Nigerian Research Journal of Engineering and Environmental Sciences 3(2) 2018 pp. 542-551

Nigerian Research Journal of Engineering and Environmental Sciences
Journal homepage: www.rjees.com

Original Research Article

Response Surface Methodology for the Optimization of Kerosene Desulphurization using Kaolinite Clay

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ARTICLE INFORMATION

Article history:
Received 06 August, 2018
Revised 03 October, 2018
Accepted 04 October, 2018
Available online 30 December, 2018

Keywords:
Sulphur
Kerosene
Desulphurization
Response surface methodology
Central composite design
Kaolinite clay

ABSTRACT

The increasing effect of climate change being experienced worldwide due to high level of sulphur compounds among other pollutants means that existing technology must be improved to isolate sulphur from petroleum products like kerosene. Adsorption is a formidable process that can be applied for kerosene desulphurization. In this study, Response surface methodology *(RSM) was applied through the central composite design (CCD) of experiment in optimizing the operating variables. The process was accomplished by a five level, three-factorial CCD with 20 runs with the operating variables (adsorbent dosage, time and temperature) using Design Expert 7.0.0. A second-order model equation was obtained for kerosene desulphurization as a function of input parameters. The analysis of variance (ANOVA) showed that the adsorbent dosage and adsorption time had a significant effect on the desulphurization process while temperature had a negligible effect. The adj. R^2 (0.9162) and the pred. R^2 (0.7830) showed that the experimental data and model predictions were in agreement. Optimization using the numerical approach gave the optimum value of 47.97% for kerosene fuel desulphurization at 0.1 g adsorbent dose, 290 minutes adsorption time and a temperature of 30.04 °C. The adsorbent can be successfully employed in the petroleum industry to reduce the sulphur level of kerosene.*

1. INTRODUCTION

The combustion of sulphur compounds are not only causing corrosion but also contributing considerably to acid rains and air pollution, deforestation, smog, and global warming, as well as several human health concerns such as cardiovascular disease, cancer, creation of asthmatic symptoms and other respiratory diseases (Adeyi *et al*., 2015). The simplest way to decrease the amount of sulphur dioxide (SO_2) emitted into the air is to reduce the amount of sulphur in fuel (Adeyi *et al*., 2015). Keeping in view the hazardous effects

of the sulphur in petroleum and regulations on fuel specifications over the years becoming increasingly stringent with respect to sulphur content, much attention has been paid to desulphurization in recent years (Shakirullah *et al.,* 2010; Javadlit and De Klerk, 2012).

Conventionally, hydrodesulphurization (HDS) is the only method used for desulphurization of petroleum products (Javadlit and De Klerk, 2012). It is however an expensive process in terms of utilizing expensive operating conditions (Ahmad *et al.,* 2014). Alternative desulphurization pathways are therefore of interest. Among different methods such as adsorption process, extractive desulphurization, oxidative desulphurization and bio-desulphurization of petroleum products, adsorption process is acceptable due to low cost, easy regeneration and operation (Gawande and Kaware 2014). In most research works, the process conditions have been merely optimized by conducting one factor-at-a-time experiments. However, the results of one-factor-at-a-time experiments do not reflect actual changes in the environment as they ignore interactions between factors that are present simultaneously. Therefore, these factors may be collectively studied to validate the optimal adsorption conditions (Giwa *et al*., 2015).

RSM has been discovered to be an effective statistical method of optimizing a process using designs such as central composite design (CCD), Box-Behnken design and D-optimal design. Apart from giving the optimum conditions with minimal number of experiments compared to the conventional method (one factor at a time), RSM gives the mathematical expression(s) showing the relationship(s) between the response(s) and the factors. It also gives a better understanding of the process, and helps the process engineer to see the effect of the control variables and the interactions among all the variables (Hashim *et al.*, 2014; Braimah *et al.,* 2016). Among the limited reports on desulphurization of kerosene via adsorption is the report by Ahmad *et al.* (2013) who conducted one-factor-at-a time method of experiment using Zn- impregnated montmorollonite clay (MMT) to obtain 76% desulphurization of kerosene. Oti and Eze (2017) reported a one-factor-at-a time method of adsorptive desulphurization without optimization using activated carbon prepared from locally sourced hardwood, and the sulphur content in dual purpose kerosene (DPK) was reduce from 1.502 to 1.317 wt %. The sulphur depletion was 0.185 wt % which was equivalent to 12.32 % desulphurization.

This research work adopted a CCD coupled with RSM to optimize the desulphurization of kerosene fuel using kaolinite clay. Analysis of the experimental data using statistical indices and the analyzed experimental data were optimized using numerical approach of response surface methodology with the aid of Design Expert 7.0.0.

2. MATERIALS AND METHODS

2.1. Materials

Pretreated and Beneficiated Kaolinite clay were obtained from Alkaleri Local Government Area, Bauchi State, Nigeria (Aroke *et al.,* 2013). Kerosene was collected locally from Kaduna Refinery and Petrochemical Company, Kaduna, Nigeria.

2.2. Methods

2.2.1. Design of experiment

Three parameters were selected for kerosene fuel: the adsorbent dose, contact time and the temperature. Low and high-level values of factors are as shown in Table 1. Before optimization, it was first necessary to choose an experimental design that would define which experiment should be carried out in the experimental region being studied. An RSM design type, CCD was the most suitable choice for this research work due to its suitability in fitting quadratic surfaces which usually works well for process optimization. Thus, a design of

20 experiments was generated for kerosene fuel desulphurization in which three factors were selected. This design comprised of eight experimental runs for factorial (2^3) points, six replicates at the central points, and six star points.

Table 1: Low and high-level values of factors

Factors	Units	Low level	high level
Time	Minutes	60	300
Adsorbent dose	g	0.5	2.0
Temperature	^oC	30	45

2.2.2. Desulphurization experiment of kerosene fuel

Batch adsorptive desulphurization experiments were performed according to the design of experiments in Table 2 for kerosene fuel using Kaolinite clay. The kerosene fuel (20 ml) was stirred separately at 120 rpm using 100 ml flask on a magnetic stirrer (HU-2) according to the design of experiments. Continuous mixing was provided during the experiments by agitating at constant speed (120 rpm) for better mass transfer with high interfacial area contact. The contact times for the experiments were between 60 and 300 minutes, and the adsorbent doses were between 0.5 and 2g. The sulphur content in each sample after adsorption at different time was determined with the aid of X-Ray Fluorescence Spectrophotometer (SLFA-60) using ASTM (D-2622) method. This was done by placing the filtered sample in an X-ray beam and intensity of the sulphur X-ray fluorescence was measured. The kerosene fuel was analyzed for physicochemical properties according to ASTM standard methods (Adeyi *et al.*, 2015). The percentage sulphur removal (desulphurization) was estimated using Equation 1.

$$\% \text{ Desulphurization} = \frac{(C_o - C_t) \times 100}{C_o} \quad (1)$$

Where C_o and C_t are the initial and final concentration in mg/ L

2.2.3. Statistical analysis and optimization

The design and analysis of the experimental data were done using Design-Expert 7.0.0. The experimental results were fitted to quadratic polynomial model as given by Equation (2) and the regression coefficients were obtained.

$$Y = \beta_o + \sum_{i=1}^{3} \beta_i x_i \sum_{i,j=1}^{3} \beta_{ij} x_{ij} + \sum_{i=1}^{3} \beta_{ii} x_i^2 \quad (2)$$

Where;β_o ,β_i, β_{ii} and β_{ij} are the regression coefficients for intercept, linear, interaction and square terms respectively. Y is the response and *x* is the independent variable. The statistical significances of the models were evaluated using the results of analysis of variance (Khuri and Mukhopadhyay, 2010; Giwa *et al.*, 2015).

Using the quadratic polynomial model, a numerical optimization was carried out and the optimum conditions of the three factors investigated for the desulphurization were obtained. The goals for the factors were in a range while that of the response was “maximize”.

Table 2: Central composite design lay out for kerosene fuel desulphurization

Run	Adsorbent Dose (g)	Time (min)	Temperature (°C)	% sulphur removal		
				Experimental	Predicted	Residual
1	0.80	108.65	33.04			
2	1.25	180.00	37.50			
3	1.70	251.35	41.96			
4	1.25	180.00	45.00			
5	1.70	251.35	33.04			
6	1.70	108.65	33.04			
7	1.25	180.00	37.50			
8	1.70	108.65	41.96			
9	1.25	180.00	37.50			
10	1.25	300.00	37.50			
11	1.25	60.00	37.50			
12	0.50	180.00	37.50			
13	2.00	180.00	37.50			
14	0.80	108.65	41.96			
15	1.25	180.00	37.50			
16	1.25	180.00	37.50			
17	1.25	180.00	37.50			
18	0.80	251.35	41.96			
19	1.25	180.00	30.00			
20	0.80	251.35	33.04			

3. RESULTS AND DISCUSSION

The main physical properties of the kerosene fuel are shown in Table 3. All these tests were conducted at ambient temperature (33°C). The physical properties show sulphur content of kerosene to be 0.0291wt% which is above the set allowable standard by Standard Organization of Nigeria. All other properties are within the ASTM standard limits.

Table 3: Physico-chemical Properties of kerosene fuel and specifications of international standard

Properties	Before	After	*Standard limits	*Method used
Specific gravity(kg/l)	0.7845	0.7847	0.78 - 0.82	D-287
API gravity	48.87	48.82	41.06 - 49.9	D-4052
Viscosity (cSt) @ 40°C	2.607	2.642	2.710	D-445
Flash point (°C)	43	43	37 – 65	D-93
Total Sulphur (wt %)	0.0291	0.0169	0.015	D-2622

*ASTM (Rick 2017)

3.1. Effects of Operating Conditions on Kerosene Fuel Desulphurization

The CCD standardization of process variables involved in kerosene fuel desulphurization was carried out in accordance with the design layout result presented in Table 4. Twenty (20) experimental runs were conducted. Between the experimental and predicted responses, low residual errors were recorded which ranged between 0.1-1.90%. Thus, the agreement proved the reliability of the model for predicting response.

Table 4: Central Composite Design responses for kerosene fuel desulphurization

Run	Adsorbent Dose (g)	Time (min)	Temperature (°C)	% sulphur removal		
				Experimental	Predicted	Residual
1	1.70	108.65	33.04	30.32	29.10	1.22
2	1.25	180.00	37.50	29.12	29.88	0.76
3	0.50	180.00	37.50	24.92	23.32	1.60
4	0.80	251.35	41.96	25.70	27.49	1.79
5	1.70	251.35	41.96	41.67	41.48	0.10
6	2.00	180.00	37.50	38.46	39.25	0.70
7	0.80	251.35	33.04	31.04	30.94	0.06
8	1.25	180.00	37.50	30.13	29.88	0.25
9	0.80	108.65	41.96	24.83	25.53	0.70
10	1.70	251.35	33.04	38.46	38.33	0.13
11	1.25	180.00	37.50	32.33	29.88	2.45
12	1.25	180.00	45.00	33.21	31.72	1.49
13	1.25	60.00	37.50	29.44	29.17	0.27
14	1.25	180.00	37.50	30.12	29.88	0.24
15	1.25	180.00	30.00	27.22	27.00	0.68
16	1.25	300.00	37.50	39.12	38.58	0.54
17	1.70	108.65	41.96	36.43	37.10	0.67
18	0.80	108.65	33.04	23.37	24.14	0.77
19	1.25	180.00	37.50	27.98	29.88	1.90
20	1.25	180.00	37.50	29.45	29.88	0.43

3.2. Experimental Data Fitting and Analysis of Variance (ANOVA) of Kerosene Fuel Desulphurization

In order to find the mathematical relationship between the selected factors and response of the desulphurization, the actual data presented in Table 4 were fitted to a quadratic regression model. The model in actual factors obtained is as given by Equation 3 and the ANOVA results are given in Table 5.

$$\%\ \text{Sulphur removal} = +28.62037 - 30.16061A + 0.058418B - 5.04633Exp - 003C + 0.019013AB + 0.82967AC - 3.81052Exp - 003BC + 2.50033A^2 + 2.77530Exp - 004B^2 - 1.21891E - 003C^2 \quad (3)$$

Where the actual factors A, B and C represents adsorbent dose (g), time (min.) and temperature (°C) respectively. It can be observed from the model equation that the linear terms B, the interactive terms AB and AC and the quadratic term A^2 and B^2 are positive which denote significant contribution in sulphur removal while the linear term A and C, the interactive term BC and quadratic term, C^2 are negative which denote an antagonistic contribution in sulphur removal. The effect of the variables such as linear, quadratic or interaction coefficients on the response were tested for significance by ANOVA as shown in Table 5. It was observed that the variables with most significant effect on the kerosene desulphurization were the linear terms of adsorbent dose A ($p<0.0001$) time B ($p<0.0001$) and temperature (0.0199), followed by the interaction term of AC (0.0117) and BC (0.0474). The least significant term that has minimal contribution in kerosene fuel desulphurization is the quadratic term C^2 (0.9528).

Table 6 gives the lack of fit test with a quadratic model having probability value (p-value) of 0.4250. The estimated coefficients of regression model are given in Table7, and the large value of the coefficient of determination (R^2 =0.9559) indicates good fitness of the results. The R^2 should be at least 0.80 for a good fit of a model. The high adjusted and predicted R^2 values of 0.9162 and 0.7830 respectively revealed that the model adequately represents the experimental results as both are in a reasonable agreement and the adequate precision of the model was 16.927, indicating that adequate signals for the model can be used to steer the design space (Bashir *et al.*, 2010).

Numerical optimization results revealed that 0.1g/ml, 290 minutes and 30.04ºC were the optimum conditions for the kerosene desulphurization. Under these conditions, 47.97% optimum desulphurization was obtained.

Table 5: Analysis of Variance (ANOVA) for kerosene fuel desulphurization

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	498.76	9	55.42	24.07	< 0.0001	Significant
A-Adsorbent dose	306.63	1	306.63	133.17	< 0.0001	
B-Time	106.85	1	106.85	46.40	< 0.0001	
C-Temp.	17.62	1	17.62	7.65	0.0199	
AB	2.93	1	2.93	1.27	0.2858	
AC	21.78	1	21.78	9.46	0.0117	
BC	11.76	1	11.76	5.11	0.0474	
A^2	3.56	1	3.56	1.55	0.2419	
B^2	28.77	1	28.77	12.50	0.0054	
C^2	0.01	1	0.01	0.00	0.9528	
Residual	23.03	10	2.30			
Lack of Fit	12.53	5	2.51	1.19	0.4250	not significant
Pure Error	10.49	5	2.10			
Cor Total	521.79	19				

Table 6: Lack of fit tests for kerosene fuel desulphurization

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Linear	80.20	11	7.29	3.47	0.0900	
2FI	43.73	8	5.47	2.61	0.1532	
Quadratic	12.53	5	2.51	1.19	0.4250	Suggested
Cubic	1.65	1	1.65	0.78	0.4163	Aliased
Pure Error	10.49	5	2.10			

Table 7: Model summary statistics for kerosene fuel desulphurization

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	2.38	0.8262	0.7936	0.7080	152.38	
2FI	2.04	0.8961	0.8481	0.7649	122.69	
Quadratic	1.52	0.9559	0.9162	0.7830	113.23	Suggested
Cubic	1.42	0.9767	0.9263	0.2755	378.05	Aliased

3.3. Response Surface Plots for Kerosene Fuel Desulphurization

The predicted versus actual, normal probability plots and 3D surface response plot were used in this section to describe the trend in kerosene fuel desulphurization responses.

3.3.1. Relationship between predicted and actual response for kerosene fuel desulphurization

Diagnostic plot such as the predicted versus actual response plot (Figure 1) helps to detect a value or group of values that are not easily predicted by the model. It can be noted from this plot that the data points split evenly by the 45 degree line, an indication of an adequate agreement between experimental data and the ones obtained from the model, hence no transformation was required to improve the model.

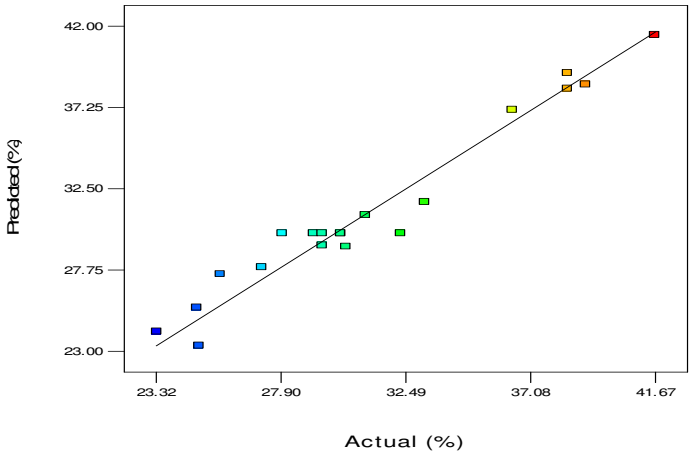
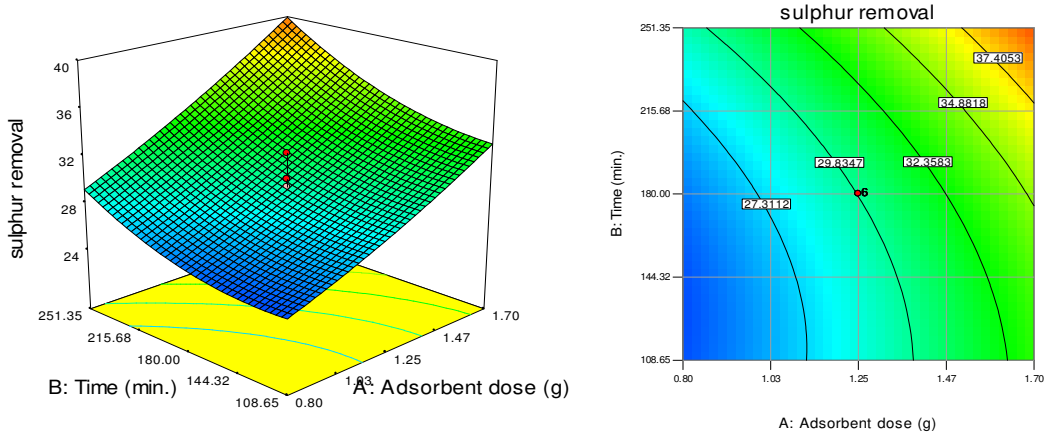


Figure 1: Predicted versus Actual response plot of kerosene fuel desulphurization

3.3.2. Interaction between adsorbent dose and time on kerosene fuel desulphurization

Figure 2 represents a contour plot and a 3D response surface plot of the interaction between adsorbent dose and time. At a fixed temperature of 37.50 ^{o}C, the sulphur removal increased from 23.37% to 41.67% as the time increased from 108 min to 251 minutes. The increase in the contact time of the adsorbent has resulted in an increase in the sulphur uptake, with a corresponding increase in adsorbent dose from 0.80g to 1.70g. This was found to be due to the availability of large surface area of the adsorbent for the adsorption of sulphur.

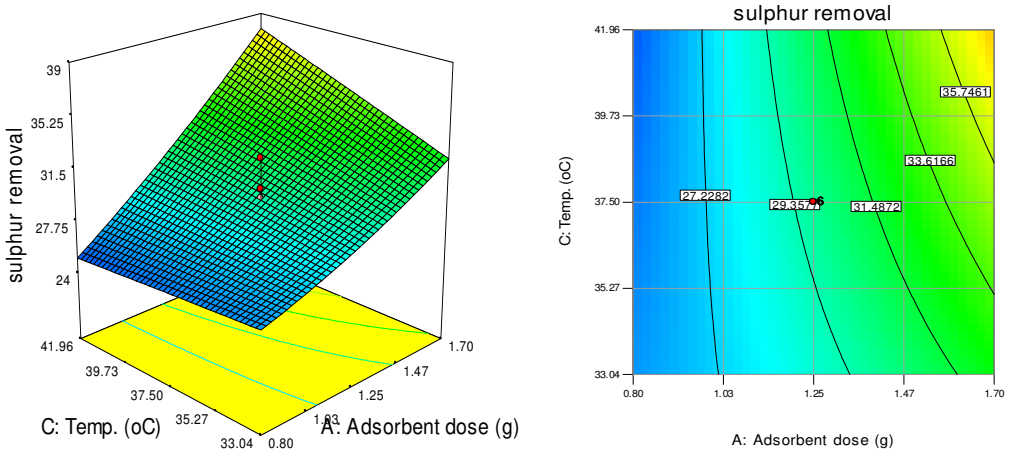


(a) (b)

Figure 2: Kerosene fuel desulphurization (a) 3D surface response plot and (b) contour plot

3.3.3. Interaction between adsorbent dose and temperature for kerosene desulphurization

Figure 3 represents a contour plot and a 3D surface response plot interaction between adsorbent dose and temperature. At a fixed time of 180.00 min, the kerosene fuel desulphurization increased from 23.37% to 41.67% as the adsorbent dose increased from 0.80g to 1.70g with an increase in temperature from 30.04 ^{o}C to 41.96 ^{o}C. It can be observed that sulphur removal is significantly dependent on the amount of adsorbent and time and less significant with regards to temperature.

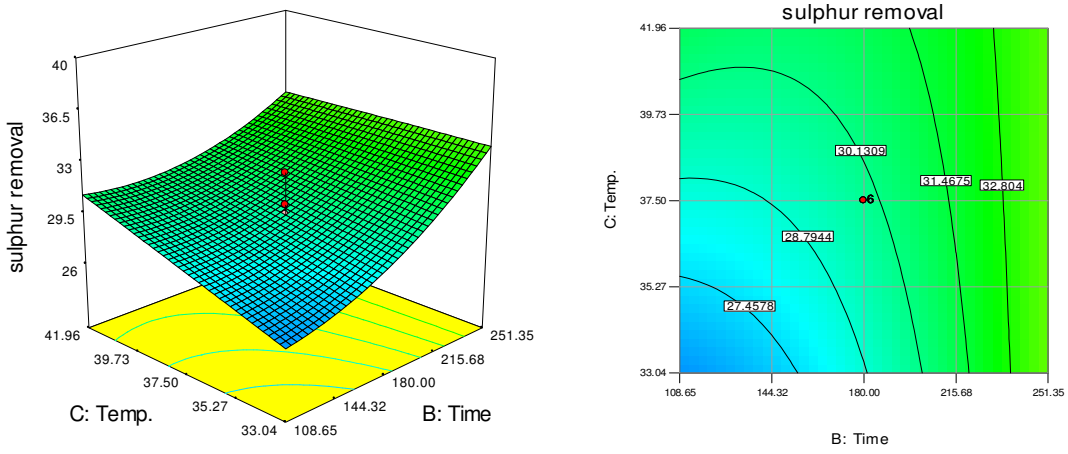


(a) (b)

Figure 3: Kerosene fuel desulphurization (a) 3D surface response plot and (b) contour plot

3.3.4 Interaction between time and temperature for kerosene fuel desulphurization

Figure 4 represents a contour plot and a 3D surface response interaction between time and temperature at a fixed adsorbent dose of 1.25g. The sulphur removal increase from 23.37% to 41.67%, as the time increase from 108 min to 251 min with an increase in temperature from 30.04 ^{o}C to 41.96 ^{o}C. The sulphur removal increases with an increase as there was enough contact time for the kerosene and the adsorbent however the temperature range was negligible to have any significant effect of the desulphurization.



(a) (b)

Figure 4: Kerosene fuel desulphurization (a) 3D surface response plot and (b) contour plot

3.3.5. Normal probability of residuals for kerosene fuel desulphurization

The normal probability plot of residuals for kerosene fuel desulphurization as presented in Figure 5 shows that the model is a good estimation of the dependent variable. The residuals (errors) are normally and independently distributed since the residuals plots are approximately along a straight line, and this is a good test for significance of regression.

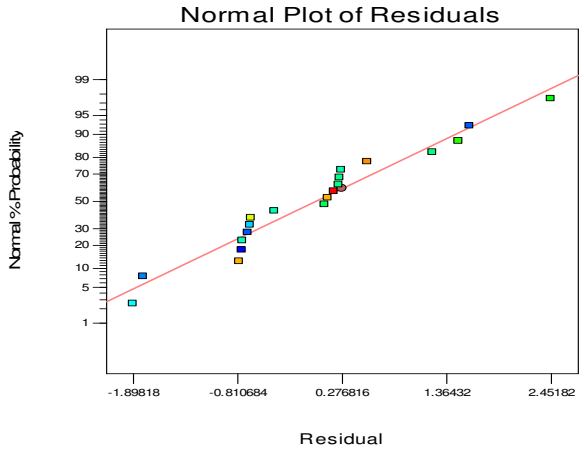


Figure 5: Normal probability plot of residuals for kerosene fuel desulphurization

4. CONCLUSIONS

The following conclusion can be drawn from the study:

i. The characterized kerosene fuel physico-chemical properties before and after desulphurization were found to be within the ASTM, however the sulphur level only met the Standard set by Standard Organization of Nigeria (SON).
ii. From the responses obtained, the central composite design of response surface methodology has been successfully applied to the desulphurization process used for the removal of sulphur from kerosene fuel.
iii. Checking the validity of the models, various relevant statistical indexes, such as F-value, coefficient of correlation (R^2), Adj-R^2 and lack of fit were determined to be statistically adequate.
iv. Numerical approach was used to obtain 47.97% as the optimum desulphurization value for kerosene fuel at the optimum process variables of 0.1g adsorbent dose, 290 minutes adsorption time and at the temperature of 30.04^{o}C.

5. ACKNOWLEDGMENT

The authors wish to acknowledge the assistance and contributions of the laboratory staff of KRPC, Kaduna, Kaduna State

6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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