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Kinetics, Modelling and Isotherms Study of Crude Oil Adsorption onto Rice Husk Ash

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Abstract. The research was conducted to develop rice husk ash adsorbent for the removal of crude oil from contaminated water. The produced adsorbent 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. 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 percentage yield obtained was 6.75%. FTIR and XRD analysis showed that the adsorbent was amorphous and could adsorbed crude oil on their surface. The effect of influencing parameters such as contact time, adsorbate concentration, and adsorbent dosage were studied. It was generally shown that adsorption process increases with time and adsorbate concentration and decreases with adsorbent dosage. ANOVA indicates that model for the prediction of adsorption capacity was significant with R^2 value of 0.9384 and P-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 5.7g/g adsorbent. The heat of adsorption b (kJ mol^{-1}) obtained from Temkin isotherm study was -52.55 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 rice husk silica with R^2 value 0.9995.

Keywords: rice husk ash, adsorption, batch studies, isotherms, kinetics

Introduction

High energy demands on petroleum based fuels has warranted need for proper transportation of this liquids to several regions across the globe from its raw state to final state of use and even afterwards. Spillage of this liquids and its fuel derivative in the biosphere is becoming increasingly inevitable via aging of pipelines, equipment failure, corrosion, accidental operational problems or by sabotage which require urgent treatment (Aisien, *et. al*., 2003).

Much more difficulties are experienced when there is oil-water emulsion due to mixing in turbulent scenarios because of its hydrophobic nature. Literature revealed 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 and spillages (Aisien, *et. al*., 2006). These materials, over time are limited in regenerability, biodegradability, efficiency, usage and economy.

There is a major need to explore the biological means of control especially agricultural waste for sustainability and consideration of economy of operation.

Many researchers have published a lot of works showing the effectiveness of numerous agricultural products for oil clean-up process. Examples are included here as straws and wood (Abdul, *et. al*., 2012), sugar cane bagasse (Sun, *et. al*., 2003), kenaf and cotton (Anthony, 1994), cotton grass fibre (Suni, *et. al*., 2004) and other natural sorbent like corn cobs saw dust, peat moss, milk weed (Sun, *et. al*., 2002) and (Choi, *et. al*., 1992).

Methods

Rice Husk Pre-Treatment

Rice husk was first washed thoroughly with tap water to remove stones and dirt. The rice husk was then dried under atmospheric condition to avoid thermal shock on the material thereby causing distortion of the structure and surface of the biomaterial. The washed dried rice husk was then soaked in 10 w/w % sulphuric acids and boiled for 1 hour and then allowed to stay for 24 hours in the boiled acid solution to removed excess carbohydrates. The rice husk was thoroughly washed with distilled water to reduce its pH to 6.6 which was close to neutrality after several washing and then dried atmospherically.

Charring and Carbonization of Rice Husk

The beneficiated and acid pre-treated rice husk was charred in the oven for two hours at 200^{o}C. This was done to ensure it does not smoke excessively during carbonization in the furnace. The charred rice husk (black in colour) was transferred to the furnace where it was carbonized at 700^{0}C for 6 hours to avoid phase transformation of silica from amorphous to crystalline surface (Kudaybergenov *et. al*., 2012).

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 RHA 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 for each runs. The same procedure was repeated for several designed conditions of RHA 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 (Thompson *et. al*., 2010).

The OSC of the sorbents were obtained with the formula.

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

Characterization

The produced chitosan and prawn source was characterized using FT-IR, XRD, AAS and Proximate analysis.

Elemental Analysis of Rice Husk

The elemental analysis of rice husk and its derivatives is given in Table 1.

Table 1. Elemental analysis of rice husk and its derivative

Materials	Ca mg/g	Fe mg/g	Nitrogen %	Carbon %
Raw Rice Husk	0.3120	0.7295	1.6	24.89
Treated Rice Husk	0.1297	0.4290	0.68	31.73
Rice Husk Silica	0.1113	0.2929	0.07	0.57

FT-IR of RH and RHA

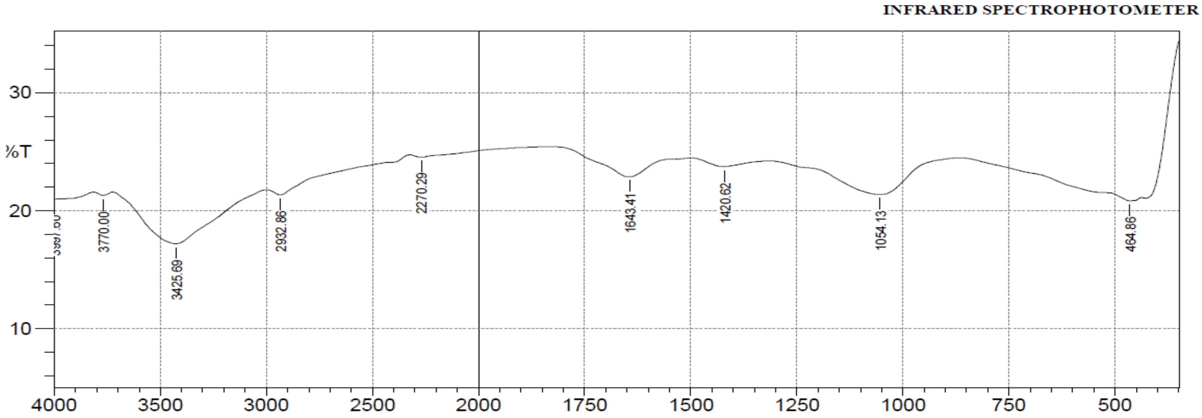

Figure 1. FTIR spectroscopy analysis raw rice husk

Hydroxyl, carbonyl and silica group are the expected functional group present in rice husk been a carbohydrate. 1054.13 cm^{-1} band corresponded to C-OH, C-O-C, C-O vibrational ring of the cellulose and hemicellulose which are polysaccharides (carbohydrates) and were reported by Ding *et al.*, (2001) to be 1060 cm^{-1} which is a bit closer. The difference may be due to origin and plant species. Band width 2909.72 cm^{-1} correspond to lignocellulosic component which was reported by to fall within 2855-2933 cm^{-1}. Also band 1643.41 cm^{-1} corresponded to C=O stretching vibration of conjugated carbonyl of lignin.

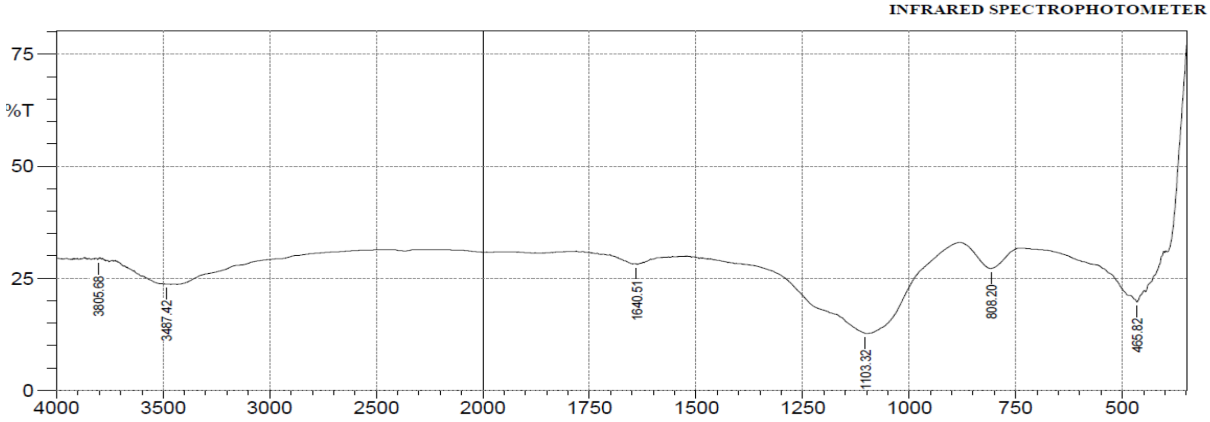

Figure 2. FTIR spectroscopy analysis rice husk silica ash

All the functional groups' associated with hydrocarbon materials had disappeared showing complete carbonization of the materials (Farook, *et. al.*, 2006). The band 8008.20 cm^{-1} shows rich presence of Silica group which is higher depicting complete removal of impurities and organic component during thermal and acid treatment. The band at 465.82 cm^{-1} in Figure 4.4b is as a result of stretching Si-H group signifying bond presence of silica.

X-Ray Diffraction of RHA

Figure 3 is the X-ray diffraction patterns of the produced rice husk silica ash.

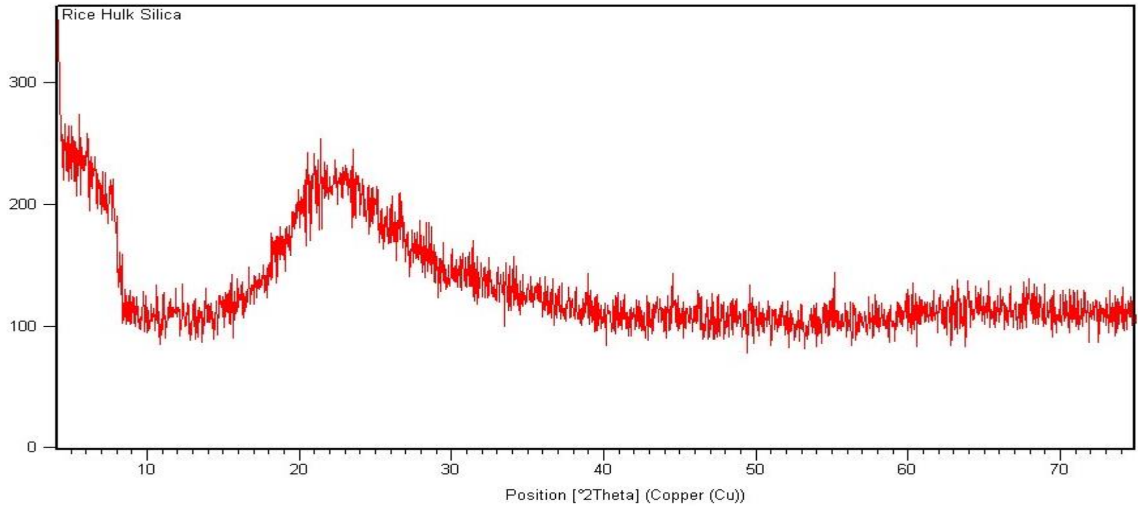

Figure 3. XRD Pattern of Rice husk silica at 700^0C

There are no sharp peaks except a broad peak observed at about 22.5º 2θ angle which generally indicates that the solid is amorphous in structures. Similar report of amorphous nature of rice husk silica produced by Farook *et al*. (2006).

Morphology of Samples

Scanning Electron Microscopy has been widely used to characterize materials, particularly their morphological properties. The main focus is the role of fiber morphology on the uptake of the hydrocarbons. Plate 1 and 2 present the SEM images of raw rice husk and rice husk silica ash respectively.

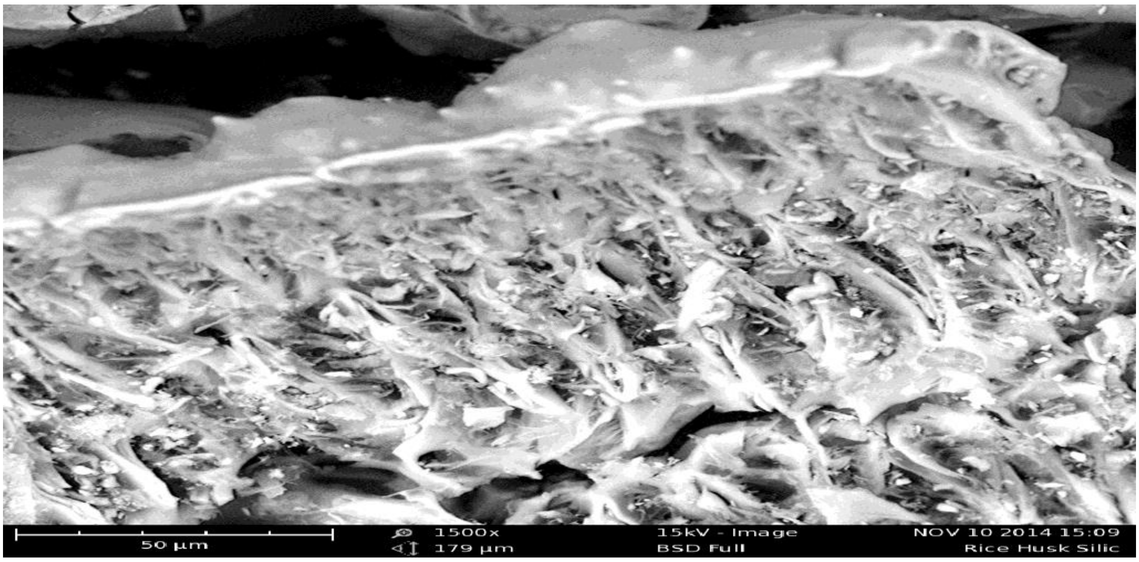

Plate 1: SEM image of raw rice husk

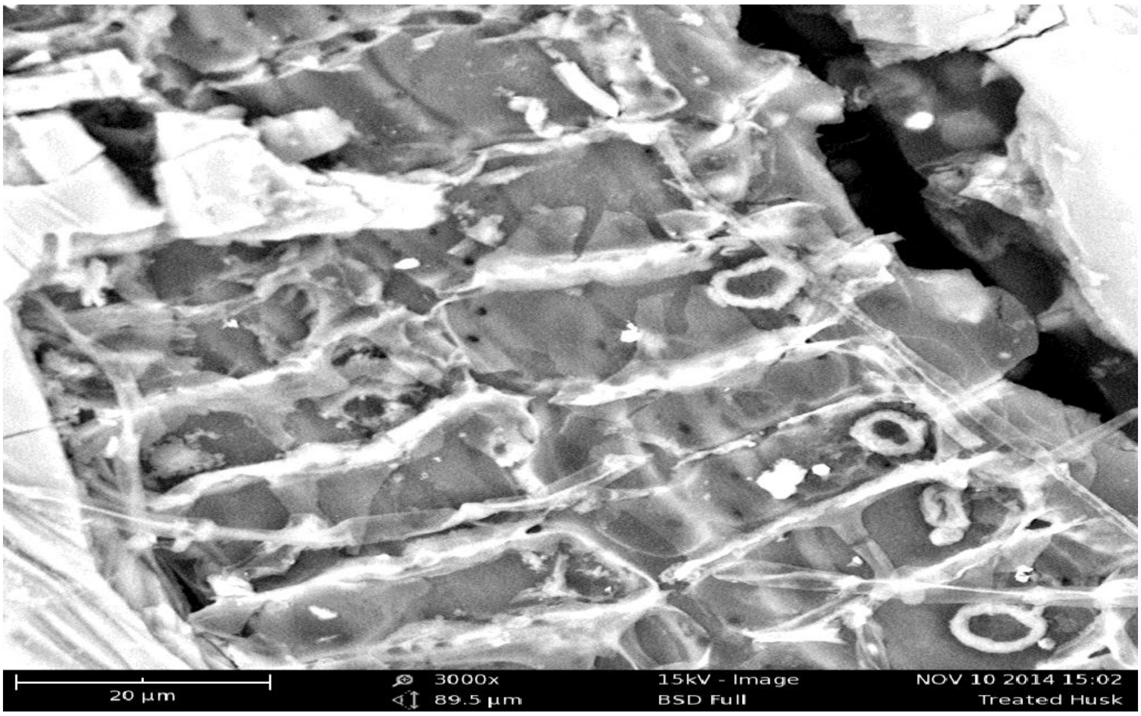

Plate 2: SEM image of rice husk ash

Plate 1 of the virgin rice husk showed that the material surface is closely tight and did not have enough pore spaces. The SEM image of virgin rice husk shows that the notable various form spherical particles of silica on the organic matrix which consists of cellulose, hemicellulose and lignin as designated on it. Plate 2 is the SEM image of thermally treated husk at 700^0C. The particle of rice husks had undergone serious changes in the process of high thermal treatment. The SEM micrograph revealed that there was increase in the pore number, size and showing a very porous tracery surface morphology with a high surface area. Also there was a rapid increase in the mesopores surface are from 5.36 to 14.20 micrometre from raw rice husk to rice husk silica respectively.

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. Silica adsorption experimental runs

Run	Silica Dosage (g)	Contact time (minute)	Oil/Water %v/v	OSC g/g
1	0.25	5.00	0.02	5.212
2	1.13	32.50	0.14	9.23
3	2.00	60.00	0.25	3.01
4	1.13	32.50	0.14	9.25
5	2.00	5.00	0.25	2.835
6	1.13	32.50	0.33	2.814
7	1.13	32.50	0.06	3.38
8	1.13	32.50	0.14	9.22
9	2.60	32.50	0.14	3.11
10	0.25	5.00	0.25	5.8
11	0.35	32.50	0.14	5.48
12	2.00	5.00	0.02	1.43
13	0.25	60.00	0.02	5.56
14	1.13	32.50	0.14	9.23
15	1.13	32.50	0.14	9.25
16	0.25	60.00	0.25	7.28
17	1.13	78.75	0.14	3.14
18	1.13	13.75	0.14	2.94
19	2.00	60.00	0.02	1.425
20	1.13	32.50	0.14	9.23

The analysis of variance statistical data is as presented in Table 3.

Table 3. ANOVA Response for quadratic model to identify the significant contributing factors

Source	Sum of Squares	DF	Mean Square	F Value	Prob>F
Model	152.96	9	17.00	16.94	< 0.0001*
A	26.82	1	26.82	26.72	0.0004*
B	0.40	1	0.40	0.40	0.5425
C	1.38	1	1.38	1.38	0.2676
A^2	34.53	1	34.53	34.41	0.0002*
B^2	57.17	1	57.17	56.97	< 0.0001*
C^2	56.02	1	56.02	55.82	< 0.0001*
AB	0.34	1	0.34	0.34	0.5714
AC	0.058	1	0.058	0.058	0.8146
BC	0.22	1	0.22	0.21	0.6532
Residual	10.04	10	1.00		
Lack of Fit	10.03	5	2.01	13379.06	< 0.0001*
Pure Error	7.500E-004	5	1.500E-004		
Cor Total	163.00	19			

Standard Deviation: 1.0a; R-Squared: 0.9384 *significant variable

Final model equation in terms of actual factors is given as:

$$OSC = +2.41436 + 3.11323A + 0.18009 * B + 40.37976C - 2.02178A^2 - 2.63366E - 003 * B^2 - 149.0778C^2 - 8.61299E - 003AB + 0.84720AC + 0.051858BC, \quad (2)$$

Where A, B and C are Silica dosage, contact time and oil water ratio respectively.

From the generated statistical data, it could also be seen that the values for most of the points are close of the predicted and actual values of the sorption capacities. This is reflected in the R^2 value which is 0.9384.

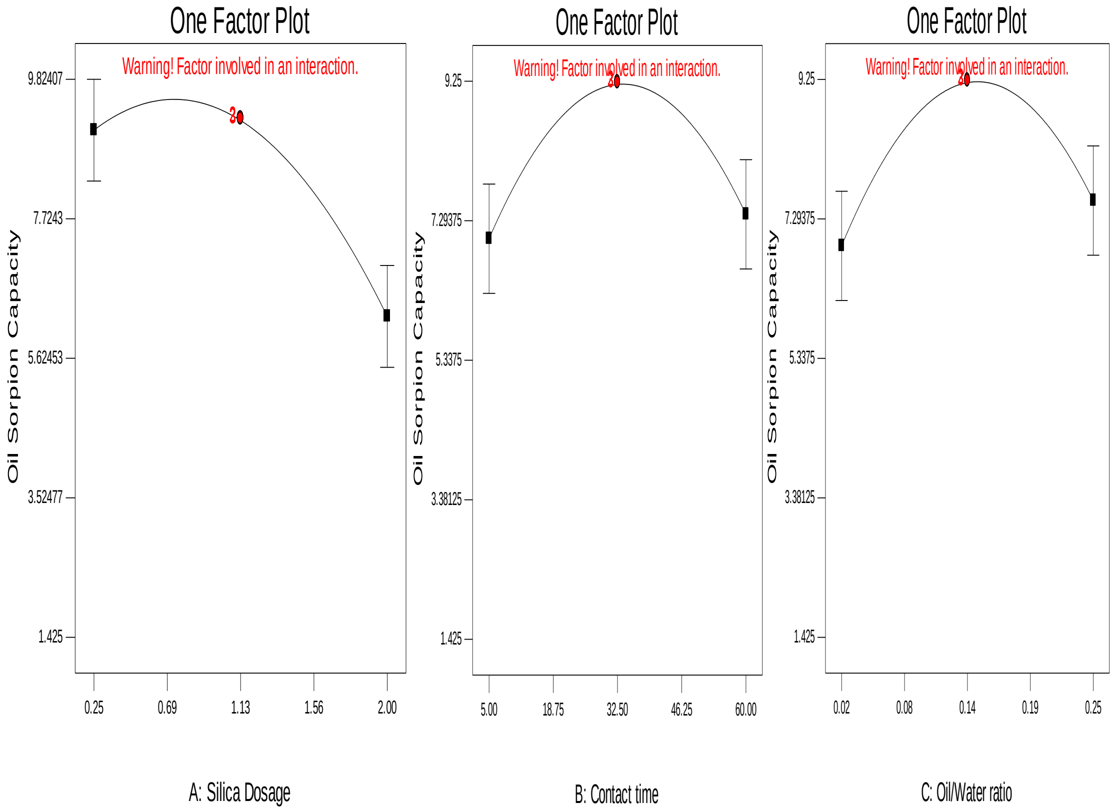

Figure 4. Silica Adsorption capacity curve against the variables

From the single variable Figure 4, it can be interpreted that OSC of silica increased with increase in contact time and oil water ratio which then get to a maximum and then fell back in a parabolic path. This may be attributed to its poor performance at anchoring lipid to its surface at saturation. Adsorbent dosage increased a little with increase in sorption capacity and then followed the same parabolic trend fall due to less available sites for adsorption. The decrease in adsorption capacity by increasing the adsorbent amount is principally due to unsaturated sites remaining during the adsorption process. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, A^2, B^2 and C^2 are significant model terms.

The model was optimised for rice husk ash adsorption giving 0.63, 31.33, 0.13, 9.46324 and 1.0 as silica dosage, Contact time, Oil/Water ratio, Sqrt(OSC) and Desirability respectively.

Isotherm and Kinetic Studies

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 (Hall, *et. al.*, 1996.

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:

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

It is linearly re-written as:

$$\frac{C_e}{q_e} = \frac{1}{q_m} Ce + \frac{1}{q_m b} \tag{5}$$

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

Where Ce= equilibrium concentration in solution qe= 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.*, 1996, as an essential feature of the Langmuir Isotherm to predict favourability of adsorption which is defined as:

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

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 7.

$$q_e = K_f Ce^{1/n} \tag{7}$$

The linearized equation is given by:

$$\log q_{e=} \frac{1}{n} logC_e + logK_f \tag{8}$$

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 Temkin, *et. al*., 1940. The equation is given:

$$q_e = \frac{RT}{b_T} In(K_T Ce) \qquad (9)$$

The linearized equation is given by:

$$q_e = \frac{RT}{b_T} InCe + \frac{RT}{b_T} InK_T \qquad (10)$$

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)

The isotherm studies of rice husk ash are shown in the Figure 5, 6 and 7. The kinetic and isotherm parameters are also as presented in Table 4 and 5 respectively.

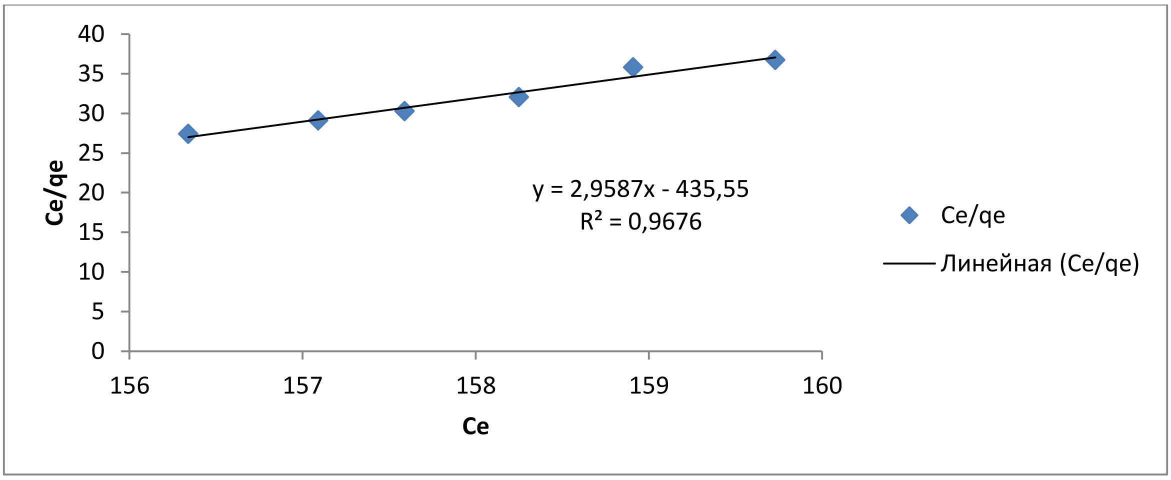

Figure 5. Silica Langmuir Plot

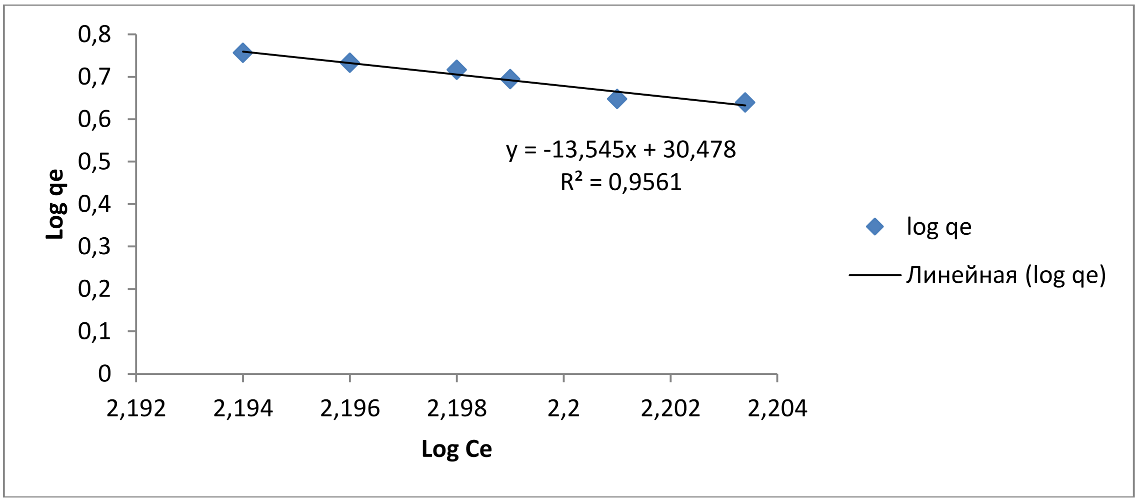

Figure 6. Silica Freundlich Plot

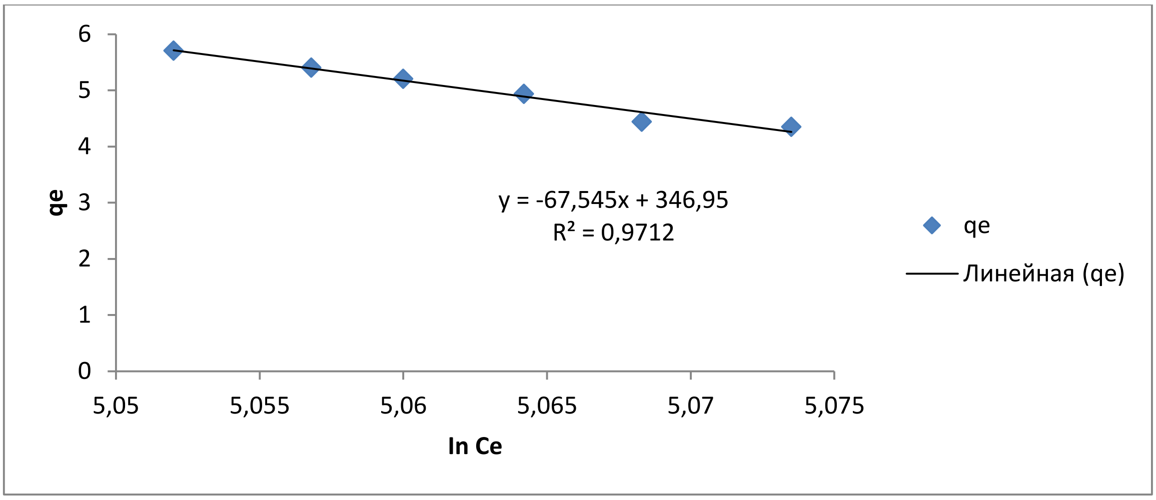

Figure 7. Silica Temkin plot

Temkin adsorption isotherm best fit the adsorption with R-squared value of 0.9712. The heat of adsorption b_T value -36.6803 J/mol is very low signifying that it is physisosorption. The Lagmuir R_L value is 0.049 showing favourable adsorption isotherm studies. R_L is vital dimensionless factor parameter. The value of R_L indicates the type of isotherm to be either unfavourable ($R_L >1$), favourable ($R_L =1$) and favourable ($0< R_L <1$) or irreversible ($R_L =0$). It is a positive number whose magnitude determines the feasibility of the carried out adsorption process.

Table 4 presents the calculated adsorption isotherm studies parameters.

Table 4. Silica adsorption isotherm parameter values

Isotherm	Parameter	Value
Langmuir	b R_L R^2	0.1138 0.049 0.9676
Freundlich	K_f 1/n R^2	6.4561 -13.565 0.9561
Temkin	K_T b_T R^2	0.915 -36.6803 0.9712

Pseudo-first-order kinetics

The non-linear form of pseudo-first-order equation is given by Equation 11.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{11}$$

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 $\text{min}^{-1}$is the rate constant of the pseudo first-order adsorption operation. The integrated rate law after application of the initial condition of qt= 0 at t= 0, is linearized to Equation 3.10

$$\log(q_e - q_t) = log q_e - \frac{k_1 t}{2.303} \tag{12}$$

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.

$$\frac{1}{C_e} = k_2 t + \frac{1}{C_o} \qquad (13)$$

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 3.12

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (14)$$

Where where h= k_2qe^2

Elovich model

Elovich model is applicable for chemisorption processes. The equation is often used valid for adsorption surface that is heterogeneous, Equation 15.

$$q_t = \frac{1}{b} In(ab) + \frac{1}{b} In\ t \qquad (15)$$

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

Figures 8 to 10 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

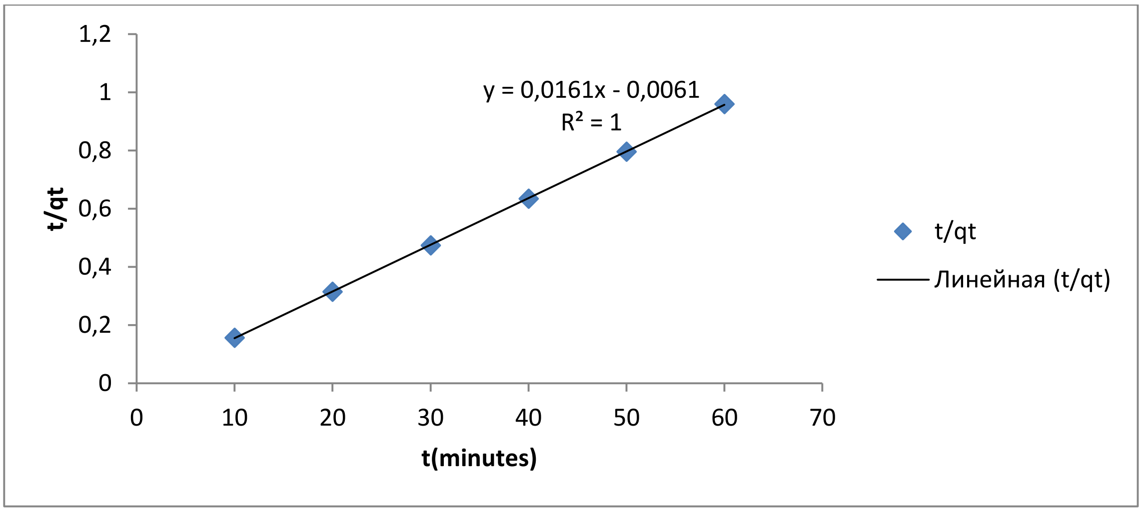

Figure 8. Rice husk silica pseudo-second order kinetic model

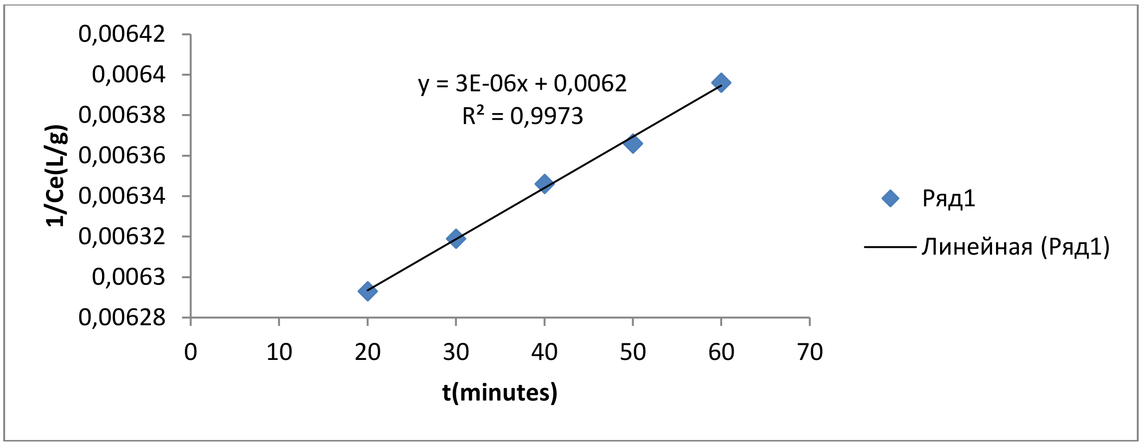

Figure 9. Rice husk silica second order kinetic model

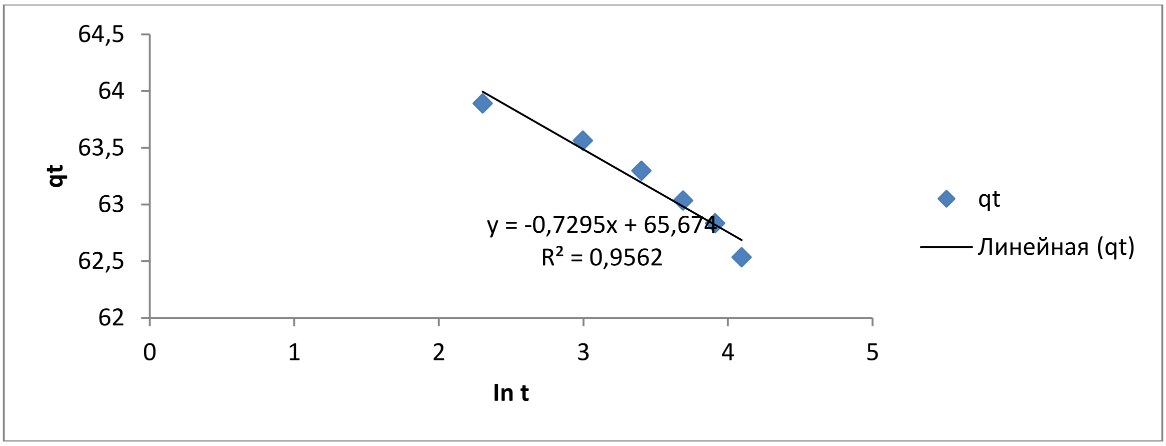

Figure 10. Rice husk silica Elovich kinetic model

The kinetic data best fitted into pseudo-second order kinetic model with highest R-squared value of 1.0. Table 5 presents the kinetic model parameters.

Table 5. Evaluated constants obtained from the tested kinetic model for rice husk silica

Kinetic model	R^2	Slope	Intercept	k	Other constants
Second order	0.9973	0.000003	0.062	0.000006	Co=161.29
Pseudo-second order	1.0000	0.0161	0.061	0.002311	qe=163.9344
Elovich	0.9562	-0.7295	65.674	b=-1.3708	a=5.8246E-40

Conclusions

The developed model for the prediction of adsorption capacity of rice husk silica ash using response surface methodology has R^2 value of 0.9384 and P-value of 0.0001 which indicated that the model was significant.

Temkin isotherm best fitted for all with R^2 value of 0.9995. The adsorption capacity from isotherm studies of the adsorbent obtained was 5.7 g/g. The heat of adsorption b (kJ mol^{-1}) obtained from Temkin isotherm studies were generally low, indicating physisorption of adsorbents to the crude oil. Pseudo-second order kinetic model best fitted for rice husk silica with R^2 value 1.0.

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