Research Article

Optimization of the preparation of *Millettia thonningii* seed pods activated carbon for use in the remediation of dye-contaminated aqueous solutions

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Abstract

An increasing research interest in the use of waste-derived activated carbon in the remediation of contaminated water as a renewable alternative to commercial activated carbon has been noted. This research evaluates the optimization of the preparation of activated carbon from *Millettia thonningii* seed pods for application in the removal of synthetic dyes from aqueous solutions. The Box–Behnken experimental design, a subset of response surface methodology is employed in this research as it provides an economical strategy to optimize the process using a minimal number of experiments. The effect of preparation factors such as activation temperature, activation time and impregnation ratio on the preparation process was evaluated and these conditions optimized by maximizing the activated carbon yield and the adsorption efficiencies of two synthetic dyes, Basic Violet 3 and Basic Blue 9. The optimal conditions established were activation temperature of 400 °C, activation time of 30 min and impregnation ratio of 2.0. The activated carbon yield, Basic Violet 3 and Basic Blue 9 adsorption efficiencies approached 39.12%, 83.25% and 91.05% respectively under these optimal experimental conditions. The optimized activated carbon was characterized via physicochemical and proximate analysis, Fourier transform infrared spectroscopy and scanning electron microscopy. *Millettia thonningii* seed pods activated carbon produced at the optimum activation conditions possessed desirable properties such as low ash content, low moisture content and suitable bulk density. The activated carbon also holds great potential for application in the removal of hazardous synthetic dyes from wastewater.

Keywords Activated carbon · Optimization · Desirability function · Box–Behnken design · *Millettia thonningii*

Abbreviations

RSM	Response surface methodology
BBD	Box–Behnken design
°C	Degrees centigrade
OFAT	One factor at a time
BV3	Basic Violet 3
BB9	Basic Blue 9
MTSP	*Millettia thonningii* seed pods
MTSPAC	*Millettia thonningii* seed pods activated carbon
ANOVA	Analysis of variance
FTIR	Fourier transform infrared
A	Activation temperature
B	Activation time
C	Impregnation ratio
Y_1	Activated carbon yield
Y_2	Basic Violet 3 adsorption efficiency
Y_3	Basic Blue 9 adsorption efficiency
D	Desirability function
DF	Degrees of freedom
Adj SS	Adjusted sum of squares
Adj MSS	Adjusted mean of sum of squares

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1 Introduction

Activated carbon is a versatile adsorbent used extensively in a wide array of industrial applications. It is the most conventional adsorbent used in treatment of water and wastewater. Its use, however, is limited in developing countries and small-scale industries due to the high cost of commercial activated carbon. This limitation has prompted research into the production of activated carbon from agricultural residues. Agricultural residues generally constitute waste with little or no economic value and often present a disposal problem [1], therefore, their sustainable conversion into valuable products such as adsorbents, is essential. Agricultural residues have the advantage of offering readily-available, low-cost, effective, and renewable precursor alternatives, thereby reducing the production cost of activated carbon. In addition to this economic benefit of providing low-cost precursors, they also provide environmental benefits because converting them into value-added products reduces the ecological burden of agricultural residues.

In this research, *Millettia thonningii* seed pods, an agricultural residue, is used as a precursor for the preparation of activated carbon. *Millettia thonningii* is a tropical deciduous plant that belongs to the family *Fabaceae* and subfamily *Papillonoideae*. It is native to Congo, Cote d'Ivoire, Democratic Republic of Congo, Ghana, Nigeria, and Togo. Its seed pods usually fall off when dry, becoming a residue, with little commercial value, except for use as wood fuel [2]. As far as known to the authors, there are no reports on the preparation of activated carbon from *Millettia thonningii* seed pods.

The experimental conditions employed in the preparation of activated carbon play a significant role in determining its suitability for use in specific applications. Optimizing these conditions for a desirable product is critical. In traditional multifactor experiments, optimization is achieved using the one-factor-at-a-time (OFAT) approach, where one factor is kept constant while varying other factors. This conventional approach is expensive because it requires a large number of experiments and is time-consuming [3]. It also cannot estimate the interactions among the factors [4]. These limitations can be overcome by applying an experimental design strategy. Response surface methodology (RSM) is one of such strategies. It is a collection of statistical and mathematical techniques used in the optimization of processes where the intended response is influenced by a number of factors [5]. The main advantages of the RSM over the OFAT method are the reduced number of experimental trials which still provide statistically valid results, and the fact that RSM evaluates the statistical significance of multiple parameters or factors and their interactions [6, 7]. It has been widely applied to various processes including the preparation of activated carbons [8–10]. One of the most common and efficient designs used in response surface methodology is the Box–Behnken design [11]. In this study, the Box–Behnken design (BBD) is employed in the preparation of activated carbon from *Millettia thonningii* seed pods with the aim of optimizing the preparation process factors in order to obtain a product with a high yield and high adsorption efficiencies for model synthetic dyes, Basic Violet 3(BV3) and Basic Blue 9 (BB9).

1.1 The Box–Behnken experimental design

The Box–Behnken design (BBD) is a class of rotatable or nearly rotatable second-order designs based on three-level, incomplete factorial designs [12]. The number of experiments (*N*) usually required for the development of the Box–Behnken Design is defined as:

$$N = k^2 + k + p \quad (1)$$

where *k*, is the number of variables or factors and *p*, is the number of the center points. The Box–Behnken design ensures that a reasonable understanding of the dependence of responses on the process or experimental factors is achieved. It helps the researcher to determine the values of the factors that will ensure that the required response parameters are optimized by carrying out a minimal number of experiments. The BBD is most advantageous when compared to other response surface designs because it requires a few experimental points for its application and has high efficiency [11]. It also does not contain combinations for which all factors are simultaneously at their highest or lowest levels, thus avoiding experiments performed under extreme conditions which may perhaps lead to unsatisfactory results [11]. Even though the Box–Behnken design is a popular optimization tool, only a few researchers have employed its use in the production of activated carbon from agricultural residues, such as coconut shell [8], *Limonia acidissima* shell [10] and banana pseudo stem [13]. The current study uses a 3-factor-3-level Box–Behnken design to evaluate the effects and interaction of activation temperature, activation time, and impregnation ratio on the production of activated carbon from *Millettia thonningii* seed pods. The ranges and levels of the process factors selected for this study are given in Table 1.

Table 1 Levels of process factors in the Box–Behnken experimental design

Factor	Code	Box–Behnken levels		
		Low (− 1)	Middle (0)	High (+ 1)
Activation temperature (°C)	A	400	500	600
Activation Time (min)	B	30	45	60
Impregnation Ratio	C	1	1.5	2

2 Methods

Millettia thonningii seed pods (MTSP) were obtained from Zaria, Kaduna State, Nigeria, washed with distilled water and air dried for 7 days to eliminate moisture. The dried seed pods were crushed in a ball mill, screened to a particle size of 2–4 mm using standard sieves and preserved in clean sample containers. All reagents used were of analytical grade. De-ionized water was used to prepare all the solutions and reagents used in this study.

2.1 Preparation of *Millettia thonningii* seed pods activated carbon (MTSPAC)

A total of 15 experimental runs, which included three replicated center points were developed by the BBD for the optimization of the preparation of MTSPAC. The complete design matrix based on the range of process variables, generated by the Minitab Software, Version 17.0 (Minitab Inc., USA) is presented in Table 2. The activated carbons were prepared as follows:

About 2.44 mL, 4.41 mL and 5.88 mL of phosphoric acid (H_3PO_4, 85%) were diluted to 10 mL and mixed separately with 5 g of raw MTSP in 30 mL porcelain crucibles in order to obtain the impregnation ratios depicted in the experimental design matrix presented in Table 2. The impregnation ratio is defined as the ratio of the mass of the activating agent to the mass of the raw sample used that will be converted into activated carbon [10]. The mixtures were left to soak for 1 h at room temperature to increase acid penetration into the raw biomass. The impregnated MTSP samples were then heated to 110 °C for 1 h in an oven and later transferred into a furnace set to temperatures and carbonization times according to Table 2. At the end of the pyrolysis process, the samples were gradually cooled in a desiccator. The resultant activated carbons were washed thoroughly with water to remove the residual acid until the pH of the filtrates reached 7. The activated carbons were set to dry for 1 h at 100 °C after which they were screened to particle size 1–2 mm and then packed in sealed bottles till further use.

2.2 Evaluation of the performance of the activated carbon preparation process

The performance of the activated carbon preparation process was evaluated by determining the percentage yield of the activated carbons produced as well as their adsorption efficiencies for BV3 and BB9 dyes. The percentage yield of the activated carbons was calculated as the ratio of the weight of dried activated carbon to the initial weight of the precursor (MTSP) expressed as a percentage. The adsorption efficiencies were derived from adsorption experiments.

2.3 Adsorption experiments

Batch adsorption experiments were performed by contacting 0.1 g of each of the prepared activated carbons with 50 mL of 20 mg/L of each dye solution in stoppered 250 mL Erlenmeyer flasks. The pH of the solutions was not adjusted. Each flask was agitated at a constant speed on a top loading orbital shaker for 60 min at ambient temperature. The mixtures were centrifuged at 1500 rpm and the supernatants analyzed for residual dye concentration at 590 nm for BV3 and 664 nm for BB9 using a UV–visible spectrophotometer (CARY 300, Agilent Technologies). The dye adsorption efficiency was calculated by using Eq. (2).

$$\textit{Adsorption}\ \text{(Removal) efficiency (\%)} = \frac{C_o - C_e}{C_o} \star \tag{2}$$

where C_o and C_e (mg/L) is the liquid phase concentrations of dye at initial and at equilibrium respectively. All adsorption experiments were carried out in two replicates.

2.4 Statistical analysis and optimization

The resulting experimental data were regressed in order to derive suitable second-order polynomial regression model equations which were used to express each predicted response (Y) as a function of the independent preparation variables (factors). A general representation of the regression model equation is expressed by Eq. (3)

$$\begin{aligned} Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 \\ + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \end{aligned} \tag{3}$$

where $\beta_{0\text{-}23}$, are regression coefficients (β_0 is a constant term which corresponds to the response when the value of β_i is zero for each parameter; β_1, β_2, and β_3 are linear effect terms; β_{11}, β_{22} and β_{33} are the square effect terms and β_{12}, β_{13} and β_{23} are cross product or interactive effect terms). A, B, and C are the coded independent variables that represent the important factors affecting the process being carried out and Y is the particular response being evaluated. The second-order polynomial equations are employed to compare and correlate the independent activated carbon preparation variables or factors (activation time, activation temperature and impregnation ratio) and the dependent variables or responses (activated carbon yield, BV3, and BB9 adsorption efficiencies). No transformation was chosen while analyzing the responses. For each response, a full quadratic model was selected after which each model was reduced by removing insignificant quadratic and interaction terms.

The adequacy of the regression models was justified via an analysis of variance (ANOVA) with the predictability of the models set at 95% (α-level of 0.05) confidence level. The ANOVA includes Fisher's F-test and its associated probability, *p (F)* which helps determine the overall model significance. Correlation coefficients (R^2) were also used to measure the goodness of fit of the regression models. Response surface plots, which are three dimensional representations of a response plotted as a function of the factors, were also generated to visualize the effects of the factors and their interactions on the responses. The predicted models were used to simultaneously determine the optimum settings of the preparation factors that can produce MTSP activated carbon of highest yield and highest adsorption efficiencies for the selected dyes. Once the optimum settings for the preparation conditions were obtained, they were validated by preparing activated carbon at those optimal conditions and the responses compared with the predicted values.

2.5 Characterization of the MTSPAC produced at optimal conditions

Physicochemical, proximate, functional group and surface morphological analyses were used to characterize *Millettia thonningii* seed pods activated carbon prepared at optimal conditions.

2.6 Physicochemical and proximate analysis

The percentage moisture content, volatile matter, ash content, pH and electrical conductivity were determined using standard ASTM procedures. The fixed carbon content was computed by subtracting the sum of moisture content, volatile matter and ash content from 100. Bulk density was determined as described by Lima and Marshall [14] while the specific surface area of the activated carbon was estimated using Sear's method [15]

2.7 Fourier transform infrared (FTIR) spectroscopy

Fourier Transform Infrared Spectrometry (FTIR) was used to analyze the organic functional groups present in the activated carbon and its precursor. The FTIR spectrum was carried out at the range of 650–4000 cm^{-1} with a spectrometer (FTIR-CARY 630, Agilent Technologies).

2.8 Scanning electron microscopy (SEM)

A Phenom Pro X scanning Electron microscope, (Eindhoven, Netherlands) was used to explore the surface morphology of the *Millettia thonningii* seed pods and the activated carbon prepared under optimal conditions.

3 Results and discussion

The complete experimental design matrix and the values of all the responses obtained from the experiments are depicted in Table 2. The yield for the different activated carbons prepared ranged from 35.26 to 41.38% while the adsorption efficiencies of BV3 and BV9 ranged from 22.11 to 97.51% and 44.16 to 97.44% respectively.

The BBD was applied to the experimental data and used to develop a second-order polynomial equation in order to compare and correlate the independent activated carbon preparation variables or factors (activation time, activation temperature and impregnation ratio) and the dependent variables or responses (activated carbon yield, BV3, and BB9 adsorption efficiencies). The ANOVA for the three quadratic models is presented in Table 3. ANOVA determines the statistical significance of the model and the effects of the individual process factors and the interactions between them on the response. It expresses the accuracy of the actual relationship between the response and significant factors as represented by the model equation, in other words, it describes the fitness of the model to experimental data. The significance of a process or experimental factor is determined by the values of Fisher's F-test (F) and *Prob > F (p)*. A larger value of *F* and a smaller the value of *p*, indicate that a factor is more significant [16]. "*p*" values less than 0.05, demonstrates that the influence of the corresponding factor on the response is statistically significant. The final empirical regression model equations in terms of activated carbon yield (Y_1), BV3 removal (Y_2) and BB9 removal (Y_3) are given in Eqs. (4–6). The suitability of the model equations in predicting the experimental responses was also assessed via the coefficient of determination (R^2) value. An R^2 value closer to 100% validates the fitness of the model. This implies that, the more the R^2 value approaches 100%, the higher the degree of correlation between the

Table 2 Box–Behnken experimental design matrix for optimization of the production of *Millettia thonningii* seed pods activated carbon

Run	A: Activation temp (°C)	B: Activating time (min)	C: Impregna-tion ratio	% Yield Y_1	% BV3 Y_2	% BB9 Y_3
1	500	60	1.0	40.78	45.47	46.30
2	500	45	1.5	39.68	55.45	47.86
3	500	60	2.0	37.76	97.51	90.60
4	600	45	2.0	35.26	90.44	94.59
5	500	45	1.5	39.60	55.56	47.53
6	500	30	1.0	40.96	45.78	44.16
7	400	45	2.0	38.58	84.45	94.30
8	500	45	1.5	39.56	55.22	47.58
9	600	60	1.5	36.36	90.33	97.44
10	600	45	1.0	37.62	74.22	88.44
11	400	60	1.5	39.40	68.89	84.02
12	500	30	2.0	38.12	87.67	85.73
13	400	30	1.5	40.50	62.89	73.76
14	600	30	1.5	36.46	82.45	92.88
15	400	45	1.0	41.38	22.11	44.73

Table 3 ANOVA for response surface quadratic model for MTSPAC yield, BV3 and BB9 uptake

Source	DF	Adj. SS	Adj.MS	*F* value	*P* value	
MTSPAC Yield						
Model	5	47.1741	9.4348	331.86	< 0.001	
A:Activationtemperature	1	25.0632	25.0632	881.57	< 0.001	
B: Activation time	1	0.3785	0.3785	13.31	0.005	
C: Impregnation, ratio	1	15.1801	15.1801	533.94	< 0.001	R-sq: 99.46%
A^2	1	6.3024	6.3024	221.68	< 0.001	R-sq(adj): 99.16%
AB	1	0.2500	0.2500	8.79	0.016	R-sq(pred): 98.44%
Error	9	0.2559	0.0284			S: 0.16861
BV3 adsorption efficiency						
Model	6	6265.66	1044.28	68.60	< 0.001	
A:Activation temperature	1	1227.76	1227.76	80.65	< 0.001	
B: Activation time	1	68.57	68.57	4.50	0.067	
C: impregnation ratio	1	3718.61	3718.61	244.27	< 0.001	R-sq: 98.09%
A^2	1	335.79	335.79	22.06	0.002	R-sq(adj): 96.66%
AC	1	531.73	531.73	34.93	< 0.000	R-sq(pred): 89.56%
Error	8	121.78	15.22			S: 3.90168
BB9 adsorption efficiency						
Model	8	6860.56	857.57	36.86	< 0.001	
A:Activation temperature	1	732.30	732.30	31.48	0.001	
B:Activation time	1	59.57	59.57	2.56	0.161	
C:impregnation ratio	1	2505.97	2505.97	107.71	< 0.001	
A^2	1	2611.14	2611.14	112.23	< 0.001	
B^2	1	602.63	602.63	25.90	0.002	
C^2	1	144.94	144.94	6.23	0.047	R-sq: 98.01%
AB	1	8.12	8.12	0.35	0.576	R-sq(adj): 95.35%
AC	1	471.32	471.32	20.26	0.004	R-sq(pred): 78.82%
Error	6	139.60	23.27			S: 4.82347

DF degrees of freedom, *Adj. SS* adjusted sum of squares, *Adj MS* adjusted mean of squares experimental and predicted values, hence the higher accuracy of the obtained model.

3.1 Evaluation of the effect of preparation factors on the responses

3.1.1 Activated carbon yield (Y_1)

The ANOVA result for activated carbon yield (Table 3) revealed that temperature had the greatest influence on the activated carbon yield as it had the highest *F* value of 881.57 closely followed by impregnation ratio with F value of 553.94 and lastly, activation time. All three linear factors had a significant effect on the activated carbon yield since their *p* values are < 0.05. The overall significance of the model was high as indicated by its low *p* value of < 0.001 thus verifying its sufficiency. The activated carbon yield as described by the model equation Eq. (4) reveals that, activation temperature (*A*), activation time (*B*) and impregnation ratio (C) and the square term of activation temperature (A^2) had an antagonistic effect on the response (Y_1), in other words, the yield decreased as these terms increased.

$$Y_1(\text{activated carbon yield}) = 39.49 - 1.77A - 0.22B - 1.38C - 1.30A^2 + 0.25AB \quad (4)$$

The magnitude of the coefficients gives an indication of the extent of influence a term or factor has on the response variable, while the sign of the coefficient depicts the direction of the influence the factor has on a response variable. The positive sign of the coefficients in a regression equation indicates a synergistic effect, while the negative sign represents an antagonistic effect on the response [17]. The suitability of the model equations in predicting the experimental responses was also assessed via the coefficient of determination (R^2) value. An R^2 value closer to 100 percent validates the fitness of the model. This implies that, the more the R^2 value approaches 100 percent, the higher the degree of correlation between the experimental and predicted values, hence the higher accuracy of the obtained model. The magnitude of the coefficient of *A* was the highest of all linear term coefficients showing that *A* (activation temperature), had the most effect on the activated carbon yield. Similar observation was made by Salman [18] and Das and Mishra [10] in the preparation of activated carbon from palm fronds and *Limonia acidissima* respectively. Interaction term, *AB* had a synergistic effect on the yield depicting that there would be an increase in carbon yield with increasing magnitude of these factors. The R^2 value (Table 3) obtained from the model was 99.46%, 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 good the model predicts a response value was 98.44%. This is in reasonable agreement with the "adjusted *R*-squared [R^2 *(adj)*] of 99.16%. The R^2 *(adj)* and R^2 *(pred)* should be within approximately 0.20 or 20% of each other to be in reasonable agreement [10, 19]. This agreement confirms the good predictability and adequacy of the model.

3.1.2 Basic Violet 3 adsorption efficiency (Y_2)

An overall model *F* value of 68.60 with *p* value less than 0.001 for BV3 adsorption verified the sufficiency of the model as shown in Table 3. The regression model equation for BV3 adsorption is given in Eq. (5)

$$Y_2(BV3\ \%\ adsorption) = 57.06 + 12.39A + 2.93B + 21.56C + 9.51A^2 + 10.81B^2 - 11.53AC \quad (5)$$

From the results of the ANOVA in Table 3 and the regression model Eq. (5), model terms; *A* (activation temperature), *C* (impregnation ratio), and square terms, A^2 and B^2 had significant synergistic effects on the BV3 removal, thus as these terms increased, there was an increase in BV3 adsorption. The interaction term, AC, had a significant antagonistic effect on the response Y_2. The magnitude of coefficient C (impregnation ratio) as seen from the model equation, and its F value (244.27) were highest indicating that the impregnation ratio had the most significant effect on the dye removal closely followed by activating temperature. It is important to note that the activating time did not significantly influence the response Y_1 having a *p*-value of 0.067, but was however still retained in the model because of hierarchy. A high R^2 value of 98.09% was obtained indicating a good correlation between the measured and the predicted BV3 adsorption efficiency values. The correlation between R^2 *(pred)* (96.66%) and R^2*(adj)* (89.56%) was satisfactory.

3.1.3 Basic Blue 9 adsorption efficiency (Y_3)

Results of the ANOVA shows the high significance of the model having a *p* value of 0.001 (Table 3). The impregnation ratio (C) was the most predominant factor with an *F* value of 107.71 and *p* values < 0.001. Amri et al, [20] reported a similar effect of impregnation ratio on BB9 adsorption efficiency in the optimization of the preparation of activated carbon from Pink Guava waste. The model equation, Eq. (6) and Table 3 also revealed a significant synergistic effect of linear terms *A* and *C*, all square terms and a significant antagonistic effect of the interaction between activation temperature and impregnation ratio (*AC*) on the BB9 removal efficiency.

$$Y_3(BB9\ \%\ adsorption) = 47.66 + 9.57A + 2.73B + 17.70C + 26.59A^2 + 12.78B^2 + 6.27C^2 - 1.42AB - 10.86AC \quad (6)$$

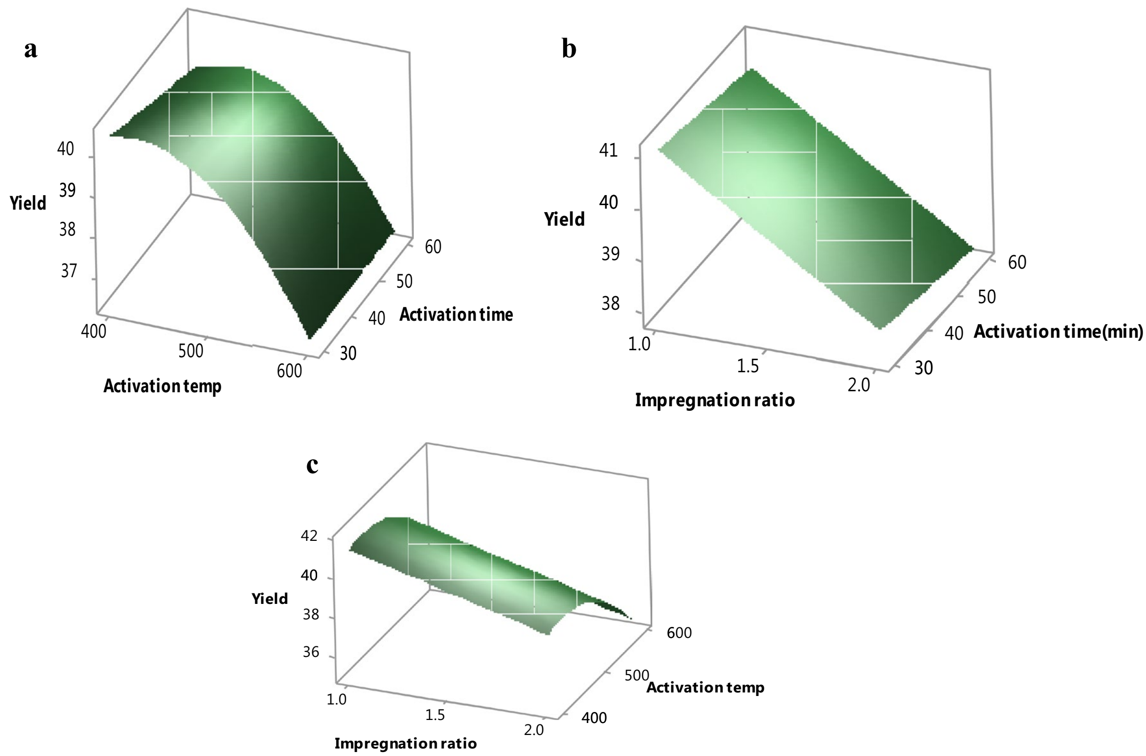

Fig. 1 3-D Response Surface Plots of Activated Carbon Yield as a function of **a** Activation temperature and Activation time. **b** Impregnation ratio and Activation time. **c** Impregnation ratio and Activation temperature at holding values of Impregnation ratio 1.5, Activation temperature 500 °C and Activation time of 45 min

The correlation between the experimental and the theoretical responses calculated by the model was also satisfactory (R^2 = 98.01% and R^2 *(adj)* = 95.35%).

The statistical results obtained showed that the three regression models developed were suitable in describing the correlation between the experimental factors and the responses within the range of factors studied.

3.2 Evaluation of the interaction effects of preparation factors on responses

3-D response surface plots as a function of two variables at a time while maintaining the third variable at fixed levels were used to show how the fitted response relates to two continuous variables. The 3-D response surface plots were generated using version 17.0 of Minitab Software, The 3-D plots are a graphical representation of the regression model equations [21] and they simplify the analysis of the effects of activated carbon preparation process factors on the responses. The effects of activation temperature, activation time and impregnation ratio on the activated carbon yield, BV3, and BB9 percent uptake are presented as response surface plots in Figs. 1, 2 and 3.

Figure 1a shows a curvature which indicates a good interaction effect between activation temperature (A) and activation time (B) on the activated carbon yield, at constant impregnation ratio (1.5). The results clearly show that the carbon yield decreases with increasing activation temperature and activation time. Figure 1b and c also show that increasing impregnation ratio had an effect on the activated carbon yield as well. The activated carbon yield was strongly affected by the temperature, where increasing temperature and impregnation ratio decreased the yield and increased the carbon burn-off. Overall, the yield of the prepared activated carbon was found to decrease with increasing activation temperature, activation time and impregnation ratio. Increase in temperature would cause an increase in the release of volatiles due to intense dehydration. This would consequently result in a decrease in carbon yield. An increase in the activation time and impregnation ratio would also cause more volatile matter to be released, leading to a decrease in carbon yield. Figure 2a–c illustrate response plots for the BV3 adsorption. The interaction between activation temperature and the impregnation ratio was found to have a significant effect on the BV3 adsorption, whereas the other combinations showed less effect. BV3 adsorption efficiency reached a maximum with increasing impregnation ratio and lower temperatures (between 400 and 450 °C).The 3-D plots for BB9 removal are shown in Fig. 3a–c. The highest BB9 percent adsorption

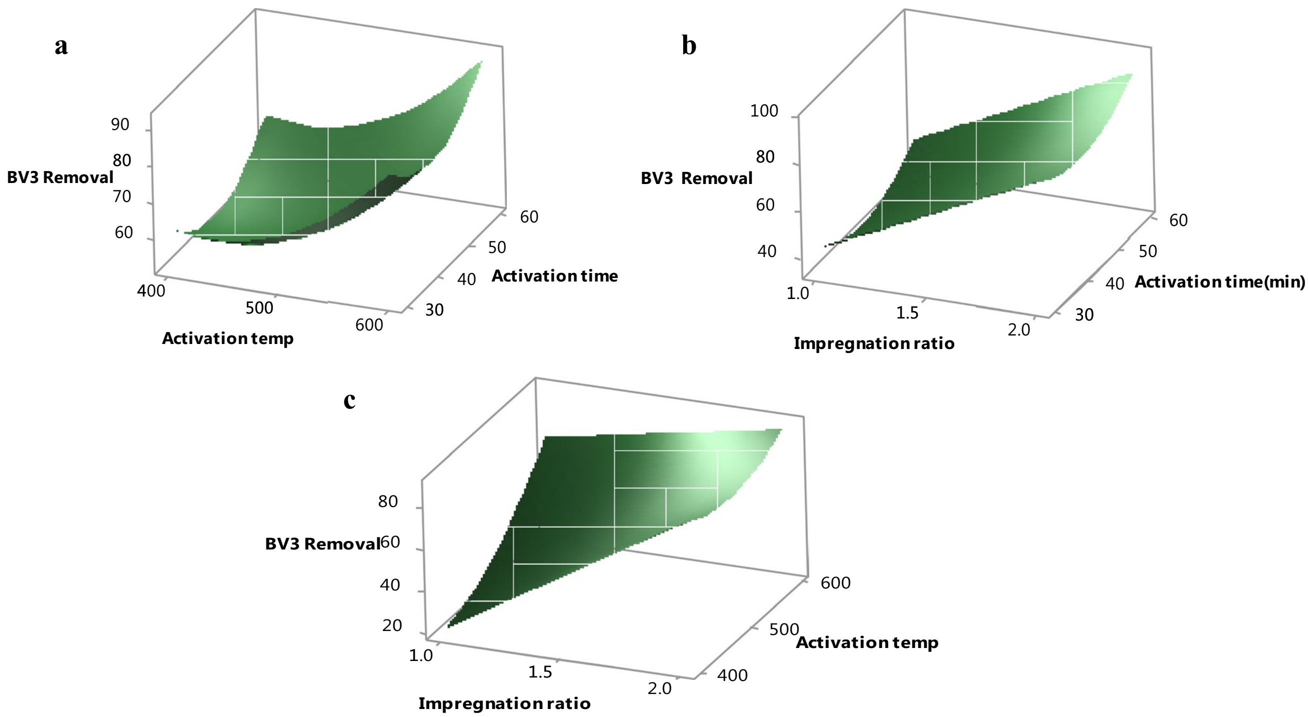

Fig. 2 3-D Response Surface Plots for BV3 removal as a function of **a** Activation temperature and Activation time. **b** Impregnation ratio and Activation time. **c** Impregnation ratio and Activation temperature at holding values of Impregnation ratio 1.5, Activation temperature 500 °C and Activation time of 45 min

was observed when both impregnation ratio and activation temperature had the highest values within the studied range. A similar observation of an increase in BB9 removal with an increase in activation temperature and impregnation ratio has been reported elsewhere [16].

3.3 Process optimization and validation

In the production of commercial activated carbon, a high product yield and high adsorption efficiencies for the target pollutants are desirable. However, optimizing both responses under the same conditions, usually poses a difficulty, because the regions of interest of each factor are quite different. For instance, at higher temperatures, a lower yield is expected but with the associated increasing pore development a higher adsorption efficiency results. Hence as Y_1 increases, Y_2 or Y_3 will decrease and vice versa. In a bid to determine an acceptable compromise between all three responses simultaneously, the desirability function approach proposed by Deringer and Suich [22] was applied where all the responses parameters were set to maximum. The desirability approach involves the conversion of each predicted response, Y_i, into an individual desirability function, d_i, on the basis of the analysts' preferences while building the optimization procedure [23]. The scale of the desirability function usually ranges between d = 0 (for an unacceptable response value) and d = 1 (for a completely desirable one). *D* is calculated combining the individual desirability values by applying the geometric mean: $D = (d_1 \times d_2 \times \ldots dm)^{1/m}$ where *m* denotes the number of responses and d_1; d_2; d_m are the desirability of various responses. An algorithm is then applied to the *D* function in order to determine the set of variable values that maximizes or minimizes it [11].

The predicted optimal settings of experimental process factors that will obtain MTSPAC with a high yield as well as high adsorption capacities for both synthetic dyes are illustrated in Table 4. The predicted optimal preparation process conditions obtained were as follows: activation temperature 400 °C, activation time 30 min and impregnation ratio 2.0 to achieve activated carbon yield of 39.055%, and BV3 and BB9 adsorption of 95.15% and about 100% respectively as shown in Table 4 with the overall desirability of 0.844. The average activated carbon yield, BV3 and BB9 adsorption efficiencies obtained in the validation experiments were, 39.12%, 83.25%, and 91.05% respectively. Generally, the experimental values obtained were in close agreement with the values calculated from the models as they fell within the predicted intervals generated by the software as shown in Table 4. Thus, the Box–Behnken Design proved to be an effective method to optimize the experimental conditions.

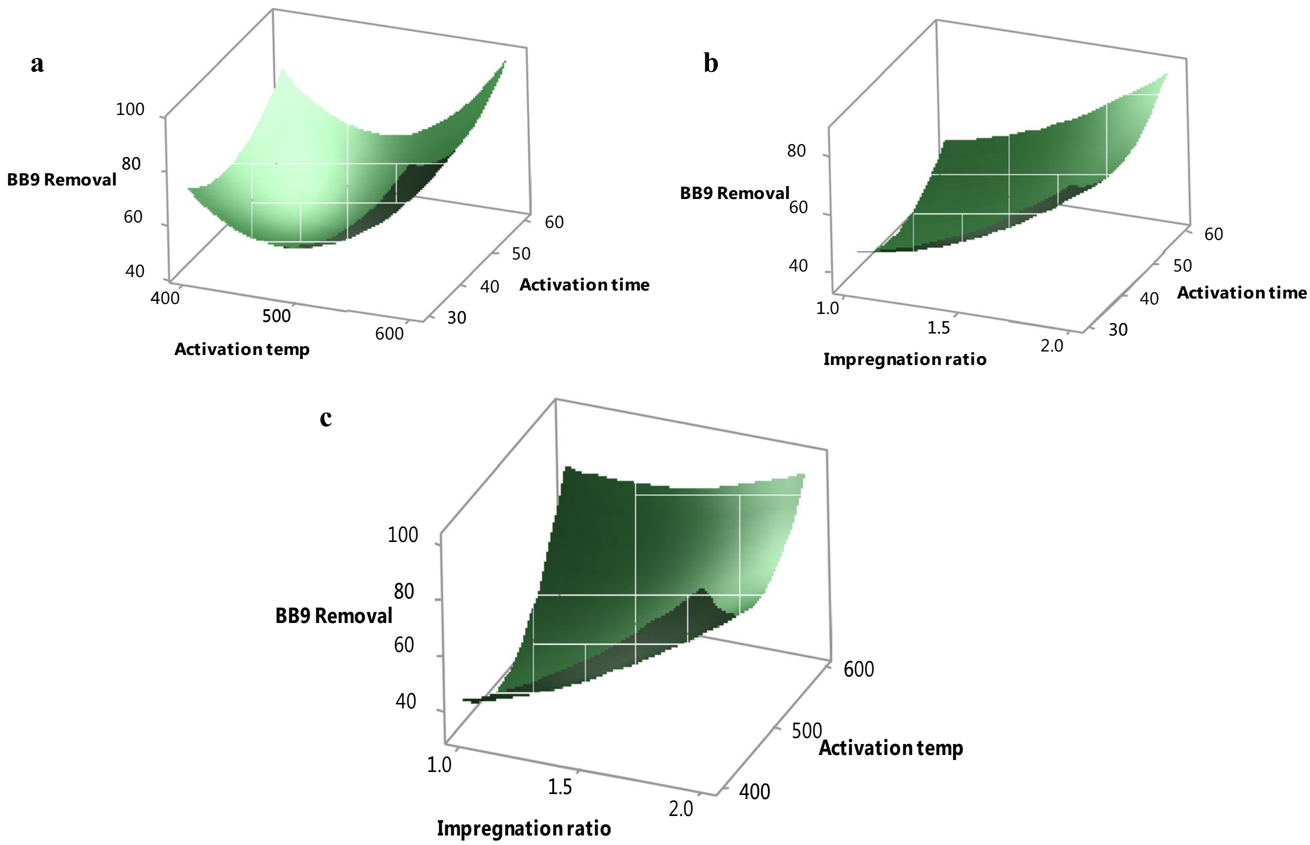

Fig. 3 3-D Response Surface Plots of BB9 removal as a function of **a** Activation temperature and Activation time **b** Impregnation ratio and Activation time **c** Impregnation ratio and Activation temperature at holding values of Impregnation Ratio 1.5, Activation Temperature 500 °C and Activation time of 45 min

Table 4 BBD predicted optimal settings for the preparation of MTSPAC

Variable	Setting				
Activation temp. (°C)	400	Composite desirability	0.843760		
Impregnation ratio	2.0				
Activation time(min)	30				
Response	Fit	SE fit	95% Confidence interval	95% Prediction interval	Experimental values
BB9% removal	103.12	5.16	(95.49,120.76)	(90.83, 125.41)	91.05
BV3% removal	95.15	3.53	(87.02, 103.29)	(83.02, 107.28)	83.25
Activated carbon yield %	39.055	0.146	(38.725, 39.385)	(38.550,39.560)	39.12

3.4 Characterization of the optimized *Millettia thonningii* seed pods activated carbon

The physicochemical and proximate characteristics of MTSPAC are shown in Table 5 while functional group characterization and surface morphology of both precursor and MTSPAC are depicted in Figs. 4a, b and 5a, b respectively.

3.5 Physicochemical and proximate characteristics of *Millettia thonningii* seed pods activated carbon

The pH of MTSPAC in water was 6.8. The useful pH for most applications of activated carbons is between 6 and 8 [23]. A low ash content of 1.8% was obtained. Activated carbon

Table 5 Physicochemical and proximate characteristics of *Millettia thonningii* seed pods activated carbon

Parameter	Value
pH	6.8
Moisture content (%)	2.4
Volatile mater (%)	24.9
Ash content (%)	1.8
Fixed carbon content (%)	70.8
Bulk density (g/cm^3)	0.4
Surface area (m^2/g)	864.6

with lower ash content is preferred for use as an adsorbent [24]. The moisture content of 2.4% was obtained for MTSPAC indicating its suitability, as moisture content of more than 3% is considered not good for standard applications [25]. High moisture content makes the activated carbon become more susceptible to degradation by fungi or other microorganisms [26].

The bulk density of the activated carbon was 0.4 g/cm^3, higher than the lower limit of 0.25 g/cm^3 set by the American Water Works Association [27] for granular activated carbon to be of practical use, while a surface area of 864.6 m^2/g was obtained. The properties of low moisture, low ash content and suitable bulk density indicate that the activated carbon produced is suitable for most applications involving adsorption from aqueous solutions.

3.6 FTIR analysis

FTIR spectroscopy is an important technique that provides basic spectra about activated carbons especially for the

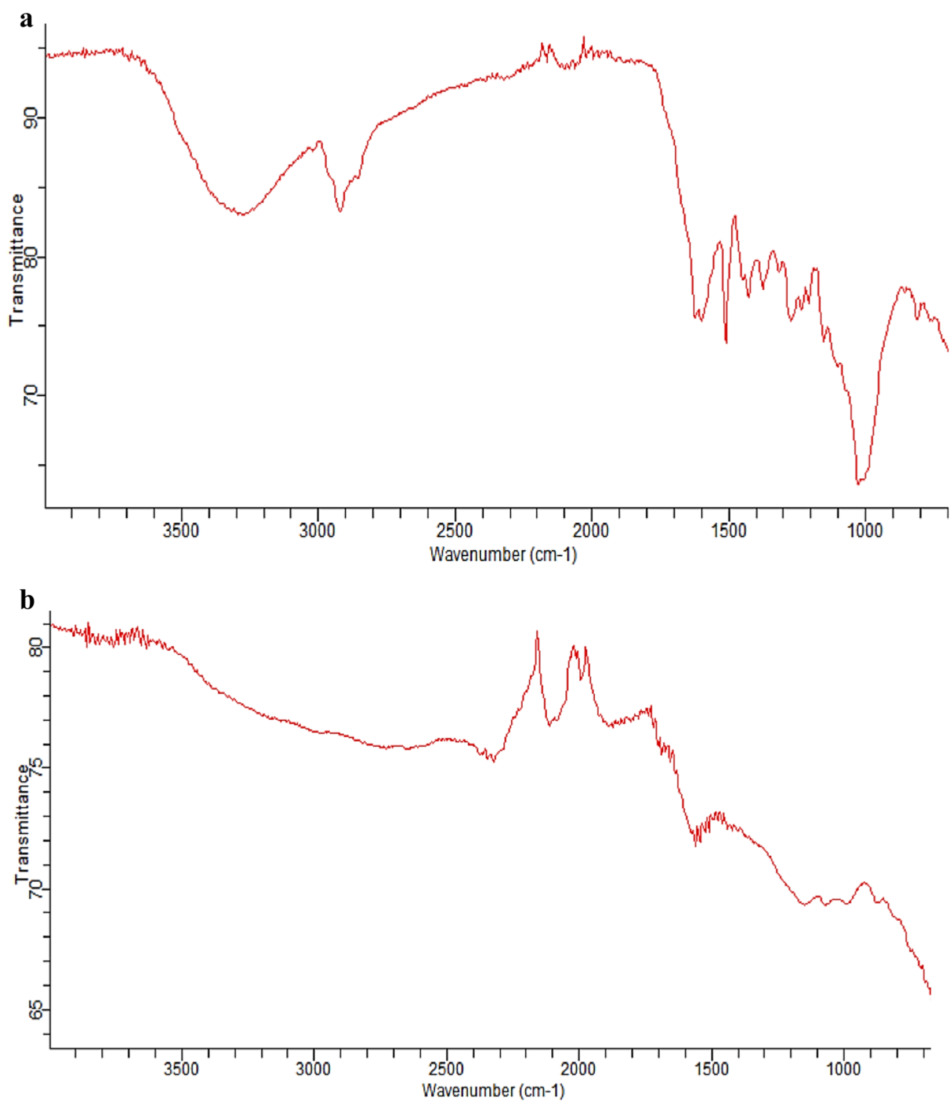

Fig. 4 FTIR Spectrum of **a** *Millettia thonningii* seed pods and **b** *Millettia thonningii* seed pods activated carbon prepared at optimal conditions

determination of types and intensities of their surface groups [28]. Figure 4b reveals significant changes in the spectrum of MTSPAC when compared to that of its precursor (Fig. 4a). The raw *Millettia thonningii* seed pods spectra contains some distinct peaks at 3280.1 cm^{-1}(characteristic absorption peak of O–H and N–H symmetric stretching vibration), 2918.5 cm^{-1} (carboxylic acid O–H), 2851.4 cm^{-1} (symmetric C–H stretching vibration from CH_2 and CH_3), 1621.4 cm^{-1} (C–O asymmetric stretching vibration) and 1021.3 cm^{-1} (S=O or C–O stretching) [29, 30]. The broad OH stretching peak present at 3280.1 cm^{-1} in the spectrum of the precursor, decreased in intensity compared to MTSPAC and this clearly indicated the loss of hydroxyls. The FTIR spectra obtained for optimized activated carbon showed fewer numbers of strong peaks due to the cracking of some bonds as a result of heating. This situation might be ascribed to the decomposition of lignin, cellulose, and hemicellulose in the *Millettia thonningii* seed pods during the carbonization and activation process. The diminution in number and intensity of peaks on the MTSPAC spectra when compared to its precursor is indicative of a successful activation.

3.7 SEM analysis

Figure 5a and b show that the surface morphology of the raw *Millettia thonningii* seed pods changed after activation and carbonization. The activated carbon prepared under optimal conditions (Fig. 5b) has well-developed pores of different sizes and shapes. The pore development on the surfaces of the activated carbon resulted from the evaporation of the activating agent, phosphoric acid, during carbonization.

4 Conclusion

Millettia thonningii seed pods can be used as a precursor to prepare activated carbon that could be used to remediate dye contaminated aqueous solutions. The Box–Behnken experimental design can be used to optimize and explain the influence of three independent preparation variables (activating temperature, activating time and impregnation ratio) on the activated carbon yield and dyes removal efficiency with suffcient statistical significance. The optimum conditions for maximum activated carbon yield, as well as maximum BV3 and BB9 adsorption efficiencies were obtained at 400 °C, 30 min and impregnation ratio of 2.0. Activation temperature had the most statistically significant effect on the activated carbon yield while the impregnation ratio had the most significant effect on the BV3 and BB9 removal efficiencies. Distinct differences such as the diminution in the number and intensity of the peaks in the FTIR spectra of activated carbon as well as the appearance of several distinct pores in the SEM micrograph of the activated carbon when compared to the precursor indicate a successful transformation of the precursor into activated carbon. The results obtained showed that *Millettia thonningii* seed pods-derived activated carbon holds great potential for application in the removal of hazardous organic dyes from industrial effuents.

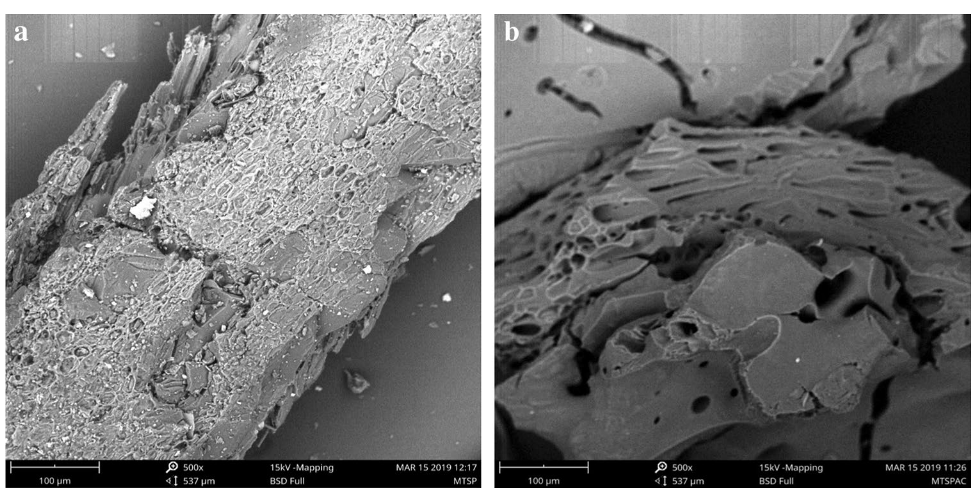

Fig. 5 **a** SEM micrographs of raw *Millettia thonningii* seed pods. **b** SEM micrograph of *Millettia thonningii* seed pods activated carbon

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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