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Adsorption of methylene blue dye onto modified activated carbon produced from groundnut shells

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In this research work, groundnut shells agricultural byproducts were utilized for the production of modified groundnut shell based activated carbon (MGSAC) through the use of phosphoric acid and ethylene-diamine tetraacetic acid disodium salt (Na_2EDTA) as an activating agent and a modifier, respectively. A three factor, two-level full factorial design (FFD) was employed for the exploratory design of experiments (DoE). The independent process variables are temperature, activation time, and activating agent concentration for the production of MGSAC in a muffle furnace. The product yield and methylene blue (MB) dye adsorption were considered as the performance indicators for the process. Regression analysis was conducted to examine the influence of process variables on the responses of the process parameters. From the analysis, it was found that the activation temperature has the most significant effects on the MGSAC product yield and the activation time for the adsorption of MB dye. The results obtained showed that the best operating conditions for production of MGSAC were carbonization temperature of 450°C, activation time of 30 min and activating agent concentration of (35 mmol Na_2EDTA; 50% H_3PO_4) which resulted in the product yield of 55.5% MGSAC, and 99.6% MB dye adsorption. It was also observed that experimental values obtained were in good agreement with the values predicted by the model. Hence, the two-level FFD DoE technique demonstrated worthwhile features in disclosing the dominant factors that affect the production of modified groundnut shell based activated carbon. The products appear to be promising adsorbents for the adsorption of cationic MB dye from wastewaters.

Keywords: Groundnut shells, Process variables, Activated carbon, Na_2EDTA modifier, Methylene blue dye.

1. Introduction

Rapid population growth and urbanization with boosted expansion of various industries across the globe resulted in the discharge of pollutants into the water bodies. Various industrial processes that produce products ranging from textile, plastic, paper, cosmetics, dyestuffs, ink, tannery, to leather starting materials use cationic dye especially methylene blue as coloring agent (Yaseen and Scholz, 2018, Genetie, 2020). The release of such dyes into the aqueous environment may cause damage to the aquatic system and food chain (Gupta, 2009, Yaqub et al., 2014, Harshananda et al., 2020, Jawad et al., 2021, Thuy et al., 2021). Hence, the treatment of industrial effluents are required in accordance with legal requirements to protect human health, sources of livelihood, and the environment.

Several techniques for treatment such as physical, chemical, or biological techniques have been used to remove dyes from wastewater. Adsorption using activated carbon (AC) has been used as an effective physical technique for the removal of pollutants from wastewater due to its low cost, and other good features for environmentally friendliness (Abdullahi 2009, Salman et al., 2012, Sekirifa et al., 2012, Oladipo et al., 2013 Mohammed et al., 2014, Sivashankar et al., 2014, Eletta et al., 2016, Das and Mishara, 2017, Zoha et al., 2020).

Activated carbons (ACs) can be produced from any potential carbonaceous material through either a chemical activation with metallic chlorides such as zinc chloride, mild acids like phosphoric acids, bases such as potassium hydroxide or sodium hydroxide prior to carbonization or simultaneous physical activation and carbonization with steam or inert gases such as nitrogen gas under high temperature operations (Abdullahi, 2009, Muhammad, 2010, Alslaibi et al., 2013, Isoda et al., 2014, Lian et al., 2016, Danish and Ahmad, 2018, Alahabadi et al., 2020, Li et al., 2020, Ping et al., 2020, Jawad et al., 2021, Eletta et al., 2018, Gao et al., 2020). The basis for the first commercial process development of activated carbon was set by von Ostreyko in 1901 (Dąbrowski, 2001). Afterwards, there are several reports for the utilization of carbonaceous materials such as coal, wood, lignite, corncorbs, and coconut shells for the commercial production of activated carbons (Li et al., 2002, Vernersson et al., 2002, Loannidou and Zabaniotou, 2007, Rafatullah et al., 2010, Sahu et al., 2010).

In recent years, surface modifications for the improvement of surface chemical properties and adsorption properties of activated carbons toward the target for effective adsorption of pollutants have been recognized (Yin et al., 2007, Igwe and Abia, 2007, Bhatnagar et al., 2013, Zizhang et al., 2016, Guo et al., 2017, and Rivera-Utrilla et al., 2011, Ezzeddine et al., 2015, Li et al., 2015). Activation followed by modification has been widely used to enhance the surface functional groups and adsorption abilities of ACs towards pollutants. Some researchers have observed that this method is tedious and time-consuming. To simplify the modification process, some researchers have deployed the in-situ modification of ACs during production process as an effective method for improving the surface group functionalities of ACs and thus resulting in the enhancement of its adsorption capacity towards organic and inorganic pollutants (Ren et al., 2013, Wang et al., 2016, Hai et al., 2021).

Therefore, the principal objective of this research was to explore the possibility of utilizing groundnut shells agricultural byproduct for the production of activated carbon with phosphoric acid (H_3PO_4) activating agent and ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) as a modifier targeted for the adsorption of methylene blue dye, and consequently employ for the examination of influence of activation time, carbonization temperature and impregnation concentration of Na_2EDTA/H_3PO_4 process variables on the product yield of MGSAC and the efficiency of methylene blue dye adsorption performance indicators with aid of two-level full factorial design.

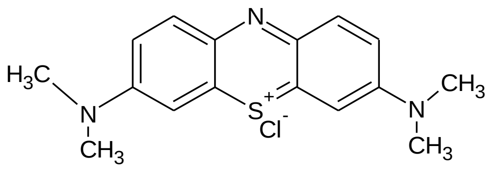
2. Material and Methods

2.1 Materials

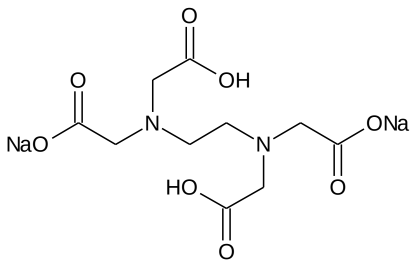
The research facilities used includes the following a Mufler tubular furnace (Gallenkamp), pH meter (pHep®), oven (Gallenkamp Hot Box Oven), and a UV-VIS Spectrophotometer (SHARCHTECH 752N). The materials used in this study are phosphoric acid from BDH Chemicals Ltd, England, Disodium ethylenediamine tetraacetate (Na_2EDTA) from Kermel, France and methylene blue from Sigma Aldrich, Germany.

2.2 Adsorbate preparation

Methylene Blue (MB) dye has a wavelength of 664 nm. It was considered to be the model adsorbate in this research investigations due to its wide applications. The molecular structures of MB, Ethylene-diaminetetraacetic acid disodium salt (Na_2EDTA), and Phosphoric acid with their molecular weights 319.85, 372. 24, and 97.95 g/mol are shown in Figure 1 (a), (b), and (c), respectively. Stock solution of Methylene Blue (MB) was prepared by dissolving 1.5 g of dye in 1L distilled water. All working solutions were prepared from the stock solution by dilution with distilled water to the needed concentration.



(a)



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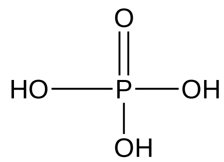


(c)

Figure 1: Molecular structures of (a) Methylene Blue (MB) dye, (b) Na_2EDTA and (c) H_3PO_4.

2.3 Design of experiments

Three factors, 2-level factorial design with four center points were used in this research. Performing replicates at center points will provide an estimate of pure error (i.e., an independent estimate of variation), which would otherwise be absent in the case of non-replicated designs. Each factor or independent process variable is denoted by A as the activation temperature, B as the activation time, and C as the concentration of the activating agent. The variables are also coded at three equally spaced levels -1, 0, +1 for low, center and high values, respectively. The levels and ranges of the examined process variables affecting the production yields of modified activated carbon and in turn the adsorption of methylene blue dye employed are presented in Table 1 with eight experimental runs and four replicated runs at the centre points. It was used for the empirical modelling of the production of modified groundnut shells based activated carbon (MGSAC), and the adsorption of methylene blue (MB) dye adsorption with the aid of a statistical software, Design-Expert® 13.0.1.0. The data ranges used were selected based on the findings of our previous studies, and the reported research (Abdullahi, 2009, Muhammad, 2010, Al Othman et al., 2013, Magdy et al., 2018, Wu et al., 2019, Kumari et al., 2020, Wang et al., 2020).

The performance indicators for the production of modified groundnut based activated carbon and the adsorption are the yield and percentage adsorption of Methylene Blue (MB) dye. The responses of the two (2) processes are designated as (Yi). Each response was used to develop an empirical model which correlated the three (3) process variables to the two (2) response by a first-order mathematical regression equation expressed in equation 1. This was achieved through analysis of variance (ANOVA), regression analysis, and the use of the statistical plots.

$$Y_i = X0 + X1A + X2B + X3C + X4AB + X5AC + X6BC + X7ABC \quad (1)$$

Where Yi is the predicted response (product yield of MGSAC and the efficiency of MB dye adsorption) $X0$ represents the global mean, Xi is the regression coefficient corresponding to the main factor effects and interactions, A is the activation temperature (0C), B is Activation time (min), and C is concentration of activating agent (mmo, %).

2.4 Production of activated carbon

In this investigation, the groundnut shells used were obtained from Zaria, Kaduna State, Nigeria. The shells of the groundnut were first washed with water to remove impurities, dried at 105°C for 24h and then crushed. 50 g groundnut shells were adequately mixed with 50 cm^3 of 35 mmol disodium ethylenediamine tetraacetate (Na_2EDTA) and then impregnated with 50 cm^3 phosphoric acid (H_3PO_4) solution with different concentrations (50, 60 and 70 wt%) overnight. Then, the mixtures were put into a Gallenkamp Mufler tube furnace with heating rate of 100 C/min for carboniztion until temperatures (350, 400 and 450°C) were reached and maintained for different activation time (10, 20 and 30 min) under a constant flow of N_2 gas of 100 mL/min and then cooled under ambient condition. The products of MGSACs were repeatedly washed with distilled water until pH falls between 6.7 and 7.0. Twelve products of activated carbon were produced by setting the experimental condition for each selected run as shown in Table 1. Finally, the products were dried at 110 °C for 24 h in an oven, grounded, packaged in an airtight container, and used for further experimental studies.

Table 1: Independent process variables

	Coded values		
Process variables	+1	0	-1
Activation temperature, A (°C)	450	400	350
Activation time, B (min)	30	20	10
Salt* and acid Concent., C (%)	70	60	50

**Salt concentration of 35 mmol were constant for all the experimental runs*

2.4.1 Activated carbon yield

Yield is a performance indicator that shows the process efficiency for the conversion of a certain raw material into product. The product yield of modified activated carbon produced from groundnut shells (MGSAC) was calculated as the ratio of the weight of dried activated carbon to the initial weight of the raw groundnut shell agricultural byproduct. This process parameter can be calculated in percentage as shown in equation (2).

$$Yield, \mathrm{Y} = \frac{W_2}{W_1} \times 100 \quad (2)$$

Where W_2 and W_1 are weights of the final modified activated carbon (g) produced, and starting material (groundnut) shell (g), respectively.

2.5 Adsorption studies

Based on the design matrix, the adsorption experiments were performed using the modified activated carbon produced from groundnut shells (MGSAC). Batch adsorption experiments were carried out by agitating 0.1 g of each MGSAC with 50 ml of 25 mg/l of MB solution in stoppered 250 ml conical flasks for 60 min at ambient temperature after which the suspensions were agitated and dye concentrations in the supernatant solutions were measured. Figure 2 displays the schematic representation of the adsorption of methylene blue (MB) dye. Calibration curve was developed based on Beer's–Lambert law at λ_{max} of 664 nm for MB dye through the measurement of the dye solution absorbance by UV/Visible Spectrophotometer (SHARCHTECH 752N UV-VIS Spectrophotometer). Determination was based on average values for each sample. The efficiency of adsorption or the percentage MB dyes adsorption at equilibrium by MGSAC was calculated using equation 3

$$Y_2 = \frac{C_0 - C_e}{C_0} \times 100 \qquad (3)$$

Where C_0 and Ce are the initial and equilibrium concentrations of MB (mg/L) before, and after adsorption, respectively.

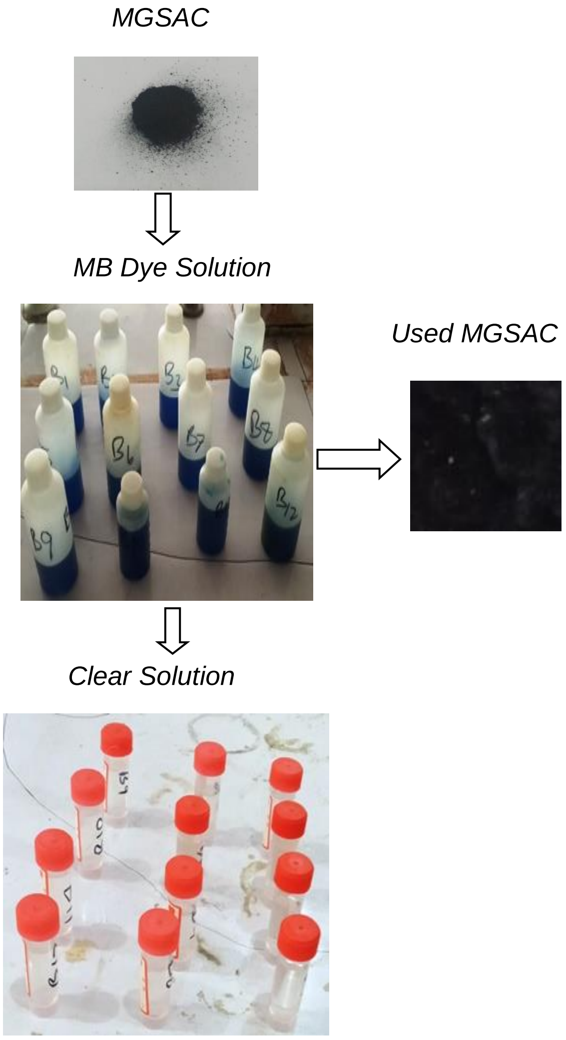


Figure 2: Adsorption of methylene blue dye onto MGSAC.

3. Results and Discussion

3.1 Half-normal plots

The half-normal plots for the product yield of MGSAC and the efficiency of MB dye adsorption are depicted in Figures 3 respectively. For activated carbon yield, the half-normal plot of this response showed that A, B and C had a negative influence on the response, with A exerting the most statistically significant effect while for the percentage adsorption MB by MGSAC, the half-normal plot shows that linear terms, A and B and interaction term AB had a significant, positive effect on the response. B (activation time) had the most significant positive influence on the response. Having identified these key factors, the settings that yield the best performance of the preparation process were further explored.

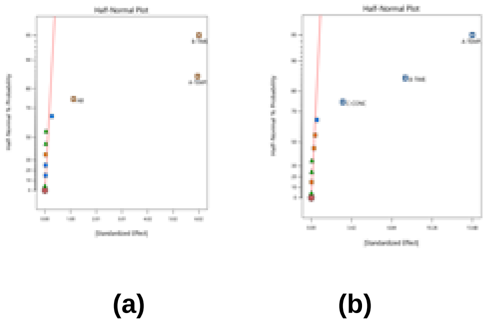


Figure 3: Half-normal plots for (a) MGSAC product yield, and (b) efficiency of MB dye adsorption.

3.2 Development of regression model

The design matrix, the responses obtained from the experimental as well as prediction from the model analysis are given in Table 3. For each response, a regression model equation was used for description of the empirical relationship between the process variables and the performance indicator after which each model was reduced by considering only the significant terms of the dominant factors. The magnitude of the coefficients in the equations shows the degree of influence a term or factor has on the process parameter, while the sign of the coefficient illustrates the direction of the influence the factor has on a performance indicator. The positive sign of the coefficients in a regression equation indicates a synergistic or positive effect, while the negative sign represents a negative or antagonistic effect on the response (Kalavathy et al. 2009).

From Table 3, it can be seen that the product yield of MGSAC and the efficiency of MB dye adsorption depend on the process conditions. The results for the main effects, and their interactions with different process variables were analyzed. The final empirical models for both product yield (Y_1) and efficiency of MB dye adsorption (Y_2) in terms of coded factor after excluding the insignificant terms are given by:

$$Y1 = 65.4 + -6.8375 * A + -3.9875 * B + -1.3375 * C \quad (4)$$

$$Y2 = 92.9458 + 2.9875 * A + 3.0125 * B + 0.5625 * AB \quad (5)$$

Where A is activation temperature, B is the activation time and C is Na_2EDTA and H_3PO_4 impregnation concentration.

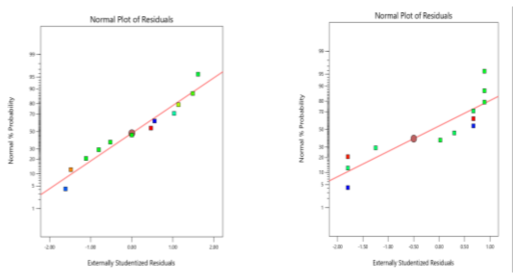
Table 3. Experimental design matrix

	Std	*Process variables* A	B	C	*Actual(a) and Predicted (p) Responses (%)* Y_2 a	Y_2 p	Y_1 a	Y_1 p
1	2	350	10	50	87.6	87.51	77.7	77.56
5	12	350	10	70	87.3	87.51	74.5	74.89
2	6	450	10	50	92.2	92.36	64.3	63.89
6	1	450	10	70	92.4	92.36	61.5	61.21
12	11	400	20	60	93.0	92.95	65.4	65.40
9	7	400	20	60	93.1	92.95	65.2	65.40
10	5	400	20	60	93.1	92.95	65.1	65.40
11	3	400	20	60	93.1	92.95	65	65.40
3	10	350	30	50	92.2	92.41	69.9	69.59
7	4	350	30	70	92.5	92.41	67.3	66.91
4	9	450	30	50	99.6	99.51	55.5	55.91
8	8	450	30	70	99.3	99.51	53.4	53.24

3.3 Model validation

3.3.1 Normal plots of residuals

It can be seen from Figures 3 to 11 that the normal plot of residuals is a straight line for both responses, indicating no abnormalities. The models appear to be good and well described even though the data doesn't have to match perfectly with the line in order to be normal.

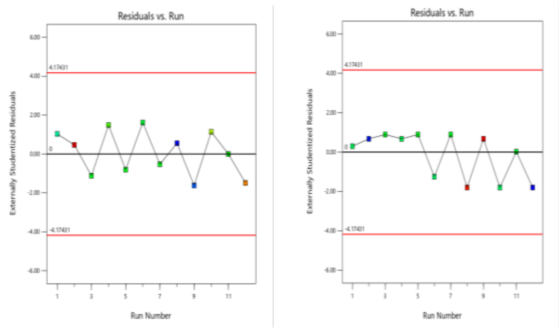


(a) **(b)**

Figure 4. Normal plots for (a) product yield of MGSAC, and (b) efficiency of MB dye adsorption.

3.3.2 Correlation of residual versus run

The "outlier t" shows the number of standard deviations (t-values) for a given run. It falls off relative to what one would expect from all the other runs. Design-Expert provides upper and lower red lines that are similar to 95% confidence control limits on the run chart. From Figure 5, none of the points stands out because this graph is plotted in randomized run order with no outliers noted as shown in the run patterns. However, by running the experiment in random order, protection was built in against trends in response biasing the results.

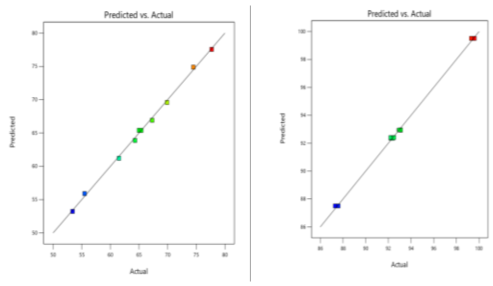


(a) **(b)**

Figure 5: Studentized residuals plots for (a) product yield of MGSAC, and (b) efficiency of MB dye adsorption.

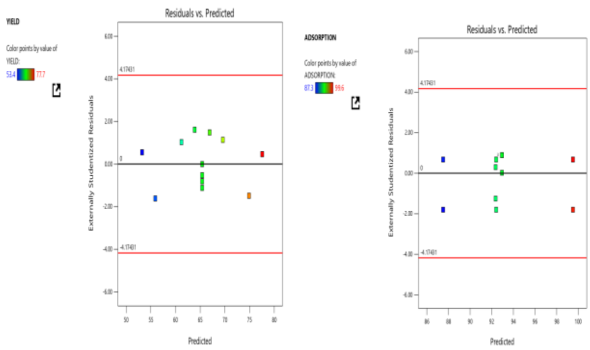
3.3.3 Experimental and predicted values

From Figure 6, the errors in the model were found to be insignificant, since the plot shows that the predicted values coincide with the actual experimental values on the model line. Therefore, the errors in the model can be considered to be negligible, and thus suggestiing suitability of the models represented by equations 4 and 5**.**



(a) **(b)**

Figure 6: Correlation between the experimental and predicted values for (a) product yield of MGSAC, and (b) efficiency of MB dye adsorption.



(a) **(b)**

Figures 7: Studentized residuals and predicted plots for (a) product yield of MGSAC, and (b) efficiency of MB dye adsorption.

3.3.4 Studentized residuals and predicted plots

In Figure 7, the data points in the plots are randomly scattered, demonstrating that the variance of experimental observations were constant for all the values of response depicted in Table 3. The data points obtained were between ±4.17431, which implied that no response transformation was needed for the experimental design of this study (Myers and Montgomery 2002).

3.4 Analysis of variance (ANOVA)

The analysis of variance (ANOVA) for the regression models equation (4) and (5) are summarized in Table 4 and 5. A model is significant at the 95% confidence level if the Fisher F-test has a probability value (Prob > F) below 0.05. The lack of fit (F-test) describes the deviation of actual points from the fitted surface, relative to pure error (Anderson and Whitcomb 2005). Coefficients of determination (R^2) values were also used to evaluate the fitness of the model equations in predicting the experimental responses. Higher the R^2 value implies higher the degree of correlation between the experimental and predicted values. A high R^2 value is desirable and a reasonable agreement with adjusted R^2 is crucial (Ghafari et al. 2009). Adequate precision (AP) is defined as a measure of the experimental signal to noise ratio (Anderson and Whitcomb 2005); an AP that exceeds 4 usually indicates that the model will give reasonable performance in prediction. PRESS, the prediction error sum of squares, is a measure on how well the model for the experiment is likely to predict the responses in a new experiment. The SD, CV and PRESS values are preferred to be small (Montgomery 2005).

Table 4: ANOVA for yield model response

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	515.52	3	171.84	1188.96	< 0.0001	Sig
A-TEMP.	374.01	1	374.01	2587.75	< 0.0001	
B-TIME	127.20	1	127.20	880.10	< 0.0001	
C-CONC	14.31	1	14.31	99.02	< 0.0001	
Residual	1.16	8	0.1445			
Lack of Fit	1.07	5	0.2138	7.33	0.0659	Not Sig
Pure Error	0.0875	3	0.0292			
Cor Total	516.68	11				
Std. Dev.	0.3802		**R²**	0.9978		
Mean	65.40		**Adj. R²**	0.9969		
C.V. %	0.5813		**Pred. R²**	0.9936		
			Adeq Precision	110.823		

The validity of the models were further justified through analysis of variance (ANOVA). Values of p less than 0.05 indicate that the model terms are significant. From Table 4, it can be seen that the prediction of the model is significant with F-value of 1188.96 and p values less than 0.0001 indicating that the regression model equation is extremely significant and highly reliable. A, B and C were significant model terms to the response. The insignificant model terms are removed from the model equation in order to view the impact of the dominant process variables on the performance indicators.

Table 5: ANOVA for percentage MB adsorption model response

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	146.53	3	48.84	1541.19	< 0.0001	Significant
A-TEMP.	71.40	1	71.40	2252.92	< 0.0001	
B-TIME	72.60	1	72.60	2290.79	< 0.0001	
AB	2.53	1	2.53	79.87	< 0.0001	
Residual	0.2535	8	0.0317			
Lack of Fit	0.2367	5	0.0473	8.41	0.0548	not significant
Pure Error	0.0169	3	0.0056			
Cor Total	146.79	11				
Std. Dev.	0.1780		**R²**	0.9983		
Mean	92.95		**Adj. R²**	0.9976		
C.V. %	0.1915		**Pred. R²**	0.9952		
			Adeq Precision	116.7514		

However, the effects of activation temperature and time process variables were more greater than the concentration on the product yield of the activated carbon. The lack of fit of 7.33 implies there is a chance that this large value of 6.59% could occur due to the noise.

Results obtained for the analysis of variance (ANOVA) for the efficiency of MB dye adsorption is shown in Table 5. It can be seen that the prediction of the model is significant with F-value of 1541.19 and p values less than 0.0001 indicating that the regression model equation in this study is extremely significant and highly reliable. A, B and AB were significant model terms to the response. However, the effects of activation temperature-A and time-B were greater than the interactive term-AB on efficiency of MB dye adsorption. The insignificant model terms are removed from the model equation in order to depict the effects of the key process variables on the performance indicators. The lack of fit of 8.41 implies there is a possibility this large value of 5.48% could occur due to the noise.

3.4.1 Interpretation of regression models and ANOVA

The product yield of activated carbon response (Y1), is described by the model equation (4), which shows that the activation temperature (A), activation time (B) and activating agent concentration (C) had a negative effect on the response (Y1), implying that the activated carbon yield decreased as these terms increased. According to the signs of their coefficients, all linear terms A, B, and AB in Equation (5) had a positive effect on the adsorption capacity of modified groundnut shell activated carbon (MGSAC) for MB dye, with B-activation time having the greatest influence as shown by the magnitude of its coefficient in the model. This implies that the activation time had the greatest influence on the percentage MB dye adsorption.

The ANOVA results for the product yield of MGSAC reveals that all three linear factors, activation temperature (A), activation time (B) and concentration of activating agent (C) had a statistically significant effect on the activated carbon yield while the interaction terms were insignificant. The insignificant model terms are removed from the model equation in order to increase the R^2 value, so as to improve the fitting. The overall significance of the model was high as indicated by its low p-value thus verifying its sufficiency. The R^2 value obtained from the model was pretty high indicating that there was a good correlation between the experimental and the theoretical values from the model. The predicted R-squared, R^2 (pred) value, which is a measure of how well the model predicts a response value was in reasonable agreement with the adjusted R-squared R^2 (adj). The R^2 (adj) and R^2 (pred) should be within approximately 20% of each other to be in reasonable agreement (Das and Mishra 2017). This agreement confirms the good adequacy and predictability of the model. Activation temperature imposed the most significant effect on the yield of activated carbon, and then followed by activation time. This can be seen from their large F-values (2587.75 and 880.09). Activation temperature and activation time plays a vital role in pores development than concentration of activating agent. This is due to the release of volatiles through pore opening and gasification at high temperatures. Essentially, groundnut shell is consisting of cellulose, lignin, and hemicellulose. Activated at high temperature, these polymeric structures decompose and liberate most of the non-carbon elements, mainly hydrogen, oxygen, and nitrogen in the form of tars and gases, leaving the rigid carbon skeleton in the form of aromatic sheets and strips. This result was in agreement with the findings of Auta and Hameed, 2011; Auta, 2012 and Ahmad et al., 2010, that at higher temperature more pores were developed hence surface area increases.

From the ANOVA results for the adsorption percentage of MGSAC for MB adsorption, it was observed that of all the three linear factors, only activation temperature-A, activation time-B and their interaction term AB had a statistically significant effect on the adsorption percentage while the concentration term-C was insignificant. The insignificant model terms were removed from the model equation in order to increase the R^2 value, so as to improve the fitting. Similar results have been reported by Jasper et al. (2021). The magnitude of the coefficient B (activation time) as seen from the model equation, and its F value were highest indicating that the activation time had the most significant effect on the percentage MB adsorption. A high R^2 value was obtained indicating a good association between the measured and the predicted percentage adsorption values. The correlation between the R^2 (pred) and R^2 (adj) were also in agreement.

It can be seen from the results of statistical analysis that the developed models are adequate for the prediction of the MGSAC product yield and the efficiency of MB dye adsorption within the range for investigation. Thus, the model can be used to navigate and explore the design space at 95% confidence level.

3.5 Effects process variables on yield

Figure 8 shows the factors A, B and C have negatively affected the product yield of MGSAC. This implies that the yield of MGSAC decreased with increase in activation temperature, activation time and concentration of activating agent and with activation temperature exerting the most effect on MGSAC yield in the studied range compared to the other factors as can be clearly seen from the nature of the slope of the plot in Figure 7a. The activation temperature is known to influence the pore structure of activated carbon with respect to adsorption capacity (Wang et al., 2020). This implies that the MGSAC produced is porous. At higher activation temperature the yield of MGSAC decreases. Ahmad et al., 2010; Auta and Hameed, 2011 reported similar findings for the preparation of activated carbon from mango-steen peel.

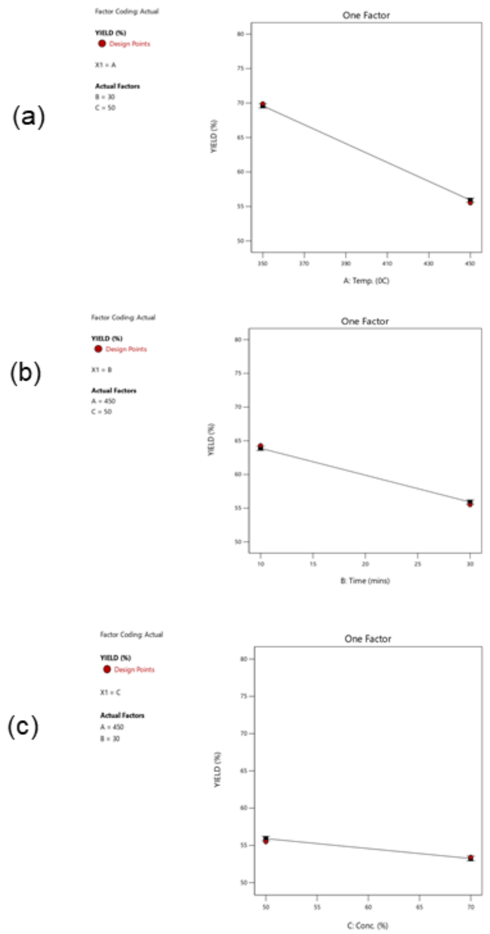


Figure 8: Effects process variables on the product yield of MGSAC (a. activation temperature, b. activation time, and c. concentration of activating agent).

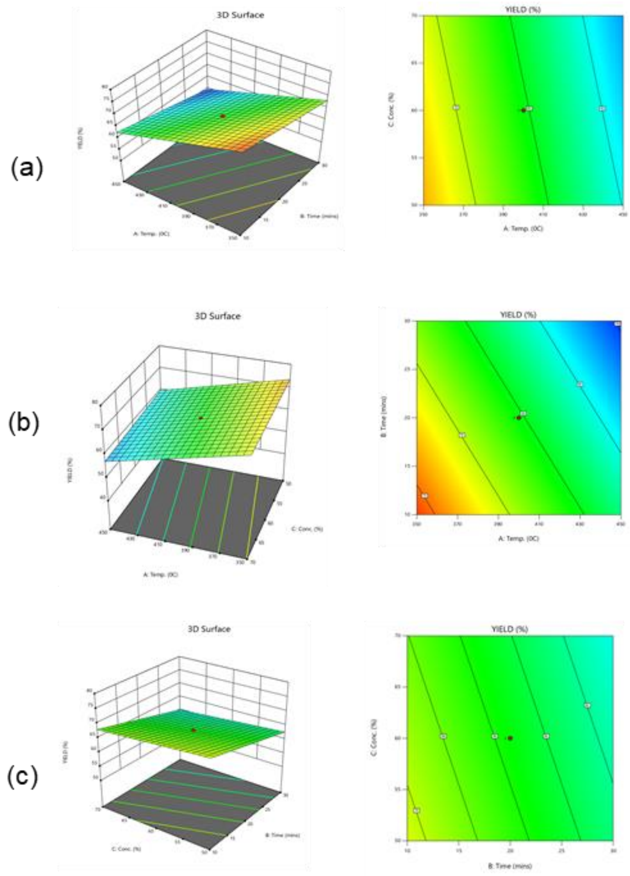


Figure 9: 3D surface and contour plots depicting the influence of process variables on the product yield of MGSAC (a. temperature and time, b. temperature and concentraton, c. concentration and time)**.**

3.6 Response surfaces of product yield

3D surface plots and its corresponding contour plots were plotted for a statistically significant model to understand the interaction of applied operating variables. Figure 9(a) represents the combined effect of activation temperature and concentration of activation agent on the product yield, where activation time was fixed at zero level (20 min). Figure 9(b) illustrates the effect of activation temperature and activation time on the response yield, where concentration of activating agent was fixed at zero level (60 %). adsorption capacity (Wang et al., 2020). Figure 9(c) illustrates the effect of concentration of activating agent and activation time on the product yield, where activation temperature was fixed at zero level (400 ^{0}C). Observing and analyzing Figure 9 completely, it can be concluded that product yield was lowered as the activation temperature and time were increased but did not change significantly as activating agent concentration was increased. By considering Figure 9(a), higher activation temperature resulted to a greater likelihood that the carbon was exposed to the vapor environment. This ultimately offered better prospects for the activation reaction to occur. It is expected that during activation, superior temperatures and prolonged reaction time provided room for more samples to react and more gasification to take place such that there was a corresponding decrease in yield. However, it is pertinent to note that with further reactions taking place at higher temperatures and longer activation times, it was noticeable that more carbon (the desired product) would have been consumed and resulted to a decreased product yield as observed in Figure 9(b). Adel et al. (2010) also observed a similar trend while utilizing beans husk and rice husk together with HCl as the activation agent for activated carbon production. Hence, activation temperature played a vital role in the production of MGSAC. From Figure 9 (c), it was evident that the yield of activated carbon did not change significantly as the concentration of activating agent was increased. When we analyzed the plot by considering the effect of concentration and time, it was observed that as activation time increases, its effects on the response yield was more significant than corresponding increase in concentration of activating agent. This is due to the fact that increase in activation time provided room for more samples to react and more release of the volatile materials from the groundnut shells which ultimately results in decrease in yield. The results obtained were in agreement with the work done by Ahmad and Alrozi (2010) where concentration of activating agent was less significant compared to activation time.

3.7 Effect of process variables on adsorption of Methylene Blue (MB) Dye

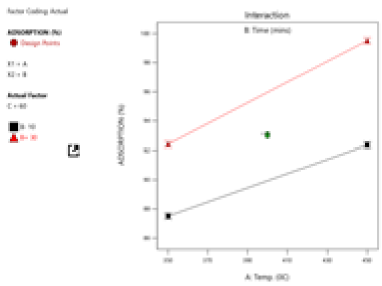


Figure 10: Effects of main process variables temperature and time on methylene blue dye adsorption.

From Figure 10, it can be observed from the nature of the slope of the plot that the activation time exerted the greatest effect on MB adsorption by the MGSAC though the activating agent concentration has no effect on percentage MB adsorption. The increase in the activation temperature from 350 ° C to 450 ° C leads to an opening and a widening of the pores, which increases the adsorption efficiency of MB on the activated carbon prepared. Indeed, when the activation time varies between 10 to 30min, the micro-porosity increases, which gives activated carbon a better percentage MB adsorption due to better development of the porosity. In the same way, it can be inferred that the concentration term has no significant effect on the percentage MB adsorption, though an increase in the concentration of the activating agent (Na_2EDTA and H_3PO_4) from 50% to 70% promotes the development of pores and surface functional groups on the surface of produced activated carbon.

3.8 Response surfaces of adsorption of Methylene Blue (MB) Dye

From Figure 11, the efficiency of MB dye adsorption by MGSAC increased progressively with increase in the activation temperature and time when the relative concentration factors were held constant. Increase in temperature promoted chemical changes that might have occurred in the precursor, resulting to the formation of more pores ready for adsorption. This is a similar trend to the findings reported by Teshome, (2015) and Jawad et al. (2021).

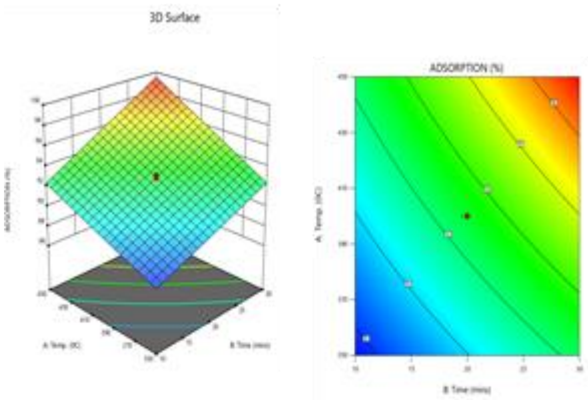


Figure 11: 3D surface and contour plots of the of methylene blue dye adsorption as a function of temperature and time at fixed concentration.

At high temperature and activating agent concentration of 70%, there was a decrease in MB adsorption. This could be attributed to the excessive carbon burnt-off at higher temperature and high concentration resulting to the widening of pore diameters and collapse of pore walls (Saka, 2012 and Atef, 2016). However, the percentage MB adsorption by MGSAC decreased again as activation time and temperature decreases. In the lower stages, the adsorption trend can be attributed to the partial conversion of the impregnated groundnut shells to activated carbon owing to inadequate activation temperature and activation time. Kundu et al., 2015 reported a similar trend in their research.

Another explanation could be that the high percentage MB adsorption by MGSAC may also be attributed to Na_2EDTA used during the impregnation since it contains two amine groups and four carboxyl groups and during activation, these chemicals would have reacted with the carbon precursor at high temperature, and the oxygen and nitrogen heteroatoms derived from Na_2EDTA were introduced into the carbon skeletons, resulting in the augmentation of the adsorption ability of the MGSAC towards MB dye. Therefore, it can be concluded that oxygen and nitrogen heteroatoms were introduced on the surface of MGSAC at high activation temperature and time which further enhanced the MB adsorption by MGSAC. Hai et al., 2021 have reported similar results in their research for enhancing the surface functionality and introducing specific surface functionalities on activated carbon from wetland biomass via in-situ modification during phosphoric acid activation. Wang et al., 2017 in their research for preparation of nitrogen-doped carbons by ammonium acetate activation for adsorption of dye reported similar trend. They concluded that after modification, some oxygen-containing and nitogen-containing functional groups were introduced into the carbon's surface, which provided more heterogeneous high-energy sorption sites, and enhanced the adsorption for pollutants. Guo et al., 2016 in their research synthesized high-quality activated carbon with enhanced porosity and functionality (acidity and basicity), large surface area, favorable surface functional groups and excellent adsorptive performance via insitu-modification of lignocellulosic precursors with (i.e. NH3H2O, urea, and NH4HCO3) while H3PO4 was used as the activating agent. They concluded that this innovative method also provides an alternative route to prepare activated carbon with a decreased impregnation concentration and activation temperature, which is preferred for industrial-scale production as it substantially reduce the costs. Hence, Na_2EDTA played a vital role in percentage MB adsorption by MGSAC.

3.9 Process optimization

The strategy employed for the optimization of the performance indicators at the expense of the dominant key process variables was multi-objective optimization approach with the aid of Design-Expert software evaluation version 13.0.1.0 (STAT-EASE Inc., Minneapolis, USA). The best solution with the highest desirability for optimization within the experimental range of the studied process variables was selected and verified (Adewoye et al., 2017; Aremu et al., 2017).The optimum MGSAC was obtained by using H_3PO_4 concentration (50%) with 35mmol Na_2EDTA, activation temperature (450 ^{0}C) and activation time (30 min) resulting in 99.508% removal of methylene blue and 55.913% of activated carbon yield.

3.9.1 Validation of model

The model validation was carried out under predicted conditions by the developed model and the predicted values were found to agree satisfactorily with the experimental values as shown in Table 7, with an error of 0.74% and 0.1% for the activated carbon yield and efficiency of methylene blue dye adsorption, respectively.

Table 6: Model validation

A (°C)	B (min)	C mmol, (%)	MGSAC Yield, Y_1 (%)		MB dye Adsorption Y_2 (%)	
			Predict.	**Experi.**	**Predict.**	**Experi.**
450	30	50	55.91	55.50	99.51	99.60

The predicted values from the models for the production of MGSAC were found theoretically and observed to be in close agreement with the values obtained from experiment. Thus, the full factorial designs can be considered as an effective technique for examining the influence of process variables.

4. Conclusions

Modification of groundnut shells based activated carbon (MGSAC) with ethylene-diaminetetraacetic acid disodium salt (Na_2EDTA) as a modifier in the course of simultaneous chemical and physical activation with phosphoric acid and nitrogen gas activation, respectively was successfully produced with the highest of yield of 77.7% at 350 ^{o}C and 30 minutes, 70% concentration of activating agent, and utilized for the adsorption of methylene blue (MB) dye under ambient condition. The indicator of the MB dye adsorption shows 99.6% percentage removal. That was obviously attributed to the modification of MGSAC with Na_2EDTA. Two-level full factorial experimental design was deployed to examine the effects of activation and carbonization temperature, activation time and concentration of activation agent on MGSAC yield and percentage MB adsorption. From the analysis of the data, the activation and carbonization temperature were found to have the most significant effect on the produced MGSAC yield. Upon optimization of the performance indicators of the product and process, the experimental values obtained for the activated carbon yield and percentage MB dye adsorption were found to be in agreement with the values predicted by the models. The optimum conditions were activation and carbonization temperature of 450 °C, activation time of 30 min and activating agent concentration of 50% H_3PO_4 with 35mmol of modifier, Na_2EDTA which gave 55.5% MGSAC yield with a wonderful performance of 99.3% MB dye adsorption under ambient condition. These promising results show that the produced MGSAC can be a good adsorbent for the adsorption of MB dye from aqueous solutions.

Conflict of Interest

The authors declare that there is no known conflict of interest.

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