Original Research Article

Application of Response Surface Methodology in Phenol red Adsorption Using Kola nut (*Cola acuminata*) Shell Activated Carbon

Abstract:

The application of response surface methodology in phenol red adsorption using kola nut shell activated carbon was studied. Chemical method of activation using zinc chloride ($ZnCl_2$) was used to prepare the carbon. The impregnated samples were kept in an oven at 383K for 24 hours. The dried samples were carbonized in muffle furnace for 1 hour at 773K. Some physical properties of the carbons such as surface area, pH, moisture content, ash content, bulk density were determined. Both the activated and non-activated carbons were characterized using the Fourier Transform Infrared (FTIR) spectroscopy to determine the functional groups and Scanning Electron Microscopy (SEM) to examine the surface morphology of the carbon. Preliminary adsorption studies were carried out to determine the significance of the parameters in adsorption process. The parameters shown to be more significant were adsorbent dosage and initial ion concentration. The adsorption process was optimized using the Central Composite Design (CCD) for three factors and the optimization results were analyzed using Design Expert 8.7.0.1 trial version. The optimum conditions for the adsorption of the dye were 303K, 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.

Keywords: Optimization, Response surface, Kola nut shell, Activated carbon, Adsorbent, Adsorbate, Charcterization,

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).

The release of large quantity of dyes into water bodies by textile industries poses serious 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 dyes and pigments are produced worldwide annually [1]. Untreated or partially treated effluents from other industries namely, paper, plastics, leather, cosmetics, food, woollen, etc also contribute to the pollution load. The colouration of the water by the presence of dyes, even in small concentrations, is easily detectable [2] and many of these dyes have an inhibitory effect on the process of photosynthesis and thus affecting the land flora and the aquatic ecosystem. The anaerobic break down of some dyes in the sediments and / or their incomplete bacterial degradation often produces toxic amines [3].

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

2.0 MATERIALS AND METHODS

2.1 Adsorbent

The kola nut shells were obtained from Ekiti State Nigeria. The kola nut shells were reduced into small pieces and dried in sunlight to reduce the moisture content. The dried sample was mixed with $ZnCl_2$ in the ratio 1:1 and kept in oven at 383K for 24 hours. The sample was washed many times with deionised water and leached with warm water to remove any trace of metal present in the sample. The sample was weighed in crucibles and placed in a furnace at 773K for one hour to undergo the carbonization process. The purpose of this carbonization process was to remove excess of the volatile matters. After cooling, it was ground using mortar and pistil and then, sieved to particle size of 75µm and kept in air tight container for further use. The process flow diagram for the production activated carbon is shown on Figure 1. This activated kolanut shell is termed KNS-AC. Equally, raw kola nut shell was dried and reduced to small pieces and termed UKNS.

The flow diagram:

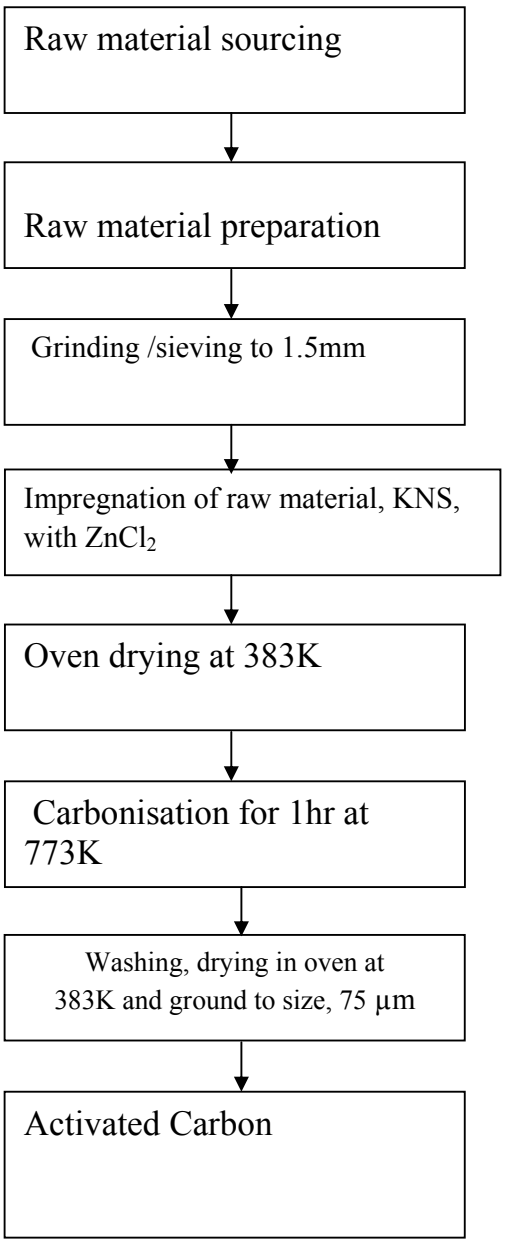


Figure 1. Process flow sheet for the activated carbon production.

2.2 Adsorbate

The phenol red used in this work was procured from Onitsha main market, Nigeria. Stock solution of the dye was prepared by accurately weighing 1.0 gram of the dye and adding 1000ml of distilled water to it to get a dye solution of concentration 1000mg/l. A given volume was then measured out and diluted appropriately to get any required concentration. The structure of the phenol red is shown in Figure 2. The chemicals used in this work were of analytical grades.

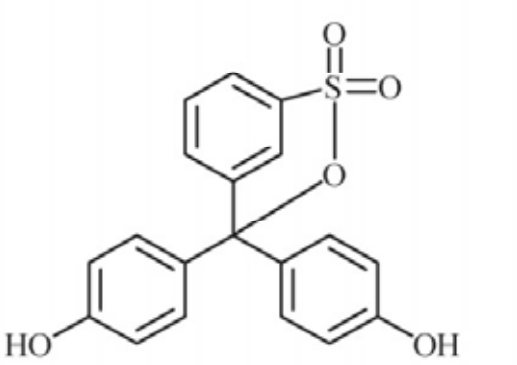


Figure 2. Molecular structure of phenol red.

2.3 Physical Properties and Characterization

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 D 28866-70 [17] and ASTMD 2867-70 [18] respectively. The pH was determined using standard test of ASTM D 3838-80 [19]. The surface area was determined using the Sears 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.

2.4 Preliminary Adsorption Study

The preliminary adsorption study for the determination of the 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.

1. pH – (2, 4, 6, 8)
2. Contact time – (10, 20, 30, 60 mins)
3. Amount of adsorbent – (0.1, 0.2, 0.3, 0.4g)
4. Concentration of dye bath – (50, 100, 150, 200 mg/L)

Plan of Experiment (Graeco – Latin Square)

$\mathbf{X}_1$ = Contact time – (τ_1, τ_2, τ_3, τ_4)

$\mathbf{X_2}$ = Adsorbent dosage – (d_1, d_2, d_3, d_4)

X_3 = Initial concentration – (α, β, γ, δ)

X_4 = pH – (A, B, C, D)

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

X_2 \ X_1	τ_1	τ_2	τ_3	τ_4
d_1	A α	B β	C γ	D δ
d_2	B β	C γ	D δ	A α
d_3	C γ	D δ	A α	B β
d_4	D δ	A α	B β	C γ

Table 1 means the number of experiments with each block representing the experimental conditions. The range of values used for the factors levels was obtained from preliminary studies and from previous works from some authors [16].

2.5 The Batch Adsorption Studies

The dye solution was prepared by dissolving appropriate mass of the dye in 1000ml of distilled water to get the required concentration of the dye solution. 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.

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

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

V is the volume of the solution (L) and

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

2.5 Optimization using Central Composite Design (CCD)

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

187 equation. The significance of each term in the equation is to estimate the goodness of fit in
188 each case. Response surfaces were drawn to determine the individual and interactive effects
189 of the test variable on the percentage removal of phenol red.
190 The high (+) and low (-) values for phenol red adsorption are dosage (0.2 and 0.4 g),
191 concentration (200 and 400 mg/l) and pH (4.0 and 8.0). The alpha (α) value used was 1.414.
192
193 **Table 2.** Factor levels of independent variables for phenol red adsorption on KNS –AC.

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

194
195 **Table 3.** Central Composite Design for adsorption of phenol red on KNS -AC (real values).

Run	**Dosage (g)**	**Concentration (mg/l)**	**pH**
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

196 **3.0 RESULT AND DISCUSSION**
197 **3.1 Proximate Analysis the Activated Carbon**
198 Some of the physical properties of the activated carbon were determined using standard
199 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.

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

Property	**UKNS**	**KNS-AC**
Surface area (m^2g^{-1})	279	570.2
pH	7.4	7.3
Moisture content (%)	5.8	0.31
Ash content (%)	6.7	2.4
Bulk density(gcm^{-3})	0.32	0.34

3.2 Adsorbent characterization using SEM.

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

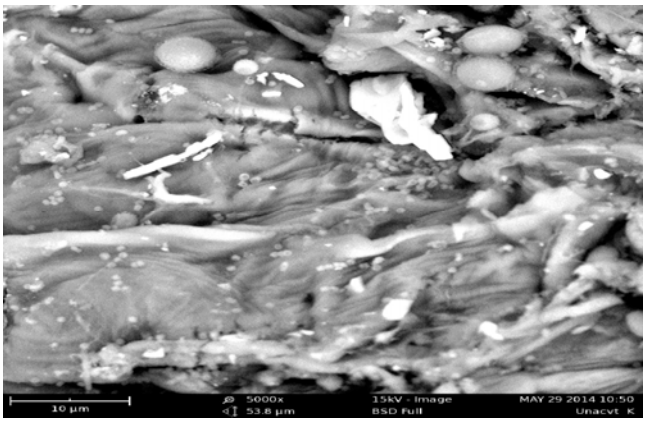


Plate 1. SEM analysis of UKNS at 75µm particle size

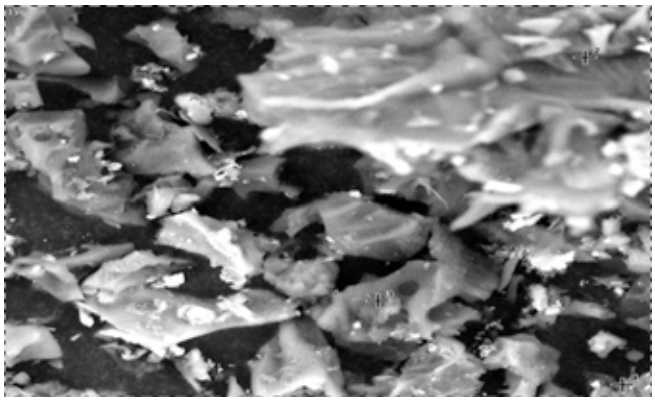


Plate 2. SEM analysis of KNS -AC at 75µm particle size (Mag.= 5000x)

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.

UKNS: The peaks between 3117.2 and 3953.7 cm^{-1} shown in Figure 3, indicate the presence of free hydroxyl groups; C-H stretching vibration around 2007.7 to 2940.5 cm^{-1} indicates the presence of alkenes. The peaks between 1742.2 and 1853.9 cm^{-1} 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^{-1} and 690.41 to 945.05 cm^{-1} correspond to Si-O-Si and Si-H groups respectively.

KNS – AC: Figure 4 shows the $ZnCl_2$ activated carbon, in which the bands at (3314.3 – 3471 cm^{-1}) indicate the existence of free hydroxyl groups [8]. The C-H stretching vibration around 2209.2 to 2911.8 cm^{-1} indicates the presence of alkenes. While the peaks between 1419.9 and 1916.6 cm^{-1} indicate the presence of alkenes and aromatic functional groups [23]. The peak around 551.64 to 878.51 cm^{-1}corresponds to Si-H group. The presence of polar

groups on the surface is likely to give considerable cation exchange capacity to the adsorbent. Analysis of the FTIR showed that the functional groups contributed to the adsorption of dyes on the surface of the adsorbents [25, 26] .

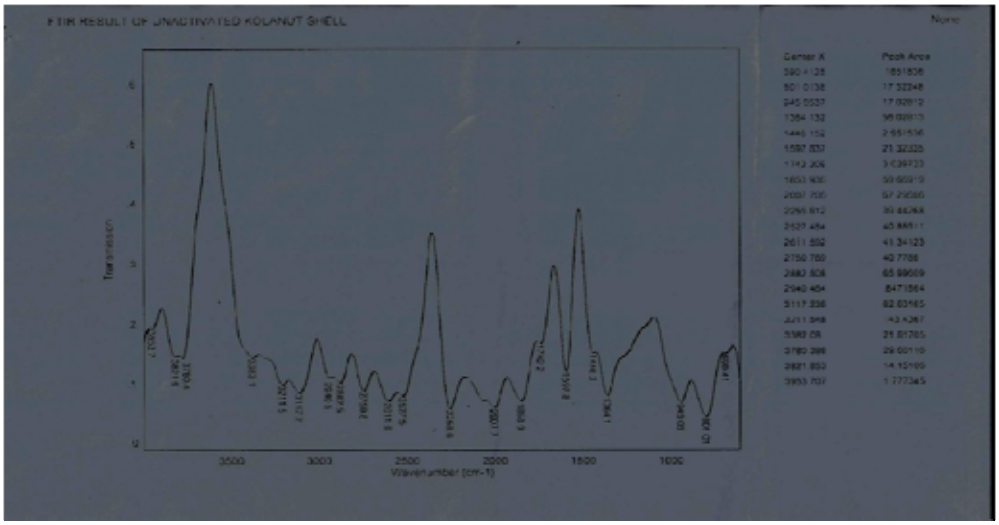


Figure 3. FTIR result of UKNS.

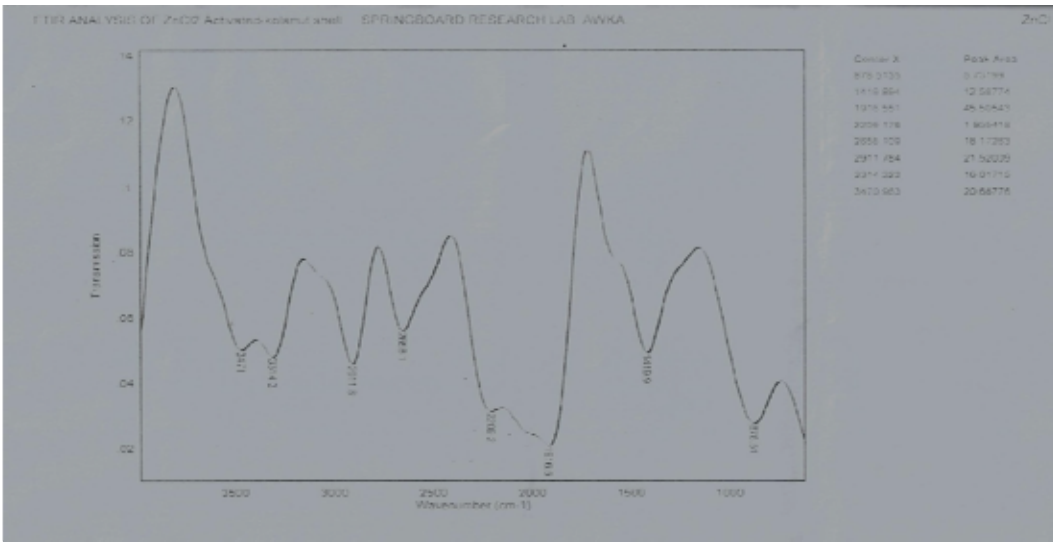


Figure 4. FTIR result of KNS - AC.

3.4 Preliminary adsorption.

The preliminary adsorption studies were carried out using the Design of Experiment (Graeco Latin Square) of 4-level factors to determine the significance of the adsorption parameters such – initial ion concentration, adsorbent dosage, pH, and contact time on the adsorption of the adsorbates. The analysis of variance (ANOVA) 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 while the adsorbent dosage and initial concentration of adsorbate significantly affected the adsorption phenol red according to the variance ratio (F-value) obtained and shown in Tables 5. This is in agreement with the result obtained by [27].

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

Source of variance	Sum of squares	No of degrees of freedom	Estimate of variance	Variance ratio (F-value)
pH	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	---	---

3.5 Optimization process using Response Surface Methodology

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

3.5.1 ANOVA analysis of the Phenol Red adsorption

Design Expert 8.7.0.1 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.

Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	Remark
Linear	< 0.0001	< 0.0001	0.8514	0.8106	Not suggested
2FI	0.3040	< 0.0001	0.8604	0.6880	Not suggested
Quadratic	< 0.0220	< 0.0001	0.9278	0.6938	Suggested
Cubic	0.4886	< 0.0001	0.9269	-3.7269	Aliased

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

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	Remark
Linear	1.81	0.8749	0.8514	0.8106	79.140	Not suggested
2FI	1.75	0.9045	0.8604	0.6880	130.390	Not suggested
Quadratic	1.26	0.9620	0.9278	0.6938	127.95	Suggested
Cubic	1.27	0.9769	0.9269	-3.7269	1975.44	Aliased

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

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

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

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

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	402.03	9	44.67	28.12	< 0.0001
A-Dosage	16.26	1	16.26	10.24	0.0095
B-Conc.	108.11	1	108.11	68.06	< 0.0001
C-pH	241.26	1	24.26	151.89	< 0.0001
AB	1	1.125E-004	7.083E-005	0.9935	< 0.0001
AC	1	0.81	0.51	0.4908	0.9276
BC	1	11.54	7.27	0.0225	0.4816
A^2	1	7.98	5.02	0.0489	0.6130
B^2	1	7.91	4.98	0.0497	0.0013
C^2	1	17.46	10.99	0.0078	0.0319
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 = 0.9278; Pred R-Sq = 0.6938; Adeq Precision = 17.429

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 adequate precision ratio above 4 indicates adequate model efficacy [30]. Hence, the adequate precision ratios of 17.429 indicates adequate model efficacy. Also, a PRESS value of127.95 indicates an adequate 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^2 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

$$Y_{KNS\text{-}AC}\ (\%) = 78.43 + 1.01A - 2.60B + 3.88C + 3.750E\text{-}003AB + 0.32AC - 1.20BC + 0.56A^2 + 0.56B^2 + 0.83C^2 \quad (2)$$

In a regression equation, when an independent variable has a positive sign, it means that an increase in the variable will cause an increase in the response while a negative sign will result in a decrease in the response [30]. Hence, an increase in dosage will cause an increase in the percentage adsorbed while an increase in concentration will cause a decrease in the percentage adsorbed and increase in pH also will cause in the percentage adsorbed. Changes in pH have the most significant effect on the response since its coefficient was highest in magnitude.

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 model equations becomes as expressed in equations 3

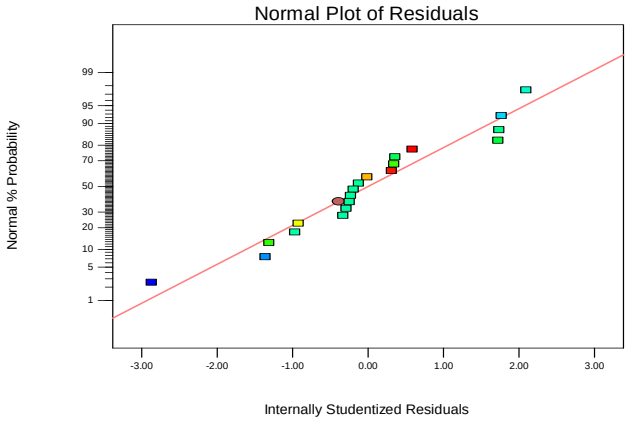
$$Y_{KNS\text{-}AC}\ (\%) = 78.43 + 1.01A - 2.60B + 3.88C - 1.20BC + 0.56A^2 + 0.56B^2 + 0.83C^2 \quad (3)$$

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 experimental response and the predicted response. Also, this close correlation confirms 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.

Std	A=Dosage	B =Conc.	C = pH	Actual Percentage Removed (%)	Predicted Percent 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 straight 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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407 **Figure 5.** Normal Plot of Residuals for Phenol Red adsorption on KNS-

408 AC.

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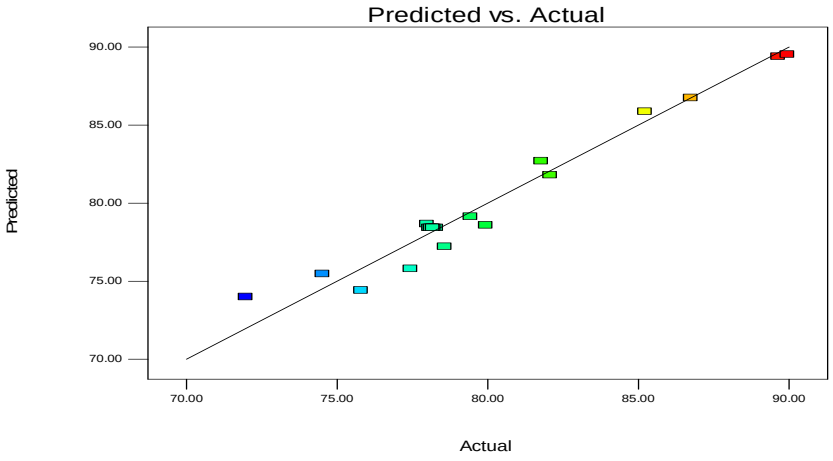

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411 **Figure 6.** Predicted Vs Actual plot for Phenol Red adsorption on KNS-AC.

412

413 **3.5.2 Three Dimensional (3D) surface plots for Phenol Red adsorption**

414 Response surface estimation for maximum removal of Phenol Red Response surface plots as

415 a function of two factors at a time, maintaining all other factors at fixed levels are more

416 helpful in understanding both the main and the interaction effects of these two factors.

417 The 3D surface and normal plots are given in Figures 7 to Figure 9.

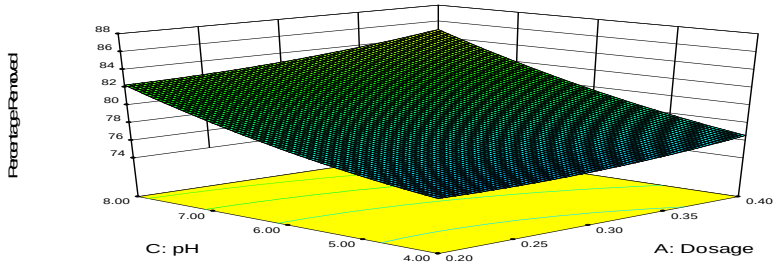


Figure 7.3D Surface plot for Phenol Red adsorption on KNS-AC showing combined effects of Dosage and pH.

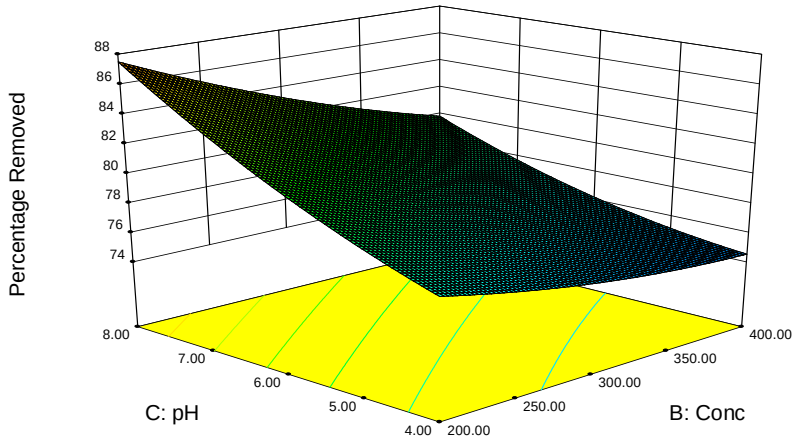
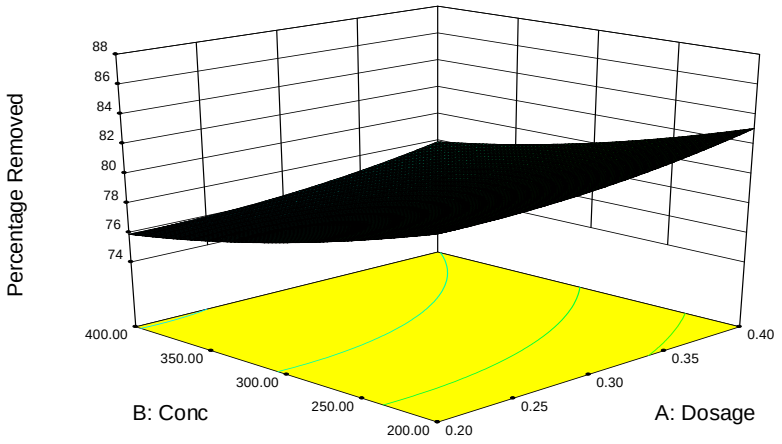


Figure 8.3D Surface plot for Phenol Red adsorption on KNS-AC showing combined effects of Concentration and pH.



425

426 **Figure 9.**3D Surface plot for Phenol Red adsorption on KNS-AC showing combined effects
427 of Dosage and Concentration.

428

429 **3.6 Conclusion**

430 The application of response surface methodology in phenol red adsorption using kola nut
431 shell activated carbon has been investigated in this work. The activated and non-activated
432 carbons were characterized using the Fourier Transform Infrared (FTIR) spectroscopy to
433 determine the functional groups present and Scanning Electron Microscopy (SEM) to
434 examine the surface morphology of the carbon. The preliminary adsorption studies were
435 carried out using the Graeco Latin Square of 4-level factors to determine the significance of
436 the adsorption parameters. The analysis of variance result of the adsorption studies at the 0.05
437 level of significance shows that time and pH did not significantly affect adsorption of phenol
438 red while the adsorbent dosage and initial concentration of adsorbate significantly affected
439 the adsorption of phenol red according to the variance ratio (F-value) obtained. Response
440 surface methodology was used to optimize the adsorption process making use of only 20
441 experimental runs. The optimum conditions for the adsorption of the dye were 30^0C, 60
442 minutes, 0.30g of adsorbent, initial ion concentration of 300 mg/l and pH 10 which resulted
443 in 89.95% removal of phenol red. The quadratic model helped to know the interactive effects
444 of the parameters. This study has shown that response surface methodology using CCD can
445 be used to study the optimization of the adsorption process of phenol red using kola nut shell
446 activated carbon.

REFERENCES

[1] N.D. Pragnesh, K. Satindar, K. Ekta, Removal of eriochrome black –T by adsorption onto eucalyptus bark using green technology, *Journal of Chemical Technology,* 18, 2011, 53-60.

[2] P. Nigam, G. Armour, I. Banat, D. Singh, R. Marchant, Physical Removal of Textile Dyes and Solid State Fermentation of Dye-adsorbed Agricultural Residues*, Journal of Bioresour Technol*, 72, 2000, 219 – 26.

[3] E. Weber, N.L. Wolfe, Kinetics Studies of reduction of aromatic azo compounds in anaerobic sediment/water systems, *Journal of Environ Toxicol Chem*, 6, 1987, 11 – 20.

[4] F.C. Wu, R.L. Tseng and R.S. Juang, Adsorption of dyes and phenols from water on the activated carbons prepared from corncob wastes*, Journal of Environ technol*, 22, 2001, 205 – 13.

[5] T. Robinson, T. McMullan, G. Marchant and P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, *Journal of Bioresource Technology* 77, 2001, 247–255.

[6] N. Ehssan and E. Yehia, Adsorption of Phenol from Aqueous Solution by Local Egyptian Bentonite, *Journal of American Science* 8(8), 2012, 1-9.

[7] K. Sunil, V. Gunasekar and V. Ponnusami, Removal of methylene blue from aqueous effluent using fixed bed of groundnut shell powder, *Hindawi Publishing Corporation Journal of Chemistry,* 1, 2012, 1-5.

[8] K.F. Al-Sultani, F.A. Al-Seroury, Characterization of the Removal of Phenol from Aqueous Solution Fluidized Bed Column by Rice Husk Adsorbent, *Research Journal of Recent Sciences,* 1, 2011, 145-151.

[9] H.A. Omar, Adsorptive removal of phenol from aqueous solution using natural immobilized Chitin by Diathiazone, *New York Science Journal* 5(8), 2012, 1- 9.

[10] T. Nestor, M. Natalia, M. Fabiana, P. Javier, P. Carina, and C. Tomas, Phenol adsorption onto powdered and granular activated carbon prepared from eucalyptus wood, *Journal of Colloid and Interface Science* 279, 2004, 357-363.

[11] M. Afshin, H. Amir, R.E. Mahvi and K. Jamil, Evaluation of Barley Straw and its Ash in Removal of Phenol from Aqueous System, *World Applied Sciences Journal*, 8(3), 2010, 369-373.

[12] O.A. Ekpette and J.M. Horsfall, Kinetic sorption study of phenol onto activated carbon derived from fluted pumpkin stem waste", *ARPN Journal of Engineering and Applied science* 6(6), 2011, 43-49.

[13] V. Srihari and D. Ashutosh, Adsorption of phenol from aqueous media by an Agro-waste (Hemidesmus Indicus) based activated carbon, *Applied Ecology and Enivronmental research* 7(1), 2009, 13-23.

[14] A. Sofia, G. Tzayhri, O. Guillermo, L. Del Socorro and G. Brenda, Adsorption of Phenol and Dichlorophenols from Aqueous Solutions by Porous Clay Heterostructure (PCH)", *J. Mex. Chem. Soc*. 49(3), 2005, 287-291.

[15] R. Rajeshkannan, M. Rajasimman, and N. Rajamohan, Decolourization of malachite green using tamarind seed: optimization, isotherm and kinetic studies, Chemical *Industry and Chemical Engineering Quarterly/CICEQ,vol*. 17, no. 1, 2011, pp. 67–79.

[16] E.C. Onu and J.T. Nwabanne, Application of Response Surface Methodology in Malachite Green Adsorption Using Nteje Clay. Open J. Chem Eng and Sci. vol 1.ISSN (online): 2014, 2374-5037.

[17] Total Ash Content of Activated Carbon, The Annual book of ASTM standards, copy right, ASTM, Race Street, Philadelphia.PA.1986, 19103.

[18] Moisture Content of Activated Carbon, The Annual book of ASTM standards, copy right, ASTM, Race Street, Philadelphia.PA.1986, 19103.

[19] pH of Activated Carbon, The Annual book of ASTM standards, copy right, ASTM, Race Street, Philadelphia.PA.1996, 19103.

[20] A.S. Alzaydian, Adsorption of methylene blue from aqueous solution onto a low cost Natural Jordanian clay*, American Journal of Applied Sci*. 6(6), 2009, 1047-1058.

[21] Z. Al-Qadah and R. Shawabkah, Production and characterization of granular activated carbon from activated sludge, *Braz.Journal of Chemical engineering*, 26(1), 2009, 6-17.

[22] P.Y. Devarly, N. Kartika, Indraswati, S. Ismadji, Activated carbon from jackfruit peel waste by H3PO4 chemical activation: Pore structure and surface chemistry characterization, *Chem.Eng.Journal*, 140, 2008, 32–42.

[23] H. Cherifi, S. Haninia and F. Bentahar, Adsorption of phenol from wastewater using Vegetal cords as a new adsorbent. *Desalination*, 244, 2009, 177-187.

[24] Y. Safa and H.N. Bhatti, Adsorptive Removal of Direct Dyes by Low Cost Rice Husk, Effect of Treatments and Modification, *African Journal of Biotechnology*, 10(16), 2011, 28 – 3142.

512 [25] I.D. Mall, V.C. Srivastavan and I.M. Mishre, Characterization of Mesoporous Rice Husk
513 Ash (RHA) and Adsorption Kinetics of Metal Ions from Aqueous Solution onto RHA, *J.*
514 *Hazard. Mater*, B134, 2006, 257 – 267.
515 [26] V.K. Garg, M. Bansal, U. Garg and D. Singh, Remomal of Cr (VI) from aqueous
516 Solutions using preconsumer processing Agricultural waste: A case study of Rice Husk",
517 *Journal of Hazard Materials*, 162, 2009, 3125 – 320.
518 [27] V.K. Vikrant and S.K. Deshmukh, Kinetic parameters and evaluation performance for
519 decolorization using low cost adsorbent, *International conference on future environment and*
520 *energy IPCBEE vol.*28, 2012, 95-99, IACSIT Press, Singapoore.
521 [28] P. Shrivastava, P. Sandagar, I. Baja and R. Singhal, Media optimization for the
522 production of U-linolenic acid by cunninghamella echinulata varielegans MTCC 522 using
523 response surface methodology, *International journal of food Engineering* 4(2), 2008, 1-32.
524 [29] Z. Alam, S.A. Muyibi and N. Kamsldin, Production of activated carbon from oil palm
525 empty fruit bunches for removal of zinc, *Proceedings of Twelfth International Water*
526 *Technology Conference, Aixeandria Egypt*, 2008, 373-382.
527 [30] A. Krumar, B. Prasad. and I.M. Mishra, Process parametric study of ethane carboxylic
528 acid removal onto power activated carbon using Box-Behnken design, *Journal of Chem. Eng.*
529 *Technol.* 30(7), 2007, 932-937
530