1	Original Research Article
2	
3	Application of Response Surface Methodology in Phenol
4	red Adsorption Using Kola nut (Cola acuminata) Shell
5	Activated Carbon
6	
7	Abstract:
8	The application of response surface methodology in phenol red adsorption using kola nut
9	shell activated carbon was studied. Chemical method of activation using zinc chloride
10	(ZnCl <sub>2</sub> ) was used to prepare the carbon. The impregnated samples were kept in an oven at
11	$110^{0}$ C for 24 hours. The dried samples were carbonized in muffle furnace for 1 hour at
12	500°C. Some physical properties of the carbons such as surface area, pH, moisture content,
13	ash content, bulk density were determined. Both the activated and non-activated carbons were
14	characterized using the Fourier Transform Infrared (FTIR) spectroscopy to determine the
15	functional groups and Scanning Electron Microscopy (SEM) to examine the surface
16	morphology of the carbon. Preliminary adsorption studies were carried out to determine the
17	significance of the parameters in adsorption process. The parameters shown to be more
18	significant were adsorbent dosage and initial ion concentration. The adsorption process was
19	optimized using the Central Composite Design (CCD) for three factors and the optimization
20	results were analyzed using Design Expert 8.1.0 trial version. The optimum conditions for

the adsorption of the dye were 30<sup>o</sup>C, 60 minutes, 0.30g of adsorbent, initial ion concentration of 300 mg/l and pH 10 which resulted in 89.95% removal of phenol red. Quadratic polynomial model was developed by the Design Expert used for the process parametric study to achieve optimal performance. The model predicted was in close agreement with the experimental result confirming the suitability of the proposed quadratic model. The study showed that CCD can conveniently be used for the optimization of phenol red adsorption using kola nut shell activated carbon.

<u>Keywords</u>: Adsorption, Phenol red, Optimization, Response surface, CCD, Kola nut,
 Activated carbon, Adsorbent, Adsorbate, Charcterization

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#### 32 **1.0 INTRODUCTION**

The over-dependence of local industries on imported raw materials is currently the bane of economy of developing countries. Thus the search and exploitation of a close substitute to such raw materials is attracting global attention. Nigeria is one of the gifted and endowed Nations with many mineral resources and economic trees, ranging from; crude oil, palm oil, palm kernel shell, coal, clay, rubber, kola nuts etc. Some of these natural mineral materials are exported, while some at times are refined for the purpose of foreign exchange.

Following the level of environmental pollution and recent moves by Federal Government towards industrialization and use of indigenous raw materials, hence the need to study the optimization of basic dye, Phenol red, used by the local industries, using cost effective adsorbent, kola-nut shell activated carbon (KNS-AC), obtained from kola nut shell (KNS).

43 The release of large quantity of dyes into water bodies by textile industries poses serious 44 environmental problems due to the persistent and recalcitrant nature of some of these dyes. According to one estimate over 7 x  $10^5$  tonnes and approximately 10,000 different types of 45 46 dyes and pigments are produced worldwide annually [1]. Untreated or partially treated 47 effluents from other industries namely, paper, plastics, leather, cosmetics, food, woolen, etc 48 also contribute to the pollution load. The colouration of the water by the presence of dyes, even 49 in small concentrations, is easily detectable [2] and many of these dyes have an inhibitory 50 effect on the process of photosynthesis and thus affecting the land flora and the aquatic 51 ecosystem. The anaerobic break down of some dyes in the sediments and / or their incomplete 52 bacterial degradation often produces toxic amines [3].

53 Thus the removal of dyes from coloured effluents, particularly from textile industries, is one of 54 the major environmental concerns these days [4]. Many physical and chemical treatment 55 methods including adsorption, coagulation, precipitation, filtration, electrodialysis, membrane 56 separation and oxidation have been used for the treatment of dye- containing effluents [5]. The 57 problems that have been associated with most of the above methods include high cost, low 58 efficiency, generation of toxic products and inability to regenerate the starting materials [6]. 59 Owing to these problems, emphasis has now been shifted to the use of adsorption for the 60 removal of wastewater pollutants, which is now one of the efficient techniques [7].

Adsorption is the process that involves the transfer of a mass of a fluid (adsorbate) to the surface of an adsorbing solid (adsorbent). The adsorption process has an edge over the other methods due to its sludge free clean operation and complete removal of dyes even from dilute solutions. Activated carbon is the most widely used adsorbent for this purpose because of its extended surface area, microporous structure, high adsorption capacity and high degree of
surface reactivity [8]. Some materials that have been used as activated carbon include rice husk
[8], chitin [9], Saw dust [10], Barley straw and its Ash [11], fluted pumpkin [12], Sveta Sariva
plant root [13] etc.

But considering the high cost of importing activated carbon and also that a substantial fraction of the activated carbon is lost during each regeneration cycle [14], there is now increase in researches that have been directed towards investigating the adsorption potentials and characteristics of cheaper, effective and efficient adsorbents from natural solid waste materials. Recently, special attention has been focused on the use of low cost adsorbents mainly from agricultural waste products such as palm kernel shell, kolanut shell etc. as an alternative to replace the conventional adsorbents [8].

Response surface methodology (RSM) is a collection of statistical and mathematical techniques used for developing, improving and optimizing processes [15]. Though there are different forms of RSM, central composite design (CCD) has been shown to be the standard form of RSM [16]. Hence, this study was aimed at optimizing the adsorption of phenol red on KNS-AC using CCD.

### 81 2.0 MATERIALS AND METHODS

#### 82 **2.1 Adsorbent**

83 The kola nut shells were obtained from Ekiti State Nigeria. The kola nut shells were reduced 84 into small pieces and dried in sunlight to reduce the moisture content. The dried sample was 85 mixed with ZnCl<sub>2</sub> in the ratio 1:1 and kept in oven at 383K for 24 hours. The sample was 86 washed many times with deionised water and leached with warm water to remove any trace 87 of metal present in the sample. The sample was weighed in crucibles and placed in a furnace 88 at 773K for one hour to undergo the carbonization process. The purpose of this carbonization 89 process was to remove excess of the volatile matters. After cooling, it was ground using 90 mortar and pistil and then, sieved to particle size of 75µm and kept in air tight container for 91 further use. The process flow diagram for the production activated carbon is shown on Figure 92 1.

93 The flow diagram:





Figure 1. Process flow sheet for the activated carbon production.

## 120 **2.2 Adsorbate**

121 The phenol red used in this work was procured from Onitsha main market, Nigeria. 0.1 gram 122 of the dye was accurately weighed and made up to 1000ml of distilled water. The structure of 123 the phenol red is shown in Figure 2. The chemicals used in this work were of analytical 124 grades.



132 Figure 2. Molecular structure of phenol red.

### 133 **2.3 Physical Properties and Characterization**

134 The physical properties of the kola nut shell before and after activation were determined

using standard methods. The ash content and moisture content were determined using ASTM

136 D 28866-70 [17] and ASTMD 2867-70 [18] respectively. The pH was determined using

137 standard test of ASTM D 3838-80 [19]. The surface area was determined using the Sears

138 method [20, 21]. The carbon was characterized using Scanning Electron Microscopy (SEM)

and Fourier Transform Infrared (FTIR) to examine the surface morphology of the carbon and

to determine the functional groups present in the carbon respectively.

### 141 2.4 Preliminary Adsorption Study

The preliminary adsorption study for the determination of significance of the various parameters was carried out on the following factors, pH, contact time, amount of adsorbent and concentration of adsorbate. The plan of the experiment using the Graeco-Latin Square is shown in Table 1.

- 146 1. pH (2, 4, 6, 8)
- 147 2. Contact time -(10, 20, 30, 60 mins)
- 148 3. Amount of adsorbent -(0.1, 0.2, 0.3, 0.4g)
- 149 4. Concentration of dye bath -(50, 100, 150, 200 mg/L)
- 150 **Plan of Experiment** (Graeco Latin Square)
- 151  $X_1 = \text{Contact time} (T_1, T_2, T_3, T_4)$
- **152**  $X_2$  = Adsorbent dosage (d<sub>1</sub>, d<sub>2</sub>, d<sub>3</sub>, d<sub>4</sub>)
- 153  $X_3$  = Initial concentration  $(\alpha, \beta, \gamma, \delta)$
- 154  $X_4 = pH (A, B, C, D)$

155 Table 1: Graeco – Latin square plan (4 factors with equal levels).

X1	T <sub>1</sub>	T <sub>2</sub>	<b>T</b> <sub>3</sub>	<b>T</b> 4
X <sub>2</sub>				
<b>d</b> <sub>1</sub>	Αα	Ββ	С γ	Dδ
d <sub>2</sub>	Ββ	C γ	Dδ	Αα
d <sub>3</sub>	С γ	Dδ	Αα	Ββ
$d_4$	Dδ	Αα	Ββ	С γ

Table 1 means the number of experiments with each block representing the experimental conditions.

### 158 **2.5 The Batch Adsorption Studies**

The dye solution was prepared by dissolving 0.1g of the dye in 1000ml of distilled water to get a solution of 100mg/l. After the adsorption, the solution was allowed to settle and the absorbance measured at its wavelength. The amount of equilibrium adsorption, qe (mg/g) was calculated as given in equation 1.

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$$q = \frac{(C_o - C_e)V}{m} \tag{1}$$

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Where,  $C_o$  and  $C_e$  (mg/l) are the liquid–phase concentrations of dye at initial and equilibrium respectively.

168 V is the volume of the solution (L) and

169 m is the mass of active carbon used (g).

### 170 **2.5 Optimization using Central Composite Design (CCD)**

The CCD was used to study the effects of the variables towards their responses and 171 subsequently in the optimization studies. This method is suitable for fitting a quadratic 172 173 surface and it helps to optimize the effective parameters with a minimum number of 174 experiments, as well as to analyze the interaction between the parameters [16]. The effects of 175 pH, adsorbent dosage and initial ion concentration on the percentage removal of Orange G 176 were conducted based on the CCD design. The range and levels of individual variables are 177 given in Table 2. The central composite design for the adsorption is shown in Table 3. The 178 regression analysis was performed to estimate the response function as a second order 179 polynomial. A statistical program package, Design Expert 8.7.0.1 version was used for 180 regression analysis of the data obtained and to estimate the coefficient of the regression 181 equation. The significance of each term in the equation is to estimate the goodness of fit in

each case. Response surfaces were drawn to determine the individual and interactive effectsof the test variable on the percentage removal of phenol red.

- 184 The high (+) and low (-) values for phenol red adsorption are dosage (0.2 and 0.4 g),
- 185 concentration (200 and 400 mg/l) and pH (4.0 and 8.0). The alpha ( $\alpha$ ) value used was 1.414.
- 186

187 **Table 2.** Factor levels of independent variables for phenol red adsorption on KNS –AC.

Independent	+α	Low level	Medium level	High level	+α
Factors		(-)	(0)	(+)	
Dosage,g	0.1	0.2	0.3	0.4	0.5
Concentration,mg/l	100	200	300	400	500
рН	2	4	6	8	10

**Table 3.** Central Composite Design for adsorption of phenol red on KNS -AC (real values).

Run	Dosage (g)	Concentration	рН
		( <b>mg/l</b> )	
1	0.2	200	4
2	0.4	200	4
3	0.2	400	4
4	0.4	400	4
5	0.2	200	8
6	0.4	200	8
7	0.2	400	8
8	0.4	400	8
9	0.1	300	6
10	0.5	300	6
11	0.3	100	6
12	0.3	500	6
13	0.3	300	2
14	0.3	300	10
15	0.3	300	6
16	0.3	300	6
17	0.3	300	6
18	0.3	300	6

19	0.3	300	6
20	0.3	300	6

#### **3.0 RESULT AND DISCUSSION**

#### 191 **3.1 Proximate Analysis the Activated Carbon**

Some of the physical properties of the activated carbon were determined using standard methods. The ash content and moisture content were determined using ASTM D 28866-70 and ASTMD 2867-70 respectively. The pH was determined using standard test of ASTM D 3838-80. The surface areas were determined using the sears method [20], [21]. The result of the physical properties of the unactivated kola nut shell (UKNS) and KNS-AC is shown in Table 4.

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Table 4: Physical properties of the UKNS and KNS-AC.

Property	UKNS	KNS-AC
Surface area (m <sup>2</sup> g <sup>-1</sup> )	279	570.2
рН	7.4	7.3
Moisture content (%)	5.8	0.31
Ash content (%)	6.7	2.4
Bulk density(gcm <sup>-3</sup> )	0.32	0.34

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#### 201 **3.2** Adsorbent characterization using SEM.

202 Plate 1 and 2 show the morphological characteristics of UKNS and KNS -AC. The large 203 pores of different shapes could be observed for the  $ZnCl_2$  activated carbon. This may be 204 because the activating agent promotes the contact area between the carbon and the activating 205 agent, and therefore, increases the surface area and porosity of carbon. The mechanism for 206 zinc chloride activation tends to produce a well developed porosity besides high carbon yield, 207 since zinc chloride degrades the cellulose, hemicelluloses and lignin. According to the 208 micrograph, it seems that the cavities on the surfaces resulted from the evaporation of the 209 activating agent during carbonization, leaving the space previously occupied by the activating 210 agent [22].



Plate 1. SEM analysis of UKNS at 75µm particle size



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**Plate 2.** SEM analysis of KNS -AC at 75µm particle size (Mag.= 5000x)

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### 218 **3.3 Adsorbent characterization using FTIR.**

The chemical structure of the adsorbent is of vital importance in understanding the adsorption process. The FTIR technique is an important tool for identifying the characteristic functional groups, which are instrumental in adsorption of organic compounds [23]. The FTIR spectra of the carbon before and after activation were used to determine the vibrational frequency changes in the functional groups present in the adsorbent.

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UKNS: The peaks between 3117.2 and 3953.7 cm<sup>-1</sup> shown in Figure 3, indicate the presence of free hydroxyl groups; C-H stretching vibration around 2007.7 to 2940.5 cm<sup>-1</sup> indicates the presence of alkenes. The peaks between 1742.2 and 1853.9 cm<sup>-1</sup> correspond to the C=O stretching that may be attributed to the hemicelluloses and lignin aromatic group

[24]. The peaks around 1364.1 to 1597.8 cm<sup>-1</sup> and 690.41 to 945.05 cm<sup>-1</sup> correspond to Si-OSi and Si-H groups respectively.

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**KNS – AC:** Figure 4 shows the  $ZnCl_2$  activated carbon, in which the bands at (3314.3 – 232 3471 cm<sup>-1</sup>) indicate the existence of free hydroxyl groups [8]. The C-H stretching vibration 233 around 2209.2 to 2911.8 cm<sup>-1</sup> indicates the presence of alkenes. While the peaks between 234 1419.9 and 1916.6 cm<sup>-1</sup> indicate the presence of alkenes and aromatic functional groups [23]. 235 The peak around 551.64 to 878.51 cm<sup>-1</sup> corresponds to Si-H group. The presence of polar 236 237 groups on the surface is likely to give considerable cation exchange capacity to the adsorbent. 238 Analysis of the FTIR showed that the functional groups contributed to the adsorption of dyes 239 on the surface of the adsorbents [25, 26].

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Figure 3:FTIR result of UKNS.

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Figure 4: FTIR result of KNS - AC.

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249 **3.4 Preliminary adsorption.** 

250 The preliminary adsorption studies were carried out using the Design of Experiment 251 (Graeco Latin Square) of 4-level factors to determine the significance of the 252 adsorption parameters such - initial ion concentration, adsorbent dosage, pH, and 253 contact time on the adsorption of the adsorbates. The analysis of variance (ANOVA) 254 result of the adsorption studies at the 0.05 level of significance and  $F_{table}$  (0.05, 3, 6) = 4.76 shows that time and pH did not significantly affect adsorption of phenol red 255 while the adsorbent dosage and initial concentration of adsorbate significantly 256 affected the adsorption phenol red according to the variance ratio (F-value) obtained 257 258 and shown in Tables 5. This is in agreement with the result obtained by [27].

### 259 Table 5: ANOVA of Phenol Red adsorption on KNS-AC

Source of	Sum of	No of degrees	Estimate of	Variance ratio
variance	squares	of freedom	variance	(F-value)
рН	489.11	4	122.28	2.205
Contact time	602.40	4	150.60	2.716
Adsorbent dosage	6291.12	4	1572.78	28.362
Concentration	4664.73	4	1166.18	21.029
Residual	1330.91	8	55.45	

Total	13378.27	24		
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### 261 **3.5 Optimization process using Response Surface Methodology**

262 The three important factors, dosage, concentration and pH were used as the independent 263 variables and their combined effects were examined while the percentage adsorbed was the 264 dependent variable or the response. This was done to determine the best conditions for 265 optimum removal of the colour from solution. Using the CCD involves varying the 266 independent variables at three different levels (-1, 0, +1). In this work, a set of 20 267 experiments were performed consisting of 14 core points and 6 centre points or null points. 268 The adsorption results of the experimental and predicted values are presented in Table 10. 269 The highest percentage adsorbed was 89.95% at the optimum conditions of adsorbent dosage 270 of 0.3g, initial ion concentration of 300mg/l and pH 10.

#### 271 **3.5.1** ANOVA analysis of the Phenol Red adsorption

Design Expert 8.0.1.7 trial version was used to analyze the results. The results were shown below. The summary of P-values indicates that a quadratic model fitted the ANOVA analysis and hence it was suggested. The linear and 2FI models were not suggested. The Cubic model is always aliased because the CCD does not contain enough runs to support a full cubic model. A significance level of 95% was used hence all terms whose P-value are less than 0.05 are considered significant. The model summary test and the lack of fit test for the adsorption of Phenol Red were also presented in Tables 6 to 8

**Table 6.** Summary of P-values for Phenol Red adsorption on KNS-AC.

280		Sequential	Lack of Fit	Adjusted	Predicted	
281	Source	p-value	p-value	<b>R-Squared</b>	<b>R-Squared</b>	Remark
282	Linear	< 0.0001	< 0.0001	0.8514	0.8106	Not suggested
283	2FI	0.3040	< 0.0001	0.8604	0.6880	Not suggested
284	Quadratic	< 0.0220	< 0.0001	0.9278	0.6938	Suggested
285	Cubic	0.4886	< 0.0001	0.9269	-3.7269	Aliased
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287						
288						
289						
290						
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	Std.		Adjusted	Predicted		
Source	Dev.	<b>R-Squared</b>	<b>R-Squared</b>	<b>R-Squared</b>	PRESS	Remark
Linear	1.81	0.8749	0.8514	0.8106	79.140	Not
suggeste	d					
2FI	1.75	0.9045	0.8604	0.6880	130.390	Not
suggeste	d					
Quadrati	c 1.26	0.9620	0.9278	0.6938	127.95	Suggested
Cubic	1.27	0.9769	0.9269	-3.7269	1975.44	Aliased

**Table 7.** Model Summary Statistics for Phenol Red adsorption on KNS-AC.

**Table 8.** Lack of Fit Test for Phenol Red adsorption on KNS-AC.

303		Sum of		Mean	F	p-value	
304	Source	Squares	df	Square	Value	Prob > F	Remark
305	Linear	52.25	11	4.75	673.15	< 0.0001	Not suggested
306	2FI	39.90	8	4.99	706.70	< 0.0001	Not suggested
307	Quadratic	15.85	5	3.17	449.17	< 0.0001	Suggested
308	Cubic	9.62	1	9.62	1362.88	< 0.0001	Aliased
309	Pure Error	0.035	5	7.057E-0	003		

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311 The ANOVA table was given in Table 9 and from the table the regression F-values of 28.12 312 implies that the model is significant which was validated by the P-values being less than 313 0.0001. A significance level of 5% was used hence all terms whose P-value are less than 0.05 314 are considered significant. The tests for adequacy of the regression models, significance of 315 individual of model coefficients and the lack of fit test were performed using the same 316 statistical package. The P-values were used as a tool to check the significance of each of the 317 coefficients, which in turn are necessary to understand the pattern of the mutual interactions 318 between the test variables [28]. The larger the magnitude of F-test value and the smaller the 319 magnitude of P-values, the higher the significance of corresponding coefficient [29]

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	Sum of		Mean	F	p-value
Source	Squares	df	Square	Value	Prob >
F					
Model	402.03	9	44.67	28.12	< 0.000
A-Dosage	16.26	1	16.26	10.24	0.009
B-Conc.	108.11	1	108.11	68.06	< 0.000
C-pH	241.26	1	24.26	151.89	< 0.000
AB	1 1	.125E-004	7.083E-005	0.9935	< 0.000
AC	1	0.81	0.51	0.4908	0.927
BC	1	11.54	7.27	0.0225	0.481
$A^2$	1	7.98	5.02	0.0489	0.613
$B^2$	1	7.91	4.98	0.0497	0.001
$C^2$	1	17.46	10.99	0.0078	0.031
Residual	15.88	10	1.59		
Lack of Fit	15.85	5	3.17	449.17	
<0.0001					
Pure Error	0.035	5	7.057E-003		
Cor Total	417.92	19			
Std. Dev. = 1.26;	Mean = 80.00;	; (	C.V. = 1.58%;	PRESS =	= 127.95
R-Squared = 0.9620;	Adj R-Sq = 0.92	278; Pred	R-Sq = 0.6938;	Adeq Prec	ision =
17.429					

**Table 9.** ANOVA analysis for Phenol Red adsorption on KNS-AC.

The adequate precision measures the signal to noise ratio and compares the range of the predicted value at the design points to the average prediction error. The adquate predicion ratio above 4 indicates adequate model efficacy [30]. Hence, the adquate precision ratios of 17.429 indicates adquate model efficacy. Also, a PRESS value of 127.95 indicates an adquate signal implying that the models can be used to navigate the design space.

The coefficient of regression  $R^2$  was used to validate the fitness of the model equation. The R<sup>2</sup> has a high value of 0.9620 showing that 96.20% of the variability in the response can be explained by the model. This implies that the prediction of experimental data is quite satisfactory. The quadratic model equation obtained for the Phenol Red adsorption is

358  $Y_{\text{KNS-AC}}$  (%) = 78.43 + 1.01A - 2.60B + 3.88C + 3.750E-003AB + 0.32AC 359 +  $0.56A^2$  $0.56B^{2}$  $0.83C^{2}$ 1.20BC + + 360 -361 (2)362 363 In a regression equation, when an independent variable has a positive sign, it means 364 that an increase in the variable will cause an increase in the response while a negative sign 365 will result in a decrease in the response [30]. Hence, an increase in dosage will cause an 366 increase in the percentage adsorbed while an increase in concentration will cause a decrease 367 in the percentage adsorbed and increase in pH also will cause in the percentage adsorbed. 368 Changes in pH have the most significant effect on the response since its coefficient was highest in magnitude. 369

Values of P less than 0.05 indicate the model term is significant. From the P values it was found that, among the test variables used in the study that A, B, C, BC,  $A^2$ ,  $B^2$ , and  $C^2$ 

are significant model terms. Therefore, eliminating the insignificant terms, the final modelequations becomes as expressed in equations 3

$$Y_{\text{KNS-AC}}$$
 (%) = 78.43 + 1.01A - 2.60B + 3.88C - 1.20BC + 0.56A<sup>2</sup> + 0.56B<sup>2</sup> + 0.83C<sup>2</sup>

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(3)

A combination of the actual experimental response and the predicted response from the mathematical equation are given in Table 10 where it can be seen that there is a close correlation between the the experimental response and the predicted response. Also, this close correlation comfirms the effectiveness of the adsorption of Phenol Red dye using KNS-AC.

**Table 10.** Actual and Predicted values of the adsorption of Phenol Red on KNS-AC.

	A=Dosage	B =Conc.	C = pH	Actual	Predicted
Std				Percentage	Percent
				Removed (%)	Removed (%)
1	0.2	200	4	78.57	77.22
2	0.4	200	4	79.93	78.59
3	0.2	400	4	75.79	74.41
4	0.4	400	4	77.43	75.80
5	0.2	200	8	86.74	86.75

6	0.4	200	8	89.64	89.40
7	0.2	400	8	79.42	79.14
8	0.4	400	8	82.07	81.80
9	0.1	300	6	77.98	78.67
10	0.5	300	6	81.77	82.70
11	0.3	100	6	85.22	85.87
12	0.3	500	6	74.51	75.48
13	0.3	300	2	71.96	74.00
14	0.3	300	10	89.95	89.53
15	0.3	300	6	78.29	78.43
16	0.3	300	6	78.05	78.43
17	0.3	300	6	78.15	78.43
18	0.3	300	6	78.10	78.43
19	0.3	300	6	78.21	78.43
20	0.3	300	6	78.17	78.43

The Normal plot of Residuals (Fig. 5) and the Predicted vs Actual plot (Fig. 6). Hence, from the figures that it can be seen that the points were closely distributed to the striaght line of the plot; it confirms the good relationship between the experimental values and the predicted values of the response though some small scatter like an "S" shape is always expected. These plots equally confirm that the selected model was adequate in predicting the response variables in the experimental values.

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Figure 5. Normal Plot of Residuals for Phenol Red adsorption on KNS-

394 395 AC.



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Figure 6. Predicted Vs Actual plot for Phenol Red adsorption on KNS-AC.

## 399 **3.5.2** Three Dimensional (3D) surface plots for Phenol Red adsorption

Response surface estimation for maximum removal of Phenol Red 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.
The 3D surface and normal plots are given in Figures 7 to Figure 9.





406 Figure 7.3D Surface plot for Phenol Red adsorption on KNS-AC showing combined effects

407 of Dosage and pH.



409 Figure 8.3D Surface plot for Phenol Red adsorption on KNS-AC showing combined effects

410 of Concentration and pH.



411

412 Figure 9.3D Surface plot for Phenol Red adsorption on KNS-AC showing combined effects

413 of Dosage and Concentration.

414

### 415 **3.6 Conclusion**

The application of response surface methodology in phenol red adsorption using kola nut shell activated carbon has been investigated in this work. The activated and non-activated carbons were characterized using the Fourier Transform Infrared (FTIR) spectroscopy to 419 determine the functional groups present and Scanning Electron Microscopy (SEM) to 420 examine the surface morphology of the carbon. The preliminary adsorption studies were 421 carried out using the Graeco Latin Square of 4-level factors to determine the significance of 422 the adsorption parameters. The analysis of variance result of the adsorption studies at the 0.05423 level of significance shows that time and pH did not significantly affect adsorption of phenol 424 red while the adsorbent dosage and initial concentration of adsorbate significantly affected 425 the adsorption of phenol red according to the variance ratio (F-value) obtained. Response 426 surface methodology was used to optimize the adsorption process making use of only 20 427 experimental runs. The optimum conditions for the adsorption of the dye were  $30^{\circ}$ C, 60 428 minutes, 0.30g of adsorbent, initial ion concentration of 300 mg/l and pH 10 which resulted 429 in 89.95% removal of phenol red. The quadratic model helped to know the interactive effects 430 of the parameters. This study has shown that response surface methodology using CCD can 431 be used to study the optimization of the adsorption process of phenol red using kola nut shell 432 activated carbon.

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