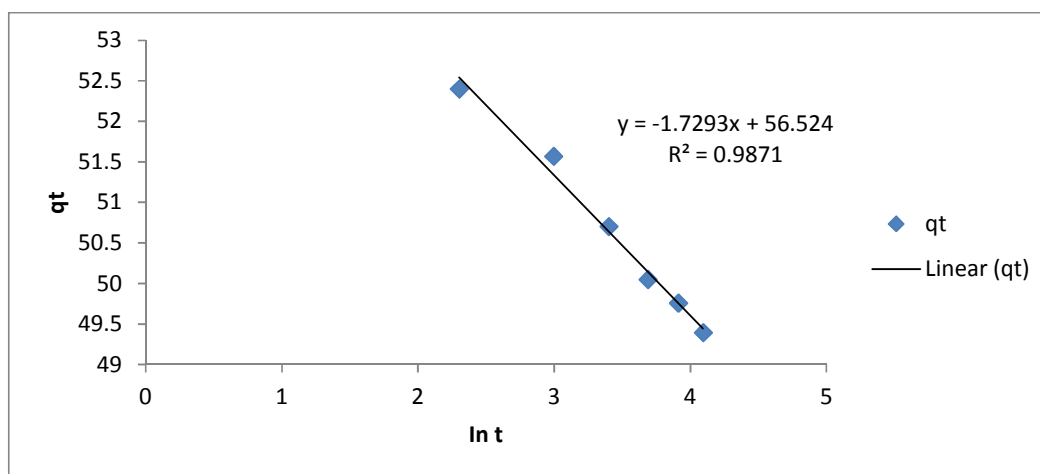


Figure 8: Composite Elovich kinetic model

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

Kinetic model	R ²	Slope	Intercept	k	Other constants
Second order	0.9641	0.000000009	0.0076	0.000000009	Co=131.579
Pseudo-second	0.9999	0.0205	0.0197	0.0189	qe=50.7614
Elovich	0.9871	-1.7293	56.524	b=-0.5783	a=1.1027E-14

Conclusion

The developed models for the prediction of adsorption capacity of rice husk silica ash using response surface methodology of Design Expert Software has R² value of 0.9384 and ANOVA model results was significant with P>F value of <0.0001.

Temkin isotherm best fitted for all with R² value of 0.9999. The adsorption capacity from isotherm studies of the adsorbents were obtained as 18.85 g/g. The heat of adsorption b (kJmol⁻¹) obtained from Temkin isotherm studies was low, indicating physisorption of adsorbents to the crude oil. Pseudo-second order kinetic model best fitted for composite with R² value 0.9999.

196 **Symbols**

- 197 b — adsorption equilibrium constant, l g^{-1}
- 198 C_e — concentration of oil at equilibrium, g l^{-1}
- 199 h — initial sorption rate, $\text{g g}^{-1}\text{min}^{-1}$
- 200 k_1 — pseudo-first-order rate constant, l min^{-1}
- 201 k_2 — pseudo-second-order rate constant, $\text{g g}^{-1}\text{min}^{-1}$
- 202 q_e — equilibrium solid phase concentration of oil, g g^{-1}
- 203 q_t — solid phase concentration of oil at time t , g g^{-1}
- 204 t — time, min

205 **References**

- 206 1) Aisien, F.A., Ebewe, R.O. and Hymore, F.K. (2003). *Potential Application of Recycled*
 207 *Rubber in Oil Pollution Control. Environmental Monitoring and Assessment.* 85, 175-
 208 190.
- 209 2) Yang, H., Viola, D., Belinda, J., Rmbo, X. and Tony, S. *Rice husks and oil pollution.*
 210 Fall 2005, Roskilde University.
- 211 3) Isa, M.T., Ameh, A.O., Tijjani, M. and Adama, K.K. (2012) 'Extraction and
 212 Characterisation of Chitin and chitosan from Nigerian Shrimps', *International Journal of*
 213 *Biological and chemical Sciences*, vol. VI, no. 1, pp. 446-453.
- 214 4) Abdul A. A, Abdulrauf R. A, Enamul H. M. (2012). 'A Novel Sustainable Oil Spill
 215 Control Technology' Dept. of Petroleum Engineering, King Fahd University of Petroleum
 216 & Minerals, Dhahran 31261, Saudi Arabia
- 217 5) Kudaybergenov K.K., Ongarbayev E.K. and Mansurov Z.A.. (2012). 'Thermally treated
 218 rice husks for petroleum adsorption'
- 219 6) Ozturk N and Kavak D, (2005) Adsorption of boron from aqueous solutions using fly ash:
 220 batch and column studies, *J. Hazard Mater.*, 127 81–88.
- 221 7) Amita Ummadisingua and Suresh Gupta. Characteristics and kinetic study of chitosan
 222 prepared from seafood industry waste for oil spills clean-up. *J.* 44 Taylor and Francis
 223 Group.
- 224 8) Tsai W.T., Chang C.Y., Wang S.Y., Chang C.F., Chien S.F., and Sun H. F., (2001),
 225 Utilization of agricultural waste corncob for the preparation of activated carbon, *Journal*
 226 *of Environmental Science and Health*, 5B(36), 677-686.

- 227 9) Hall, K.R., Egleton, L.C., Acrivos, A. and Vemeulen, T. (1966). *Pore and solid diffusion*
228 *kinetics in fixed bed adsorption under constant pattern conditions*. Industrial and
229 Chemical Engineering Fundamentals, 5, 212-223.
- 230 10) Temkin, M., & Pyzhev, J. A. V., (1940). *Kinetics of ammonia synthesis on promoted iron*
231 *catalysts*. Acta Physiochim 12: 217-222.