Original Research Article

Optimization of process parameters for the treatment of Crude oil spill polluted water surface by sorption technique using fatty acid grafted ogbono shell as a sorbent

ABSTRACT

This work focuses on the optimization of the adsorption technique using fatty acid grafted ogbono shell for the removal oil from polluted water surface. The shell was carbonized at a temperature of 600^{o}C for 4hours and then further modified with stearic acid. The surface morphology of raw and grafted ogbono shell was studied Scan Electron microscope (SEM) while Fourier Transform Infra-red Spectroscopy (FTIR) was used to investigated the functional group of different minerals. Proximate analysis was carried out to determine the surface area of the agro wastes before and after modification. The process parameters were optimized using response surface methodology. Physiochemical characterization of the adsorbents showed that surface area increased significantly after carbonization and modification. SEM and FTIR results revealed that more micro porous surfaces were created on the surface of the adsorbent after modification. The optimum time, temperature, dosage, pH and percentage oil removal were; Time of 10mins, temperature of 60^{o}C, dosage of 1.4g, pH of 3 at the theoretical percentage removal of 78.77%

Key words: Optimization, ogbono shell, crude oil, adsorption

INTRODUCTION

Crude oil is a combustible liquid found in the earth's sedimentary mantle and is basically composed of a complex mixture of hydrocarbons with its color ranging from brown to almost black depending on the content and structure of the resinous substances it contains (Uzoije et al., 2011). Over the years, crude oil spill and its concomitant pollution have been in front burner in environmental issues over the world and in particular the rich Niger Delta of Nigeria (Uzoije et al., 2011). Crude oil spillage results when oil has been released into the environment (Ali et al., 2012). The oil spills in seawater and soil are usually as a result of exploration or transportation or storage activities (Annunciado et al., 2005; Baars, 2002). Spillage is broadly categorized into four groups, namely minor, medium, major and disaster (Banerjee, 2006). The most frequent of these is the minor spillage which is oil discharge less than 25 barrels in land waters or less than 250 barrels on land, offshore and coastal water (Behnood et al,., 2013). This category of spill contributes more to the total volume of annual spillage than other categories (Chung et al., 2011).

Clean-up is necessary after a spill for the protection of the environment and human health. In control of spillages, a wide range of tool and techniques are used to clean oil spills. Among the techniques include; chemical remediation, bioremediation, phytoremediation, thermal desorption, adsorption and land fill in the case of soil spillage. Adsorption technique is of great interest due to its cheapness and convenience (Sayed et al., 2003). Natural sorbents and varieties of organic vegetable waste products, such as peat moss, wood, cotton, rice straw, corncobs and kapokshave been recently gained an appraisal both internationally and locally as an effective sorbents in oil spill treatment (Nwadiogbu et al., 2016; Choi and Cloud, 1992; Deschamop et al., 2003) These agro wastes are at no cost and available locally. Optimization of the process parameters was done in this work using response surface methodology (RSM). Response surface methodology is a statistical tool designed specifically for optimization studies. Its usage depicts the effect of independent factors on the results or expected results. The input elements or factors are the independent variables while the response(s) or the outputs are the dependent variables (Datta, 2011). RSM relates item properties by utilizing regression equation that portrays interrelations between information factors and item properties (Adeyanju et al., 2016). The most often used type of RSM is central composite design (CCD) and Box Behnken design (BBD). Therefore, the aim of this study is to optimize the use of esterified ogbono shell (agro wastes) as an adsorbent in the remediation of crude oil layer polluted water surface using Box Behnken design.

Materials and method

Materials

The major raw material (Ogbono shells) was collected from Akpoga Nike in Enugu State Nigeria. The shells were first washed and dried under the sun for one week. After which, the shells were grounded using a commercial grinder at Oye Market in Emene, Enugu State Nigeria. Other materials used included; Crude oil, distilled water, sodium hydroxide (NaOH), H_2SO_4, HCL, Sieving net, stearic acid, n-hexane.

Methods

Preparation of Carbonized Adsorbent (Ogbono Shells)

The dried biomass (Ogbono shells) was carbonized in a muffle furnace at 600^{o}C for 4 hours respectively. After the carbonization, the samples were cooled and stored in dry transparent containers for further use (Angelova et al., 2011).

Activation of the carbonized ogbono shell by Esterification

Carbonized samples of the biomass (ogbono shell) were treated differently with 0.5g of fatty acid (stearic acid) in 200ml of n-hexane containing two drops of concentrated H_2SO_4 as catalyst. The mixture was refluxed in dean stark apparatus at 65± 2^{o}C for 4 hrs. After reaction, the esterified acid–grafted ogbono shells were washed severally with n- hexane. The fatty acid grafted biomass was oven dried at 110^{o}C for 12hrs respectively (Banerjee et al., 2006). They were then kept in dry tightly closed bottles respectively.

. They were then kept in dry tightly closed bottle for further use.

$$Weight\ percentage\ gain = \frac{Weight\ gain}{Original\ weight} \times 100 \quad (1)$$

Characterization of the raw and modified biomass

The surface morphology of the (raw and modified) biomass was studied using Model 302 Hitachi High Field Emission Scanning Electron Microscope and the images at 1mm and 150 magnifications. The method employed by Nwabanne and Igbokwe (2008) was adopted to carry out Fourier Transformed Infrared analysis of raw and modified biomass (Ogbono shell) using BUCK model 500 M infrared spectrophotometer. The sample was prepared using KBr and the analysis was done by scanning the sample through a wave number range of 500 to 4000 cm^{-1}. The proximate analysis parameters and the method of analysis were according to the American Society for Testing and Materials (ASTMD 5142, 3174, 872 and 3175 for moisture, ash, volatile and fixed carbon respectively) (Diadem, 2012)

Adsorption Experiment

The sorption of crude oil contaminated water was carried out following the method described by Banergee et al. (2006). Exactly 50ml of water was measured inside a 100ml beaker. A certain amount of crude oil (0.1-1.4g) depending on the oil/water ratio for a particular run was added into the beaker. The oil/water mixture was manually stirred for at varying minutes to ensure proper dispersion of the oil in water. 0.2g of the modified adsorbent was weighed into the beaker. The beaker containing the sorbent, oil and water was put into a water bath at a varying temperature. The mixture was stirred for a period of time, depending on the particular run. After which the mixture was filtered through a net of approximately 250µm. The weight of the net before and after the filtration was recorded. Meanwhile, the net after the filtration was allowed to stay for 24hours before the final weight was taken.

Percentage removal was also calculated according to the equation below

$$\%\ \text{removal} = \frac{(\text{Co} - \text{Ce})}{\text{Co}} \times 100 \quad (2)$$

$$\text{qe} = \frac{(\text{Co} - \text{Ce})}{\text{M}} V \quad (3)$$

C_o = Initial oil concentration (mg/l)

C_e = Equilibrium Concentration oil at certain time

Qe = Equilibrium adsorption in (mg/g)

V = Volume of the aqueous mixture in cm^3

M = Mass of the activated biomass (Esterified ogbono shell) in (g)

BBD Design of Experiment using RSM

The sorption of the crude oil layers by activated ogbono shell was optimized using Box Benkhen design (BBD) and RMS methods. The independent variables studied were Time X_1 (mins), temperature X_2 (°C), adsorbent dosage X_3 (g), and pH X_4. The time range of 10 to 60 minutes, the temperature range of 30 to 70 °C, dosage range of 0.2 to 1.4 and pH range of 3 to 11 were selected. The coded and uncoded levels of these independent variables are shown in Table 1. The experimental design was based on BBD. This was done to determine the best conditions for optimum sorption of the oil onto activated biomass. Equally, this helps to examine the interactive effects of the four important factors (Time, Temperature, dosage and pH). These factors were the independent variables while the percentage of oil adsorbed or removed (%R) were the dependent variables or responses. Using the Box Benkhen design (a statistical package in Minitab software version 17.1.0) involves varying the independent variables at three different levels (-1, 0, +1). In this work, a set of 27 experiments were performed. Table 2 shows the run order, variable conditions and the columns for the experimental, predicted and residual values of the oil layer sorption unto activated biomass.

Table 1: Independent variables with three different levels

Variables	Symbol	Level		
		Low	Centre	High
Time (mins)	X_1	10	35	60
Temperature (^oC)	X_2	30	60	90
Dosage (w:w)	X_3	0.2	0.8	1.4
pH	X_4	3	7	11

Table 2: Design matrix with responses for the sorption of oil from surface water onto Esterified Ogbono shell

Std	Run	Time: X_1 mins	Temp:X_2 ^oC	Dosage:X_3 g	pH:X_4	Coded values X_1 X_2 X_3 X_4	%Sorption Experimental	%Sorption Predicted
5	1	35	60	0.2	3	1 0 0 -1 -1	21.34	23.56
13	2	35	30	0.2	7	1 0 -1 -1 0	36.10	32.56
20	3	60	60	1.4	7	1 1 0 1 0	27.30	23.11
9	4	10	60	0.8	3	1 -1 0 0 -1	28.90	30.12
1	5	10	30	0.8	7	1 -1 -1 0 0	55.75	56.22
10	6	60	60	0.8	3	1 1 0 0 -1	17.30	17.00
3	7	10	90	0.8	7	1 -1 1 0 0	26.34	23.66
14	8	35	90	0.2	7	1 0 1 -1 0	26.11	26.77
7	9	35	60	0.2	11	1 0 0 -1 1	21.88	21.34
24	10	35	90	0.8	11	1 0 1 0 1	29.55	28.97
12	11	60	60	0.8	11	1 1 0 0 1	14.20	14.79
26	12	35	60	0.8	7	1 0 0 0 0	28.07	29.66
16	13	35	90	1.4	7	1 0 1 1 0	26.11	26.78
21	14	35	30	0.8	3	1 0 -1 0 -1	37.23	36.97
19	15	10	60	1.4	7	1 -1 0 1 0	76.40	78.77
2	16	60	30	0.8	7	1 1 -1 0 0	15.80	16.34
25	17	35	60	0.8	7	1 0 0 0 0	24.80	29.66
11	18	10	60	0.8	11	1 -1 0 0 1	30.45	27.89
22	19	35	90	0.8	3	1 0 1 0 -1	12.33	10.14
18	20	60	60	0.2	7	1 1 0 -1 0	22.55	23.11
8	21	35	60	1.4	11	1 0 0 1 1	19.60	21.34
4	22	60	90	0.8	7	1 1 1 0 0	29.40	29.89
23	23	35	30	0.8	11	1 0 -1 0 1	12.34	13.70

6	24	35	60	1.4	3	1	0	0	1	-1	24.23	23.56
15	25	35	30	1.4	7	1	0	-1	1	0	61.67	62.56
17	26	10	60	0.2	7	1	-1	0	-1	0	32.33	36.22
27	27	35	60	0.8	7	1	0	0	0	0	31.23	29.66

Results and Discussion

Proximate analysis of the raw and modified biomass

The characteristics of raw and modified biomass were shown in Table 3. From the Table, it can be seen that the raw biomass (ogbono shell) have low fixed carbon, surface area and high volatile content and as such suggest that the sample requires activation. Increase in fixed carbon and reduction in volatile matter of the activated biomass shows that activation improved the surface area of the biomass for adsorption. As observed from table 3, the surface area of ogbono shells increased from 114cm^2 (raw ogbono shell) to 190.5cm^2 (esterified ogbono shell) after modification with strearic acid thereby increasing the number of micropores within the surface the biomass for oil sorption and further validates the effectiveness of biomass modification by esterification and ogbono shells as a good sorbent for oil removal. Similar results on acetylated ogbono shell (199.3cm^2) has been reported by Alothman et al., (2011)

Table 3: Physical properties of the raw and modified ogbono shell

Adsorbents	Ash content (%)	Volatile matter (%)	Carbon content (%)	Surface area(m^2/g)	pH
Raw ogbono shell	7.4	28.6	56.5	114	6.9
Carbonized ogbono shell	5.7	21.4	64.2	129.4	7.1
Esterified ogbono shell	5.6	19.3	69.4	190.5	7.2

SEM Analysis Results

SEM Analysis is used to study the morphological compositions of the biomass before modification and after modification. There were more pore spaces in the carbonized and activated adsorbents than in the unmodified biomass. Availability of pore spaces favors adsorption process since it is a surface reaction. The surface morphologies of the raw biomass (Ogbono shells), and esterified biomass were presented as shown in fig 1 and 2. It was observed from fig 1 that the samples were internally bonded together. It can be observed from the figures that a bulk of microstructure which in turn is composed of a homogeneously distributed network comprised of small filamentous and fistulous crystallites showing the presence of minerals. In the matrix, Luminous and non-luminous features can be seen. These features indicate the presence of minerals distributed in the organic matrix and as surface coverage. From fig 2, the surface is loosed and some features such as fissures, cleats, cracks and veins can be seen showing that the action of heat and acid did lots of harm to the surface and the surface is no longer as intact as shown in fig 1. Some minute fissures and cracks, however an evident. These changes in microstructures may not be unconnected to the removal of some minerals from the activated biomass thereby increasing the micro porous surface. The surface is bright and mostly protracted. That micrograph reveals that the activation has undergone properly. The porosity has been increased and provides strong evidence that significant amounts of organic elements are being removed thereby increasing the number of micro pores

Fig 1: SEM image of un-carbonized ogbono shell @ 100µm

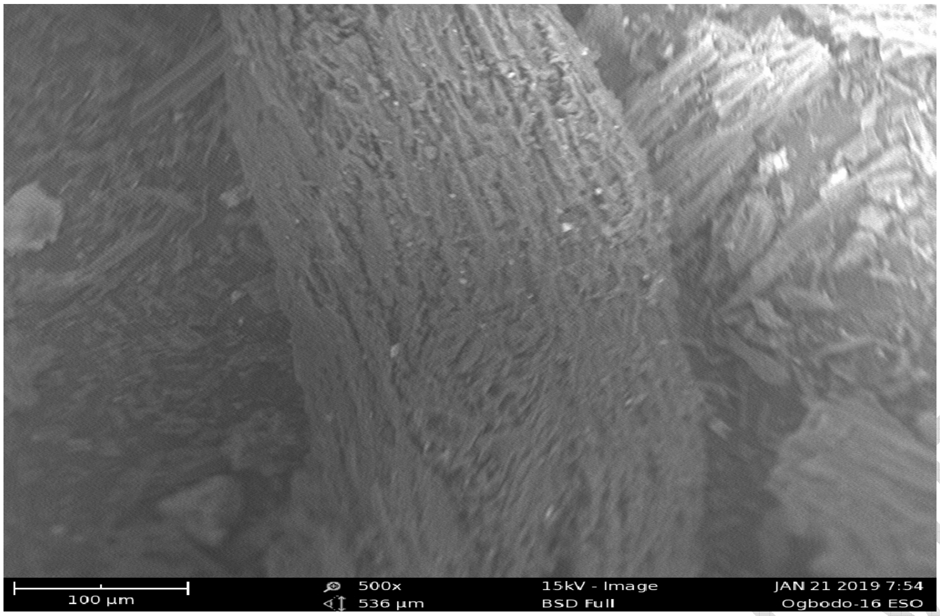

Fig 2: SEM image of esterified ogbono shell@ 100µm

Fourier Transform infrared (FTIR) of the modified and unmodified biomass

Bands were assigned according to the published article (Starsinic et al., 1984; Supaluknari et al., 1998). Fourier transforms infrared spectra of the raw biomass, carbonized biomass, and esterified biomas are presented in Fig 3 to 5. The frequencies were assigned to the respective functional ground and interpreted. It was observed that the biomass sample (ogbono shell) have numerous functional groups and the major functional groups present are O-H, N-H, N-CH_3, C=C-C, C-Cl, Si-O-Si. Petroxides bands stretches between 9650-1095cm^{-1}, Aromatic phosphate P-O-C stretches between 1300-1390cm^{-1}, Aromatic C-H in plane bend, Silicon ozy compounds Si-O-Si stretches between 1125-1295cm^{-1} , C-Cl stretch, alkyne C-C bend lies between 700-900cm^{-1}, hydroxyl group OH stretch was observed between 4000-3650cm^{-1}, primary amine group NH stretches between 3200-3450cm$^{-1,}$ Aliphatic secondary amine NH stretches between 3150-3200cm-^{1}, Normal polymetric stretch of hydroxyl group lies between 3050-3100cm^{-1},Methylamino acids N-CH, C-H stretches between 2550-2950cm$^{-1,}$ Cyanide ion, thiocyanide ion stretches between 1990-2000cm^{-1} , Isocyanate N=C=O stretches between 2290-2550cm-^{1}, Isothiocynate –CNS bond stretches between 1600-1795cm-^{1}, Conjugated keton, open chain acids anhydrides stretches between 1600-1750cm^{-1}, the bending of the hydroxyl group was further observed at the stretch between 1450-1595cm^{-1}. Fig 3 showed that the entire spectrum had more or less similar broad characteristic absorption bands. All the absorption bands were unresolved indicating that the material constituents had either large particle size or a contained polymeric unit which shows that the volatile matter is still intact. Esterification of the carbonized biomass has better modification with removal of volatile matter thereby creating more pores for oil adsorption as shown in fig 5 indicating that the picks are more resolved than the picks as shown in Fig 3, this further proved that esterification is effective in removing volatile matter and increasing micro pores on the surface of the adsorbents. The change in absorption and frequency in the spectrum peaks shows how the several treatment conditions affect the structure of the biomass .The functional groups indicate that the biomasses are organic compound which are hydrophobic and olephilic. This could be the reasons while they were able to remove the oil from water surface. Upon comparing the spectrum; it was observed that all the samples showed a remarkable absorption near 1440cm^{-1}. This indicated the strong presence of ethylene and methyl groups in the samples. The bands at 1541cm^{-1} and 1442cm^{-1} is normally present in organic substance (biomass) with more Lignin content. The band was shifted from strong absorption to medium intensity in the spectra of stable product. This reveals the effectiveness of modification of biomass using esterification.

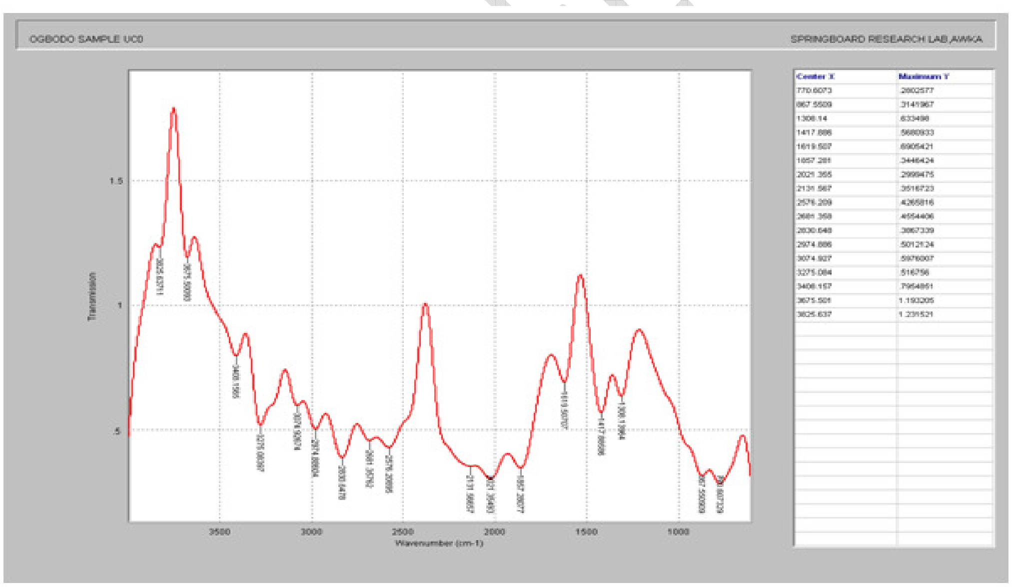

Fig 3: FTIR spectra for uncarbonized ogbono shell

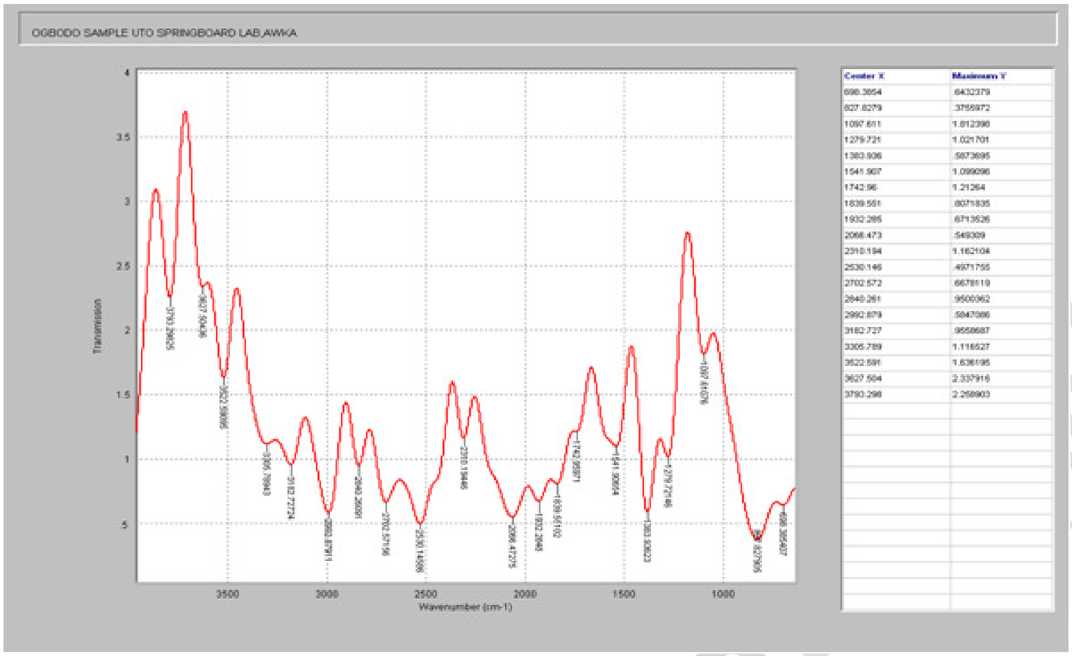

Fig 4: FTIR spectra for carbonized ogbono shell

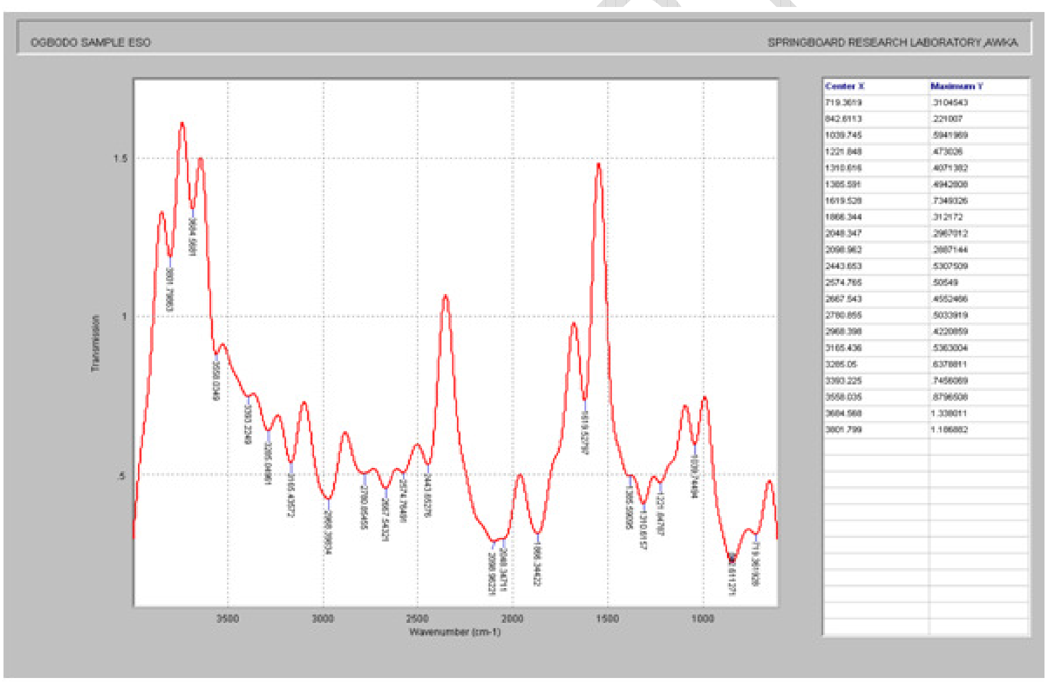

Fig 5: FTIR spectra for esterified ogbono shell

Statistical analysis of the sorption process using RSM

The process was optimized using Box Benkhen Design. This was done to determine the best conditions for optimum sorption of the crude oil. In this work, a set of 27 experiments was performed with the adsorbent (esterified ogbono shell) using a statistical package Minitab software version 17.0. During analysis, it was discovered that the major response in which the main parameters or factors were significant at 0.05 was percentage removed (%R). The optimization analysis was therefore based on percentage removal as the major response. The experiments were performed in random to avoid systematic error. The design matrix and output responses for the sorption of crude oil were given in Table 2. The responses obtained from various runs are significantly exceptional which implies that each of the factors have substantial effect on the response.

Analysis of variance (ANOVA) for the sorption of oil layer onto fatty acid grafted ogbono shell

The response values in Table 2 were analyzed using statistical package Minitab software (Minitab version 17.0). The F-value tests were performed using the ANOVA to calculate the significance of each type of model. Based on the results of F-value, the highest order model with significant terms which shows the most accurate relationship between parameters was be chosen. Besides evaluating the significance, the adequacy of the models was evaluated by applying the lack-of-fit test. This test was used in the numerator in an F-test of the null hypothesis and indicates that a proposed model fits well or not. The test for lack-of-fit compares the variation around the model with pure variation within replicated observations. This test measured the adequacy of the different models based on response surface analysis (Chauhan and Gupta, 2004)). The sum of square, the degree of freedom, the mean square, the F-values were shown in Table 4.

Table 4: Analysis of Variance (ANOVA) for the sorption of oil onto esterified ogbono shell

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	6	1794.50	93.98%	1794.50	299.084	52.08	0.000
Linear	3	630.20	33.01%	630.20	210.065	36.58	0.000
X_1	1	515.09	26.98%	515.09	515.092	89.70	0.000
X_2	1	100.34	5.26%	100.34	100.341	17.47	0.000
X_4	1	14.76	0.77%	14.76	14.763	2.57	0.025
X_4^2	1	347.35	18.19%	347.35	347.346	60.49	0.000
X_1X_2	1	373.65	19.57%	373.65	373.649	65.07	0.000
X_2X_4	1	443.31	23.22%	443.31	443.313	77.20	0.000

Error	20	114.85	6.02%	114.85	5.742		
Lack-of-Fit	18	94.17	4.93%	94.17	5.232	0.51	0.832
Pure Error	2	20.67	1.08%	20.67	10.337		
Total	26	1909.35	100.00%				

R-sq	R-sq(adj)	PRESS	R-sq(pred)
93.98%	92.18%	209.018	91.05%

Multiple regression analysis was employed as a tool in this work to for the assessment of the effect of independent variables (Time, temperature, dosage and pH) on the dependent variables (%Sorption). % Sorption by the activated biomass (esterified ogbono shell) was analyzed using multiple regression method to fit second order polynomial equations. The second order polynomial equations developed after analysis of percentage sorption as a function of the actual values of Time (X_1), temperature (X_2), dosage (X_3) and pH (X_4) are as follows;

$$(\%\text{Sorption})_{\text{esterified ogbono shell}} = 88.36 - 1.0353\, X_1 - 1.1615\, X_2 + 0.77\, X_4 + 0.01289\, X_1X_2 + 0.08773\, X_2X_4 - 0.4511\, X_4^2 \quad (4)$$

Regression coefficients of the intercept, linear, quadratic and interaction terms of each model were presents in Table 4. The coefficient of determination (R^2) obtained for the percentage sorption of oil by esterified ogbono shell was 93.98%. These result shows that more that 93% of the overall system variables can be explained by the quadratic models of equation 4. Higher values of F-ratio and lower p-values indicated higher significance of the model or model terms. The models significance was tested at $p<0.05$.

It was observed that the model p-value was 0.000. This indicates that the model is very significant and could be very efficient in predicting the system response (sorption of oil by activated biomass). The F-values was also observed to be 52.08 for acetylated ogbono shell. This value was found to be very high and as such, show that the model is highly significant above 93% confidence level. Table 4 shows that the linear terms of time (X_1), temperature (X_2) and pH (X_4) as well as interactive terms of time and temperature (X_1X_2), temperature and pH (X_2X_4) together with quadratic term of pH (X_4^2) were all significant with p-values ($p<0.05$). However, the adjusted coefficient of regression (Adj R^2) and the predicted coefficient of regression (Pred R^2) were found to be, 92.18% and 91.05%. These results are indication of the model significance and also indicate that the quadratic model provided an excellent explanation for the relationship between the independent variables and the corresponding response.

The models adequacy was additionally checked from the normal residual plots as shown in Fig 6. It can be seen from the figure that the residual followed the normal distribution and the assumption of normality is somewhat valid. The data were also analyzed to check the correlation between the experimental and predicted sorption (%R). The experimental values were the measured response data for the runs designed by the Box Benkhen model on the platform of Minitab software version 17.0, while the predicted values were obtained by calculation from equation 4. Also, the points were closely distributed to the striaght line of the plot (R^2 = 93.98%). This confirms the good relationship between the experimental values and the predicted values as shown in Table 2. Some small scatter like an “S” shape is always expected which shows a normal distribution of experimental data points within the straight line. These plots equally confirmed that the selected model was adequate in predicting the response variables.

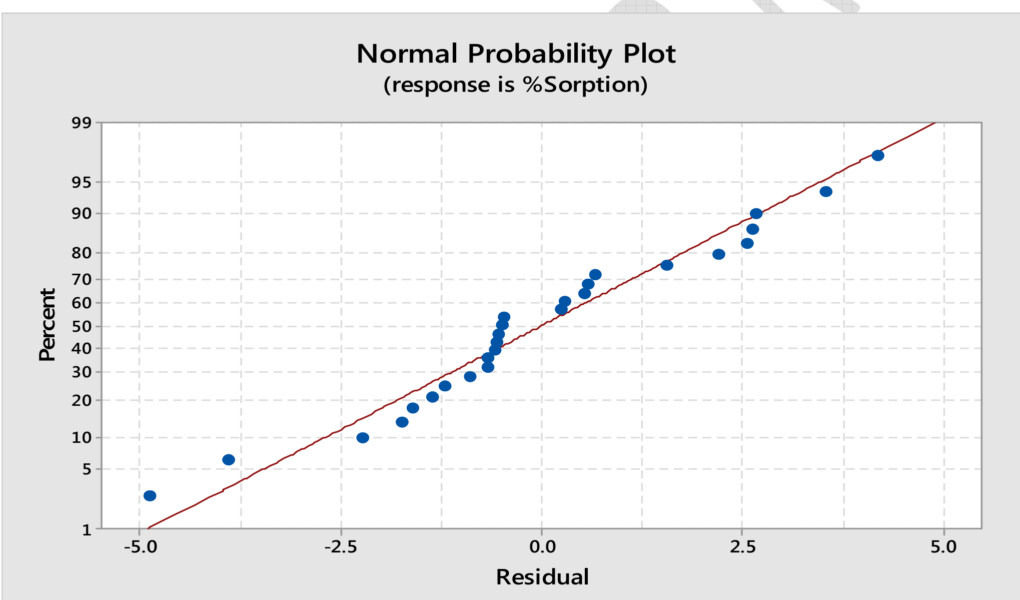

Fig 6: Normal plot of residual for the sorption of oil onto esterified ogbono shell

The Three Dimensional (3-D) response surface plots for crude oil adsorption onto fatty acid grafted ogbono shell.

The 3-D response surface and contour plots are presented in Fig 7 and 8.The 3-D response surface and contour plots are graphical representation of the interactive effects of any two variable factors. Response surface plots as a function of two factors at a time, maintaining all other factors at fixed levels are more helpful in understanding both the main and the interaction effects of these two factors. These plots can be easily obtained by calculating from the model, the values taken by one factor where the second varies with constraint of a given Y value. The response surface curves were plotted to understand the interaction of the variables and to determine the optimum level of each variable for maximum responses.

The nature of the response surface curves shows the interaction between the variables. The elliptical shape of the curve indicates good interaction of the two variables. From figures, it was observed that the elliptical nature of the contour in graphs depicts the interactions of all the variables. There was a relative significant interaction between every two variables, and there was a maximum predicted yield as indicated by the surface confined in the smallest ellipse in the contour diagrams.

Temperature – Time interaction effect

The temperature –time interaction effect was plotted against oil sorption and presented as shown in fig 7. Keeping every other factor constant, it was observed that the contour lines for the effect of temperature and time interactions were somewhat curve and circle indicating a good interaction. The contour lines showed that the interactions are significant. The significant level was proven by the p-values as shown in Table 4 which indicates that the p-values were less than 0.05. It can be concluded that increase in temperature and time, increases the rate of oil sorption by the activated biomass. The interaction of temperature and time (X_1X_2) was included in the model equation 4 for improvement of the model performance since the interactions are significant.

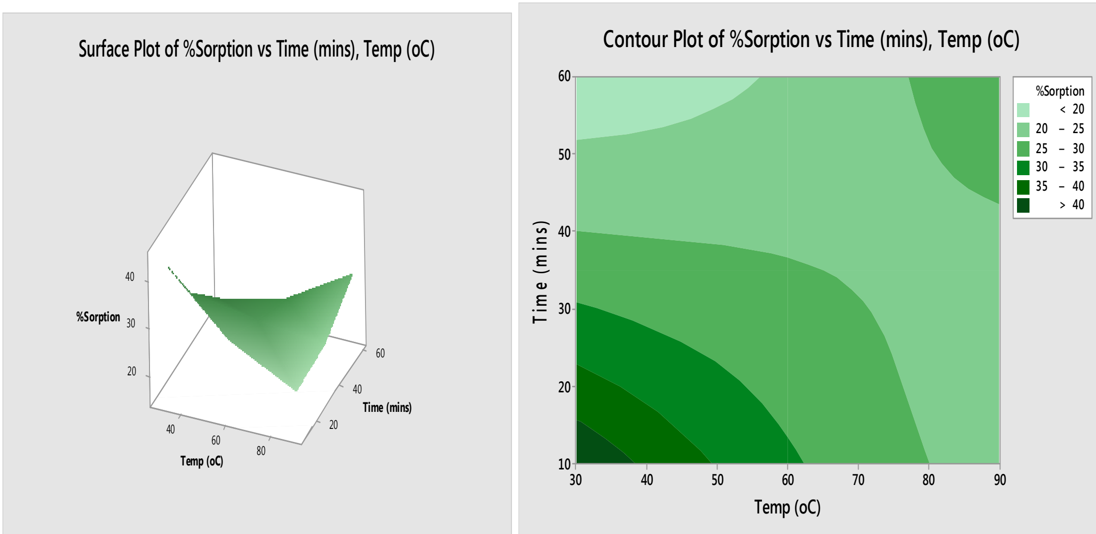

Fig 7 : Response surface and contour plots for the effect of time and temperature on sorption of oil by fatty acid grafted ogbono shell.

pH- Temperaure interaction effect

The pH- temperature effect (X_2X_4) was included in equation 4 to improve the model performance. Fig 8 shows the response surface plot and contour plot for the effect of pH-temperature interaction on the percentage sorption of oil by the activated biomass. From the figure, the shape of the contour is curve showing a good interaction. The 3D plots also showed that almost equal percentage sorption could be obtained at low temperature, low pH; low temperature, high pH, high temperature, low pH; and high temperature, high pH. The height of the 3D seems to be the same at the four edges of the curve. The p-value of the curve is less than 0.05 which indicates that the interaction is statistically significant.

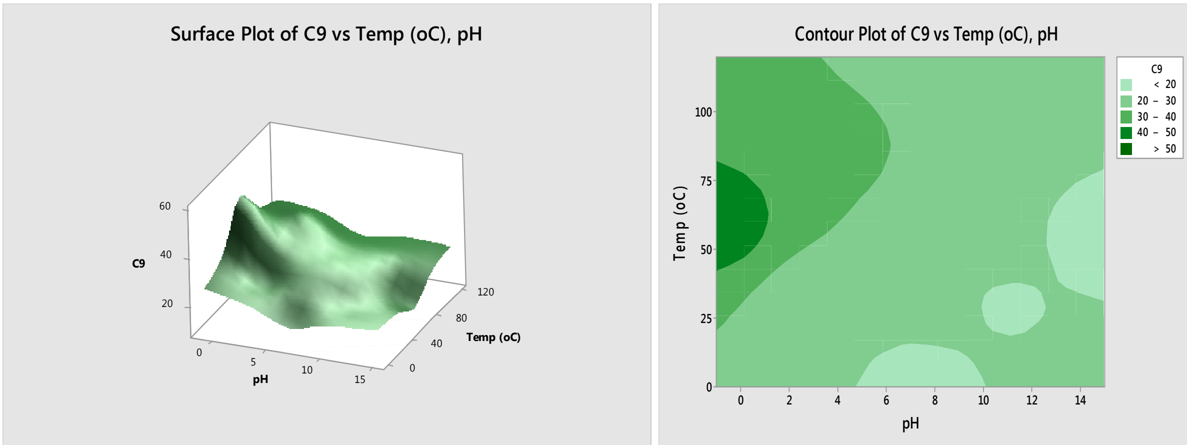

Fig 8: Response surface and contour plots for the effect of pH and temperature on soption of oil by esterified ogbono shell

The numerical optimum conditions

The developed model as shown in equation 4 for the process parameters was optimized using response optimizer facility that is available on Minitab software version 17.0 which provided several numerical optimum solutions. The optimization is also interactive and allows for the compromise among the various independent variables and responses (Yuksel et al., 2006; Yi et al., 2010). The optimum solutions are given in Table 5. the optimum time, temperature, dosage, pH and percentage removal were; time of 10mins, temperature of 60^{o}C, dosage of 1.4g, pH of 3 at the theoretical percentage removal of 78.77%. The theoretical percentage removal was verified by carrying out adsorption process using the optimum parameters. The result of the verified experiment was recorded as the actual percentage removal. The actual percentage removal was in close agreement with the theoretical value as shown in table 5.

Table 5: The theoretical optimum solution using esterified ogbono shell

No.	Time (min)	Temp (°C)	Dosage (g)	Predicted (%R)	Actual (%R)	
1	10.0	60	1.4	78.77	76.40	Selected

Conclusion

Comparative study of data in this research revealed that carbonized ogbono shell modified by esterification process using steric acid can be used as an eco-friendly adsorbent for the maximum removal oil layer from oil polluted water surface. FTIR analysis of activated and uncarbonized biomass (ogbono shell) shows that they consist mainly of organic compounds such as hydroxyl group, amino group, amine, isocyanate, conjugated ketons, silicon, peroxide. Surface morphological analysis of raw and esterified ogbono shell using Scan electron microscope (SEM) revealed that activation of the biomass increased the surface area significantly. Statistical analysis of the sorption of oil onto activated biomass such as (esterified ogbono shell) showed that the process can be modeled by central composite design with all the four variables affecting the process such as .time, temperature, dosage and pH been statistically significant

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