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Optimization of activated carbon preparation conditions from *Prosopis africana* seed hulls for the removal of 2,4,6-Trichlorophenol from aqueous solution

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ABSTRACT

Optimum conditions for activated carbon preparation from *Prosopis africana* seed hulls (PASH) were investigated for the removal of 2,4,6-Trichlorophenol (2,4,6-TCP) by employing central composite design (CCD) to study the effects of three preparation variables which were activation temperature, activation time, and impregnation ratio (IR) on 2,4,6-TCP percentage removal and PASH-derived activated carbon yield (PASH-AC yield). Based on the CCD, a quadratic model and a two-factor interaction model were developed for 2,4,6-TCP removal and PASH-AC yield, respectively. The optimum conditions for preparing activated carbon from PASH for the removal of 2,4,6-TCP were found as follows: activation temperature of 800°C, activation time of 58 min, and IR of 2.70, which resulted into 93.64% of 2,4,6-TCP removal and 22.13% of PASH-AC yield. The experimental results obtained agreed satisfactorily with the model predictions. The optimum activated carbon was mesoporous with BET surface area, micropore volume, total pore volume and average size of 1,071.89 m^2/g, 0.35 cm^3/g, 0.46 cm^3/g, and 3.19 nm, respectively. The surface morphology and elemental composition of the activated carbon were determined by scanning electron microscopy and electron dispersive X-ray, respectively.

Keywords: *Prosopis africana* seed hulls; Activated carbon; Response surface methodology; 2,4,6-Trichlorophenol; Adsorption

1. Introduction

Significant attention was focused towards recovery and reuse of wastewater due to the ever-increasing demand for water [1]. Chlorophenols constitute a prominent class of pollutants that can be an obstacle to the reuse of wastewater, because of their wide use in the pesticides, woods, pharmaceuticals, dye manufacturing, paper, textile, paint, and pulp industries [2–4]. Highly chlorinated phenol derivatives such as 2,4,6-Trichlorophenol (2,4,6-TCP) are commonly found in wastewaters from such industrial activities. These phenolic compounds are classified as pollutants [5]. Adverse effects on the human nervous system such as respiratory, cardiovascular, gastrointestinal effects as well as cancer have been reported to be caused by 2,4,6-TCP [6,7]. As a result of its high toxicity, carcinogenic properties, and structural stabilization in the environment, the removal of 2,4,6-TCP from the environment is very crucial.

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Many treatment processes such as adsorption [8–10], photo-Fenton degradation [11], catalytic wet oxidation [12], photocatalytic degradation [13,14], and biodegradation [15–20] were applied for the removal of chlorophenols from wastewater. Among these processes, adsorption was shown to be the most effective in removing suspended solids, odors, organic matter, dyes, and oil from aqueous solutions [21,22]. Due to fast adsorption kinetics, high adsorptive capacity, and simplicity of design of activated carbon, it is the most widely used adsorbent in the removal of heavy metals, hydrocarbons, dyes, and other hazardous chemicals [23,24] such as chlorophenols that may be found in wastewater.

Many researchers produced activated carbons for the removal of various pollutants [25] using renewable and cheaper precursors which were mainly industrial and agricultural byproducts, such as *Borassus aethiopum* shells [26], almond shell [27], date palm seed [28], date pits [29], apricot shell [30], bean pod [31], rice husk [32], cherry stone [33], sunflower seed hull [34], charcoal ash [35], and coconut husk [36,37].

One of the significant problems troubling agrarian and developing countries such as Nigeria is managing many agricultural byproducts lying as wastes, littering, and polluting the environment. One of such wastes is the seed hulls of *Prosopis africana*. *P. africana* is a perennial tree in the genus *Prosopis* that grows very well in Nigeria and other parts of West Africa. In many areas, its fermented seeds are used to prepare a food condiment called daddawa, a locally fermented product that is widely used as a food condiment in Nigeria and many parts of West Africa. The seed hulls from this process lie as wastes and constitute environmental concern; therefore, usage of the waste materials generated from this process could result in waste minimization and tremendous cost saving. Preliminary studies have shown that the seed hulls of *P. africana* contain high carbon and low ash content which make it a good precursor material for preparing activated carbon as adsorbent [38]. As far as we know, no study has been done on the preparation of activated carbon from *Prosopis africana* seed hulls (PASH) by physiochemical activation method for the adsorption of 2,4,6-TCP from aqueous solutions, especially by applying response surface methodology (RSM).

The goal of this study, therefore, was to optimize the preparation conditions of activated carbon from a novel PASH precursor for the removal of 2,4,6-TCP. The effects of activation temperature, activation time, and chemical impregnation ratio (IR) as preparation variables were studied simultaneously to obtain a high activated carbon yield as well as high 2,4,6-TCP percentage removal from aqueous solution using central composite design (CCD), a subset of RSM.

2. Materials and methods

2.1. Materials and sample collection

The seed hulls of *P. africana* were collected locally from Zaria and Kano, Nigeria. They were washed with distilled water to remove dirt, dried at 105°C for 24 h, ground using a locally made grinder, and sieved to generate the precursor for the activated carbon preparation. All the chemicals/reagents used in this work were of analytical grade.

2.2. Adsorbate

The adsorbate (2,4,6-TCP) was supplied by Aldrich. Deionized water was used to prepare its solution. 2,4,6-TCP has a chemical formula of $C_6H_2Cl_3OH$ with molecular weight of 197.45 $gmol^{-1}$. The chemical structure of 2,4,6-TCP is shown in Fig. 1

2.3. Preparation of activated carbon

The activated carbon was prepared with potassium carbonate (K_2CO_3) as activating agent by considering the following factors: temperature of activation, time of activation, and IR. The dried PASH of the desired particle size was measured and mixed with the K_2CO_3, and activated at temperature and time determined by the design of experiment (DOE) table. The detailed preparation method is contained in our previous work [38]. The product was cooled to room temperature, washed with distilled water until a neutral pH was attained, oven dried, and finally stored in an airtight container for further use. A flow chart describing the activated carbon preparation procedure is shown in Fig. 2.

The IR of the activating agent with the precursor was computed using the following relationship:

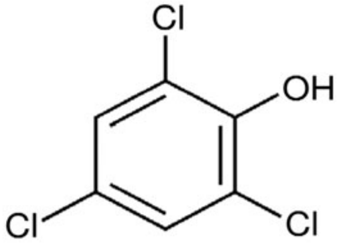

Fig. 1. Chemical structure of 2,4,6-Trichlorophenol.

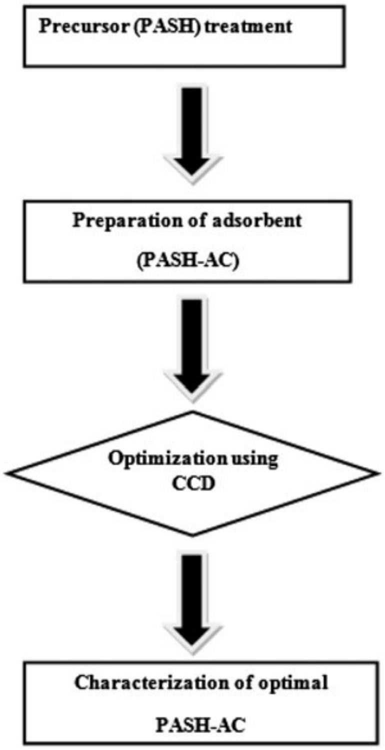

Fig. 2. Flow chart for the activated carbon preparation.

$$\text{Impregnation ratio} = \frac{\text{dried weight of } K_2CO_3}{\text{dried weight of precursor (PASH)}} \quad (1)$$

The adsorbent preparation was strictly adhered to the DOE table as shown in Table 1.

2.4. DOEs using RSM

In this work, CCD, a subset of RSM, was applied to study the variables for preparing the activated carbons from PASH. CCD was chosen because it is suitable for fitting a quadratic surface and reduces the number of experimental trials needed to evaluate multiple parameters and their interactions. It is characterized by three operations namely: 2^n factorial runs, $2n$ axial runs, and six center runs [39]. In this case, it translated into eight factorial points, six axial points, and six replicates at the center which give a total of 20 experiments.

$$\text{Total number of experiments } (N) = 2^n + 2n + n_c \quad (2)$$

where n is the number of factors, and n_c is the number of center points (six replicates).

Table 1
Experimental design matrix for preparation of PASH-AC and responses

Run	Level			PASH activated carbon preparation variables			2,4,6-TCP removal, Y_1 (%)	PASH-AC yield, Y_2 (%)
				Temperature (℃)	Time (min)	IR		
1	+1	+1	−1	842	148	0.97	86.41	13.66
2	0	0	0	750	100	2.10	92.28	21.91
3	−1	−1	+1	658	52	3.23	92.18	21.17
4	0	0	+1.682	750	100	4.00	84.78	21.15
5	0	0	0	750	100	2.10	91.15	23.22
6	0	−1.682	0	750	20	2.10	74.24	27.88
7	0	0	0	750	100	2.10	92.23	22.78
8	0	0	0	750	100	2.10	92.32	21.76
9	+1	+1	+1	842	148	3.23	95.15	12.35
10	0	0	0	750	100	2.10	92.37	21.83
11	+1	−1	+1	842	52	3.23	94.09	20.72
12	0	+1.682	0	750	180	2.10	91.96	21.91
13	0	0	0	750	100	2.10	91.23	22.43
14	−1	+1	−1	658	148	0.97	55.33	26.53
15	−1	+1	+1	658	148	3.23	91.39	20.96
16	+1.682	0	0	905	100	2.10	84.09	19.04
17	−1	−1	−1	658	52	0.97	39.09	27.51
18	+1	−1	−1	842	52	0.97	77.43	22.73
19	−1.682	0	0	595	100	2.10	72.88	25.75
20	0	0	−1.682	750	100	0.20	21.66	28.86

The two level-independent variables were coded as +1 and −1 for high and low values, respectively, and were used to represent the eight factorial points. The six axial points were located at (±α, 0, 0), (0, ±α, 0), and (0, 0, ±α), and the six replicates were at the center (0, 0, 0).

Rotatability value, α, which depends on the number of points in the factorial portion of the design, was obtained as 1.682 using Eq. (3) [40]:

$$\alpha = N_{\mathrm{p}}^{1/4} \tag{3}$$

where $N_{\mathrm{p}} = 2^n$ is the number of points, and n is the number of factors.

In this work, the activated carbons were prepared using physicochemical activation method and the variables studied were activation temperature (x_1), activation time (x_2), and IR (x_3). These three variables with their respective ranges were chosen based on literature as given in Table 2.

Optimal conditions for the responses (yield of PASH-AC and percentage removal of TCP) were determined using the optimal predictor quadratic model using the following equation:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i\right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \tag{4}$$

where Y is the predicted response, b_0 is the constant coefficients, b_{ii} the quadratic coefficients, b_{ij} the interaction coefficients, and x_i and x_j are the coded values of the activated carbon preparation variables considered.

Percentage yield for the adsorbent prepared was determined using the following equation:

$$\text{Yield}\,(\%) = \frac{\text{weight (g) of dried activated carbon produced}}{\text{weight (g) dried precursor used}} \times 100 \tag{5}$$

2.5. Batch adsorption for the removal efficiency of 2,4,6-TCP in aqueous solution

About 0.1 g of the prepared activated carbon was added into 250 mL reagent bottle containing 100 mL of 100 ppm 2,4,6-TCP solution. Each sample was kept in an isothermal water bath shaker at 140 rpm at 30˚C until equilibrium was reached. All samples were filtered prior to analyzing the solution to separate the activated carbon from the adsorbate in order to minimize interference of the carbon fines with the analysis. The concentration of the 2,4,6-TCP in the supernatant solutions was determined before and after adsorption using ultraviolet–visible (UV–vis) spectrophotometer (JASCO V-530) at its maximum wavelength of 296 nm.

The design expert statistical software (version 6.0.8 Stat Ease, Inc., Minneapolis, MN 55413, USA) was employed for model fitting and significance for the PASH-derived activated carbon yield (PASH-AC yield) and percent removal of the 2,4,6-TCP.

2.6. Characterization of the prepared activated carbon

The Brunauer–Emmett–Teller (BET) surface area, micropore volume, total pore volume, and the pore size of the PASH activated carbon prepared under optimum preparation conditions were determined using BET equation and Quantachrome Nova Win2©1994–2002. As a comparison, a sample of QRëC commercial activated carbon (CAC) was also characterized under same condition. The surface morphology of the samples was examined using a scanning electron microscope (SEM) (FEI QUANTA PEG 60), while electron dispersive X-ray (EDX) was used to determine the elemental composition of the samples (precursor and the prepared activated carbon).

3. Results and discussion

3.1. Development of regression model equation

The complete design matrix together with the values of both the responses (PASH-AC yield and 2,4,6-TCP removal) obtained from the experimental works

Table 2
Independent variables and their coded levels for the CCD of PASH-activated carbon (PASH-AC) preparation

Adsorbent	Variable	Code	Unit	Coded variable levels				
				$-\alpha$	−1	0	+1	$+\alpha$
PASH-AC	Activation temperature	x_1	˚C	595	658	750	842	905
	Activation time	x_2	min	20	52	100	148	180
	Impregnation ratio	x_3	–	0.20	0.97	2.10	3.23	4.00

is given in Table 1. CCD, a subset of RSM, was used to develop a correlation between the activated carbon preparation variables to the two responses. The 2,4,6-TCP removal ranged from 21.66 to 95.15%, while the activated carbon yield ranged from 12.35 to 28.86%. Runs 2, 5, 7, 8, 10, and 13 at the center point were used to determine the experimental error. According to the sequential model sum of squares, the models were selected based on the highest order polynomials, where the additional terms were significant and the models not aliased. For the response of 2,4,6-TCP removal, quadratic model was chosen as recommended by the software. On the other hand, two-factor interaction (2FI) model was selected as the best model for PASH-AC yield response.

The final empirical formula models for the 2,4,6-TCP removal (Y_1) and the activated carbon yield (Y_2) in terms of coded factors after excluding the insignificant terms are represented by Eqs. (6) and (7), respectively.

$$Y_1 = 91.66 + 6.88x_1 + 4.05x_2 + 16.16x_3 - 2.96x_1^2 - 1.32x_2^2 - 11.89x_3^2 - 0.68x_1x_2 - 7.97x_1x_3 - 3.12x_2x_3 \quad (6)$$

$$Y_2 = 22.21 - 2.78x_1 - 2.10x_2 - 2.06x_3 - 2.03x_1x_2 + 1.07x_1x_3 + 0.18x_2x_3 \quad (7)$$

From Eqs. (6) and (7), the coefficients with one factor represent the effect of the particular factor, while the coefficients with two factors and those with second-order terms represent the interaction between two factors and quadratic effect, respectively. Positive sign in front of the terms indicates synergistic effect, while the negative sign indicates antagonistic effect.

The quality of the models developed was evaluated based on the correlation coefficients, R^2 value. The R^2 values for Eqs. (6) and (7) were 0.9411 and 0.8224 as deducted from Figs. 3 and 4, respectively. The R^2 value of 0.9411 for Eq. (6) was considered relatively high as the value was close to 1, which indicates that there was a very good agreement between the experimental and the theoretical 2,4,6-TCP percentage removal values while the R^2 value of 0.8224 for Eq. (7) was considered as moderate to validate the fit, which might lead to larger variation in the theoretical PASH-AC yield values from the model. Nevertheless, the standard deviation for this model (2.10) is lower than the model for 2,4,6-TCP percentage removal (6.67), which indicates that the theoretical values for this model is still considered as suitable to correlate the experimental data [40].

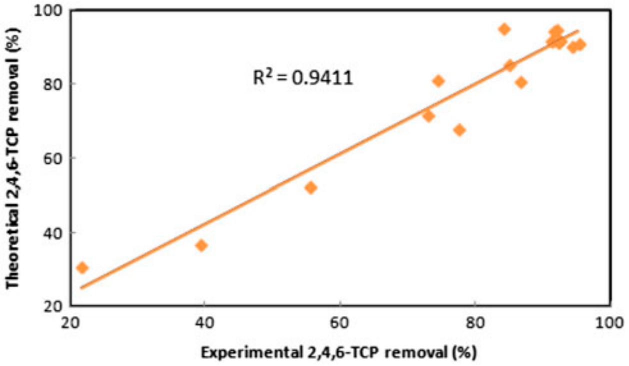

Fig. 3. Relationship between theoretical and experimental data for 2,4,6-TCP removal.

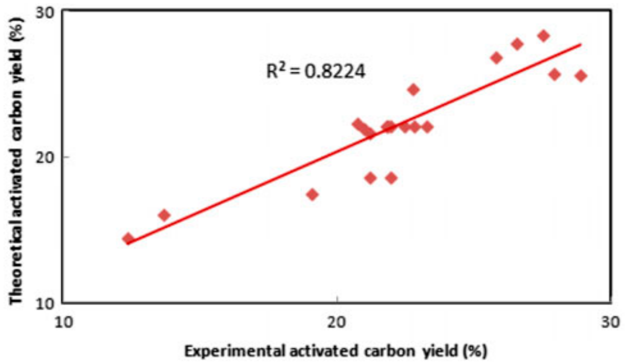

Fig. 4. Relationship between theoretical and experimental data of PASH-AC yield.

3.2. Statistical analysis

The significance and adequacy of the models were further verified through analysis of variance (ANOVA). ANOVA is required to validate the importance and how adequate the models are. The mean squares were obtained by dividing the sum of the squares of each of the variation sources with the respective degrees of freedom. If the value of Prob. > F is less than 0.05, the model terms are considered as significant [38,39]. The surface quadratic model resulting in the form of ANOVA for 2,4,6-TCP percentage removal is given in Table 3. It can be seen from the table that the model has F-value of 17.75 and Prob. > F of <0.0001 indicating that this model was significant. x_1, x_2, x_3, x_3^2, and $x_1x_3$were the significant model terms, whereasx_1^2, x_2^2, x_1x_2 and x_2x_3 were insignificant to the response.

From the ANOVA for 2FI model of the PASH-AC yield shown in Table 4, the model F-value of 10.03 and Prob. > F value of <0.0001 indicate that the model

Table 3
ANOVA for response surface quadratic model of 2,4,6-TCP removal by PASH-AC

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	Prob. > *F*
Model	7,109.28	9	789.92	17.75	<0.0001
x_1	646.22	1	646.22	14.52	0.0034
x_2	223.85	1	223.85	5.03	0.0488
x_3	3,566.75	1	3,566.75	80.16	<0.0001
x_1^2	125.98	1	125.98	2.83	0.1233
x_2^2	25.30	1	25.30	0.57	0.4682
x_3^2	2,037.06	1	2,037.06	45.78	<0.0001
x_1x_2	3.66	1	3.66	0.08	0.7802
x_1x_3	508.01	1	508.01	11.42	0.0070
x_2x_3	77.81	1	77.81	1.75	0.2155
Residual	444.93	10	44.49	–	–

Table 4
The ANOVA for response surface 2FI model of PASH-AC yield

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	Prob. > *F*
Model	266.61	6	44.44	10.03	0.0003
x_1	105.71	1	105.71	23.86	0.0003
x_2	60.19	1	60.19	13.59	0.0027
x_3	58.22	1	58.22	13.14	0.0031
x_1x_2	33.01	1	33.01	7.45	0.0172
x_1x_3	9.22	1	9.22	2.08	0.1727
x_2x_3	0.27	1	0.27	0.06	0.8088
Residual	57.59	13	4.43	–	–

was significant. In this case, x_1, x_2, x_3, and x_1x_2 were the significant model terms, while x_1x_3 and x_2x_3 were the insignificant model terms for the response. From the statistical results obtained, it was shown that both models [Eqs. (6) and (7)] were adequate to predict the 2,4,6-TCP removal and PASH-AC yield, respectively within the range of variables studied. In addition, Figs. 3 and 4 show the predicted values vs. the experimental values for 2,4,6-TCP removal and PASH-AC yield, respectively. The developed models were able to capture successfully the relationship between preparation variables and responses, when the theoretical values obtained were quite close to the experimental values.

3.3. Removal of 2,4,6-TCP

Based on the *F*-values from the ANOVA data in Table 3 for 2,4,6-TCP percentage removal, it can be seen that IR showed the largest *F*-value of 80.16 among all the factors, indicating that this variable portrayed the most significant effect on the 2,4,6-TCP percentage removal by the PASH-AC. The effect of activation temperature was significant as well with *F*-value of 14.52. However, the effect of activation time on the response was relatively insignificant compared with other two variables studied (*F*-value of 5.03). The quadratic effect of IR showed the most significant effect with *F*-value of 45.78 while those of activation temperature and activation time had the least effect (*F*-values of 2.83 and 0.57, respectively). The interaction effect between activation temperature and IR had *F*-value of 11.42, whereas the interaction effect between activation time and IR as well as interaction effect between activation temperature and activation time were relatively insignificant with *F*-values of 1.75 and 0.08, respectively.

As can be seen from the 3D plots in Fig. 5, the 2,4,6-TCP percentage removal increases with increase

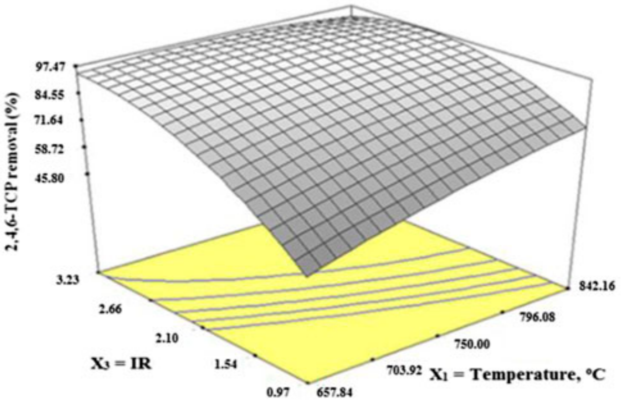

Fig. 5. Three-dimensional response surface plot of 2,4,6-TCP removal (effect of activation temperature and IR, *t* = 100 min) on PASH-AC.

in activation temperature and IR which agrees with works reported by Tan et al. [36], Ahmad and Alrozi, [40] as well as Sudaryanto et al. [41]. Increasing activation temperature and activation time also entailed an opening and enlargement of the pores which enhanced the 2,4,6-TCP adsorption [42–44]. Moreover, increase in the activation temperature also caused the CO_2 and the surface metal complex to further gasify the carbon, leading to widening of pores [45].

3.4. PASH-AC Yield

From Table 4, it can be seen that activation temperature has the greatest effect on PASH-AC yield with the highest *F*-value of 23.86, whereas IR and activation time produced similar effects on this response with *F*-values of 13.14 and 13.59, respectively.

The interaction effects between IR with temperature and that of IR with time were lower and slightly insignificant with *F*-values of 2.08 and 0.06, respectively, while that of interaction between temperature and time was more significant with *F*-value of 7.45.

Fig. 6(a) and (b) showed the 3D response surface plots for the studied variables with Fig. 6(a) demonstrating the effect of activation time and activation temperature with IR fixed at zero level (IR = 2.10) whereas Fig. 6(b) demonstrates the effect of temperature and IR with activation time fixed at zero level (t = 100 min). From both figures, the PASH-AC yield was found to decrease with increase in activation temperature, activation time, and IR due to the increase in C–K_2CO_3 and C–CO_2 reaction. The results obtained in this study were in agreement with the works done and reported by Tan et al. [36], Ahmad and Alrozi, [40] as well as Sudaryanto et al. [41] where activation temperature was found to play a significant role on the yield of activated carbon with activation time showing little effect on the activated carbon yield.

The activated carbon yield was also strongly affected by the chemical IR where increasing IR decreased the yield and increased the carbon burn off according to Tan et al. [36]. This was because when higher IR was used, the weight losses occur due to increasing release of volatile products as a result of intensifying dehydration and elimination reactions [46].

Table 5 compared various activated carbon yields from different precursors. The results obtained in this study work compared well with the works reported in the literature. Different precursors used to prepare the activated carbons might be responsible for the variation in the activated carbon yields.

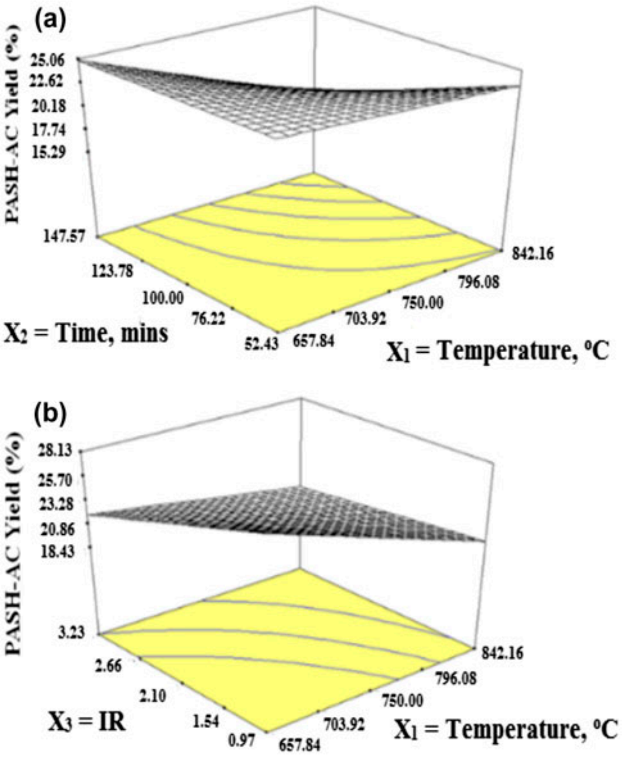

Fig. 6. Three-dimensional response surface plot of PASH-AC yield; (a) effect of activation temperature and activation time, IR = 2.10, (b) effect of activation temperature and IR, t = 100 min.

3.5. Process optimization

The prepared activated carbon should have relatively high yield for economic feasibility with the most important property of activated carbon being its adsorption capacity [36]. CCD has been used to optimize the parameters affecting the percentage removal of 2,4,6-TCP and PASH-AC yield responses. In this case, it is difficult to optimize both responses because the interest regions of factors are dissimilar; therefore, the function of desirability was applied using Design-Expert software (Stat-Ease, Inc., Minneapolis, MN 55413, USA) so as to compromise between these responses. The theoretical and experimental results of 2,4,6-TCP percentage removal and PASH-AC yield obtained at optimum conditions are shown in Table 6. The optimum PASH-AC was obtained using activation temperature of 800˚C, activation time of 58 min, and IR of 2.70.

The optimum activated carbon showed 2,4,6-TCP removal of 93.64% and PASH-AC yield of 22.13%. It was observed that the experimental values obtained were in good agreement with the theoretical values

Table 5
Comparison of carbon yield for various activated carbons

Activated carbon precursor	Method of activation	Activated carbon yield (%)	References
Prosopis africana seed hulls	Physico chemical	13.66–28.86	This study
Mangosteen peel	Physico chemical	11.38–26.59	[40]
Rambutan peel	Physico chemical	13.67–21.75	[47]
Rattan sawdust	Physico chemical	11.98–42.43	[48]
Tea waste	Physico chemical	23.45–39.10	[39]
Palm oil fronds	Physico chemical	4.21–23.00	[49]

Table 6
The PASH-AC preparation parameters optimization

Parameters		PASH-AC
2,4,6-TCP removal (%)	Theoretical	94.10
	Experimental	93.64
	Error	0.49
Activated carbon yield (%)	Theoretical	23.01
	Experimental	22.13
	Error	3.82
Model desirability		0.90
x_1, ℃		800
x_2, min		58
x_3, IR		2.70

from the model with relatively small percentage errors, which were only 0.49 and 3.82% for 2,4,6-TCP percentage removal and PASH-AC yield, respectively.

3.6. Characterization of the optimized PASH-AC

3.6.1. Surface morphology

Fig. 7(a) and (b) show the morphology of the raw PASH and PASH-AC prepared under the optimum conditions, respectively. As can be seen from Fig. 7(a), the surface texture of the raw PASH was irregular, rough, and with very little pores available on the surface. However, after activation, large pores can be observed on the sample surface as shown in Fig. 7(b). This might be due to the activation process used [36], which involved both chemical and physical activating agents (K_2CO_3 and CO_2, respectively). The high 2,4,6-TCP removal in this study was attributed to the well-developed pores of the prepared activated carbon.

3.6.2. Elemental analysis

Table 7 shows the results of the different elements weight percent (wt%) obtained. The raw material of the PASH showed the presence of carbon, oxygen, sodium, chlorine, and silicon with 51.06, 47.14, 0.94,

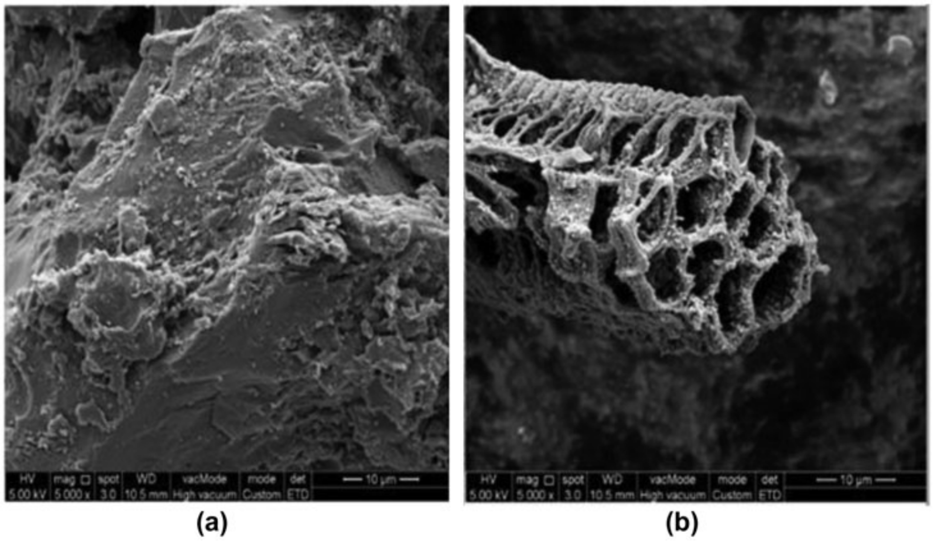
(a)
(b)

Fig. 7. SEM micrograph of (a) raw PASH sample and (b) PASH-based activated carbon.

Table 7
EDX of raw PASH sample and PASH-AC

Activated carbons	Element weight (%)						Total wt %
	C	O	Na	K	Cl	Si	
PASH sample	51.06	47.14	0.94	–	0.39	0.47	100
PASH-AC	79.54	14.84	–	5.62	–	–	100

0.39, and 0.47 wt%, respectively, while the activated carbon prepared with K_2CO_3 (PASH-AC) showed only three elements which are carbon, oxygen, and potassium with 79.54, 14.84, and 5.62 wt%, respectively. The raw PASH sample demonstrated lower carbon content and higher oxygen content compared with the PASH-AC. The carbon content increased from 51.06 to about 79.54 wt%, while the percentage of oxygen decreased to about 14.84 wt% from 47.14% with the disappearance of sodium, chlorine, and silicon after the activation process suggesting that the chemical activating agent removed the interfering elements (sodium, chlorine, and silicon) from the raw PASH sample.

3.6.3. BET surface area and pore volume

The N_2 adsorption–desorption isotherms and the pore size distribution by BJH method for PASH-AC was shown in Fig. 8. The sample presents an isotherm of I–IV hybrid shape from Fig. 8, according to the IUPAC classification. As the relative pressure increases, the adsorption isotherm of both samples increases gently and a hysteresis loop appears, pointing to a vast majority of micropores associated with a considerable development of mesoporosity.

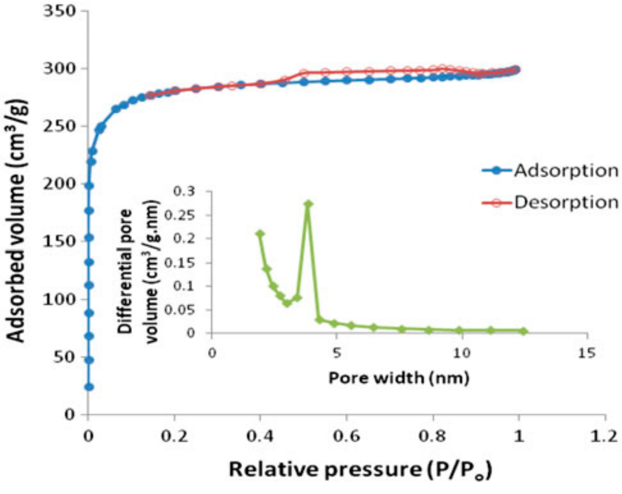

Fig. 8. N_2 adsorption-desorption isotherms at 77 K and BJH pore size distribution (inset plot) for the optimized PASH-AC.

Table 8
The BET characterization of the optimized waste tea activated carbon

BET surface area (m^2/g)	Micropore volume (cm^3/g)	Total pore volume (cm^3/g)	Average pore size (nm)
1,071.89	0.35	0.46	3.19

The BET surface area, micropore volume, and total pore volume were found to be 1,071.89 m^2/g, 0.35 cm^3/g, and 0.46 cm^3/g, respectively, as shown in Table 8. According to the pore size distribution shown in Fig. 8 (inset), the presence of significant mesopores together with micropores can be found in the PASH-AC, giving rise to an average pore size of 3.19 nm in the mesopores region according to the IUPAC classification [50].

Overall, the activated carbon prepared from PASH under optimum conditions showed characteristics which were comparable with CACs, such as F300 and QRëC CAC which are widely used grades of activated carbons in the wastewater treatment industry. F300 was reported to have BET surface area of 960 m^2/g, micropore volume of 0.46 cm^3/g, and total pore volume of 0.56 cm^3/g [43], while QRëC have BET surface area of 632.48 m^2/g, micropore volume of 0.18 cm^3/g, and total pore volume of 0.29 cm^3/g.

4. Conclusions

The effects of PASH-AC preparation variables (activation temperature, activation time and IR) on the 2,4,6-TCP percentage removal and PASH-AC yield has been studied using CCD, a subset of RSM. IR was found to impose the greatest effect on the 2,4,6-TCP percentage removal, whereas activation temperature was found to have the most significant effect on PASH-AC yield. The optimum PASH-AC preparation conditions were obtained as 800℃ activation temperature, 58 min activation time, and 2.70 IR resulting into 93.64% of 2,4,6-TCP removal and 22.13% of PASH-AC yield. The experimental values obtained were in good agreement with the values predicted from the models with relatively small errors. The optimum activated carbon was found to be mesoporous, demonstrating heterogeneous type of pore structure. The results confirmed *P. africana* seed hulls to be a promising low-cost precursor for activated carbon production.

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Nomenclature

PASH	—	*Prosopis africana* seed hulls
2,4,6-TCP	—	2,4,6-Trichlorophenol
RSM	—	response surface methodology
CCD	—	central composite design
BET	—	Brunauer–Emmett–Teller
BJH	—	Barrett, Joyner and Halenda
IR	—	impregnation ratio
2FI	—	two-factor interaction
PASH-AC	—	activated carbon prepared from *Prosopis africana* seed hulls
DOE	—	design of experiment
%*R*	—	percentage removal of 2,4,6-Trichlorophenol
ANOVA	—	analysis of variance
CAC	—	commercial activated carbon
ppm	—	parts per million
IUPAC	—	international union of pure and applied chemistry
wt%	—	weight percentage

References

[1] G. Annadurai, S.R. Babu, K.P.O. Mahesh, T. Murugesan, Adsorption and bio-degradation of phenol by chitosan-immobilized *Pseudomonas putida* (NICM 2174), Bioprocess Eng. 22 (2000) 493–501.

[2] A.P. Annachhatre, S.H. Gheewala, Biodegradation of chlorinated phenolic compounds, Biotechnol. Adv. 14 (1996) 35–56.

[3] H. Bae, T. Yamagishi, Y. Suwa, Evidence for degradation of 2-chlorophenol by enrichment cultures under denitrifying conditions, Microbiology 148 (2002) 221–227.

[4] K.A. Short, J.D. Doyle, R.J. King, R.J. Seidler, G. Stotzky, R.H. Olsen, Effects of 2,4-dichlorophenol, a metabolite of a genetically engineered bacterium, and 2,4-dichlorophenoxyacetate on some microorganisms-mediated ecological processes in soil, Appl. Environ. Microbiol. 57 (1991) 412–418.

[5] K. Akhrib, F. Kaouah, T. Berrama, Z. Bendjama, Kinetic and thermodynamic study of removal of o-chlorophenol from potable water using activated carbon prepared by Date Pits, Desalin. Water Treat. 51 (2013) 6049–6057.

[6] B.H. Hameed, Equilibrium and kinetics studies of 2,4,6-trichlorophenol adsorption onto activated clay, Colloids Surf., A 307 (2007) 45–52.

[7] P. Howard, Handbook of Environmental Degradation Rates, Lewis, Chelsea, MI, 1991.

[8] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon, J. Hazard. Mater. 164 (2009) 473–482.

[9] K.H. Bakhtiar, M.N. Ahmad, A.R. Afidah, Removal of 4-chloro-2-methoxy phenol by adsorption from aqueous solution using oil palm shell carbon activated by K_2CO_3, J. Phys. Sci. 22 (2011) 41–58.

[10] S.E. Agarry, C.N. Owabor, A.O. Ajani, Modified plantain peel as cellulose-based low-cost adsorbent for the removal of 2,6-dichlorophenol from aqueous solution: Adsorption isotherms, kinetic modeling, and thermodynamic studies, Chem. Eng. Commun. 200(8) (2013) 1121–1147.

[11] S.G. Poulopoulos, M. Nikolaki, D. Karampetsos, C.J. Philippopoulos, Photochemical treatment of 2-chlorophenol aqueous solutions using ultraviolet radiation, hydrogen peroxide and photo-Fenton reaction, J. Hazard. Mater. 153 (2008) 582–587.

[12] S. Chaliha, K.G. Bhattacharyya, Catalytic wet oxidation of 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol in water with Mn(II)-MCM41, Chem. Eng. J. 139 (2008) 575–588.

[13] S.P. Devipriya, S. Yesodharan, Photocatalytic degradation of phenol in water using TiO_2 and ZnO, J. Environ. Biol. 31 (2010) 247–249.

[14] N.A. Laoufiy, D. Tassalit, F. Bentahar, The degradation of phenol in water solution by TiO_2 photocatalysis in a helical reactor, Global Nest J. 10 (2008) 404–419.

[15] A.P. Annachhatre, S.H. Gheewala, Biodegradation of chlorinated phenolic compounds, Biotechnol. Adv. 14 (1996) 35–56.

[16] H. Bae, T. Yamagishi, Y. Suwa, Evidence for degradation of 2-chlorophenol by enrichment cultures under denitrifying conditions, Microbiology 148 (2002) 221–227.

[17] P.M. Armenante, D. Kafkewitz, G.A. Lewandowski, C.J. Jou, Anaerobic–aerobic treatment of halogenated phenolic compounds, Water Res. 33 (1999) 681–692.

[18] D.C. Yee, T.K. Wood, 2,4-Dichlorophenol degradation using *Streptomyces viridosporus* T7A lignin peroxidase, Biotechnol. Prog. 13 (1997) 53–59.

[19] A.Z. Elkarmi, K.H. Abu-Elteen, A.A. Atta, N.A. Abu-Sbitan, Biodegradation of 2,4-dichlorophenol originating from pharmaceutical industries, Afr. J. Biotechnol. 8 (2009) 2558–2564.

[20] P. Steinle, P. Thalmann, P. Höhener, K.W. Hanselmann, G. Stucki, Effect of environmental factors on the degradation of 2,6-dichlorophenol in soil, Environ. Sci. Technol. 34 (2000) 771–775.

[21] G. Annadurai, M. Chellapandian, M.R.V. Krishnan, Adsorption of basic dye from aqueous solution by

chitosan: Equilibrium studies, Ind. J. Environ. Prot. 17 (1997) 95–98.

[22] G. Hisarli, C. Tezcan, G. Atun, Adsorption kinetics and equilibria of basic dyes onto zeolite in single and binary component systems, Chem. Eng. Commun. 199 (2012) 1412–1436.

[23] B.H. Hameed, Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solution, J. Hazard. Mater. 161 (2009) 253–259.

[24] F. Zeinali, A.A. Ghoreyshi, G. Najafpour, Removal of toluene and dichloromethane from aqueous phase by granular activated carbon (GAC), Chem. Eng. Commun. 199 (2012) 203–220.

[25] Y. Min, G. Huijuan, C. Zezhi, Z. Mengqun, Adsorption characteristics of activated carbon for siloxanes, J. Environ. Chem. Eng. 1 (2013) 1182–1187.

[26] Z.N. Garba, A.R. Afidah, S.A. Hamza, Potential of *Borassus aethiopum* shells as precursor for activated carbon preparation by physico-chemical activation; optimization, equilibrium and kinetic studies, J. Environ. Chem. Eng. 2 (2014) 1423–1433.

[27] E. Demirbas, M. Kobya, A.E.S. Konukman, Error analysis of equilibrium studies for the almond shell activated carbon adsorption of Cr(VI) from aqueous solutions, J. Hazard. Mater. 154 (2008) 787–794.

[28] A. El Nemr, A. Khaled, O. Abdelwahab, A. El-Sikaily, Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed, J. Hazard. Mater. 152 (2008) 263–275.

[29] M. Belhachemi, F. Addoun, Adsorption of congo red onto activated carbons having different surface properties: Studies of kinetics and adsorption equilibrium, Desalin. Water Treat. 37(1–3) (2012) 122–129.

[30] B. Karagozoglu, M. Tasdemir, E. Demirbas, M. Kobya, The adsorption of basic dye (Astrazon Blue FGRL) from aqueous solutions onto sepiolite, fly ash and apricot shell activated carbon: Kinetic and equilibrium studies, J. Hazard. Mater. 147 (2007) 297–306.

[31] B. Cabal, T. Budinova, C.O. Ania, B. Tsyntsarski, J.B. Parra, B. Petrova, Adsorption of naphthalene from aqueous solution on activated carbons obtained from bean pods, J. Hazard. Mater. 161 (2009) 1150–1156.

[32] J.N. Sahu, S. Agarwal, B.C. Meikap, M.N. Biswas, Performance of a modified multi-stage bubble column reactor for lead(II) and biological oxygen demand removal from wastewater using activated rice husk, J. Hazard. Mater. 161 (2009) 317–324.

[33] J. Jaramillo, V. Gómez-Serrano, P.M. Álvarez, Enhanced adsorption of metal ions onto functionalized granular activated carbons prepared from cherry stones, J. Hazard. Mater. 161 (2009) 670–676.

[34] N. Thinakaran, P. Baskaralingam, M. Pulikesi, P. Panneerselvam, S. Sivanesan, Removal of acid violet 17 from aqueous solutions by adsorption onto activated carbon prepared from sunflower seed hull, J. Hazard. Mater. 151 (2008) 316–322.

[35] İ. Özbay, U. Özdemir, B. Özbay, S. Veli, Kinetic, thermodynamic and equilibrium studies for adsorption of azo reactive dye onto a novel waste adsorbent: Charcoal ash, Desalin. Water Treat. 51 (2013) 6091–6100.

[36] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Preparation of activated carbon from coconut husk: Optimization study on removal of 2,4,6-trichlorophenol using response surface methodology, J. Hazard. Mater. 153 (2008) 709–717.

[37] B.H. Hameed, I.A.W. Tan, A.L. Ahmad, Adsorption isotherm, kinetic modeling and mechanism of 2,4,6-trichlorophenol on coconut husk-based activated carbon, Chem. Eng. J. 144 (2008) 235–244.

[38] Z.N. Garba, A.R. Afidah, Process optimization of $K_2C_2O_4$-activated carbon from *Prosopis africana* seed hulls using response surface methodology, J. Anal. App. Pyrol. 107 (2014) 306–312.

[39] M. Auta, B.H. Hameed, Optimized waste tea activated carbon for adsorption of Methylene Blue and Acid Blue 29 dyes using response surface methodology, Chem. Eng. J. 175 (2011) 233–243.

[40] M.A. Ahmad, R. Alrozi, Optimization of preparation conditions for mangosteen peel-based activated carbons for the removal of Remazol Brilliant Blue R using response surface methodology, Chem. Eng. J. 165 (2010) 883–890.

[41] Y. Sudaryanto, S.B. Hartono, W. Irawaty, H. Hindarso, S. Ismadji, High surface area activated carbon prepared from cassava peel by chemical activation, Bioresour. Technol. 97 (2006) 734–739.

[42] A. Bacaoui, A. Yaacoubi, A. Dahbi, C. Bennouna, R. Phan Tan Luu, F.J. Maldonado-Hodar, J. Rivera-Utrilla, C. Moreno-Castilla, Optimization of conditions for the preparation of activated carbons from olive-waste cakes, Carbon 39 (2001) 425–432.

[43] G.G. Stavropoulos, A.A. Zabaniotou, Production and characterization of activated carbons from olive-seed waste residue, Micropor. Mesopor. Mater. 82 (2005) 79–85.

[44] A.C. Lua, T. Yang, Effect of activation temperature on the textural and chemical properties of potassium hydroxide activated carbon prepared from pistachio-nut shell, J. Colloid Interface Sci. 274 (2004) 594–601.

[45] F.C. Wu, R.L. Tseng, Preparation of highly porous carbon from fir wood by KOH etching and CO_2 gasification for adsorption of dyes and phenols from water, J. Colloid Interface Sci. 294 (2006) 21–30.

[46] D. Adinata, W.M.A.W. Daud, M.K. Aroua, Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3, Bioresour. Technol. 98 (2007) 145–149.

[47] M.A. Ahmad, R. Alrozi, Optimization of rambutan peel based activated carbon preparation conditions for Remazol Brilliant Blue R removal, Chem. Eng. J. 168 (2011) 280–285.

[48] A.A. Ahmad, B.H. Hameed, A.L. Ahmad, Removal of disperse dye from aqueous solution using waste-derived activated carbon: Optimization study, J. Hazard. Mater. 170 (2009) 612–619.

[49] J.M. Salman, Optimization of preparation conditions for activated carbon from palm oil fronds using response surface methodology on removal of pesticides from aqueous solution, Arab. J. Chem. 7 (2013) 101–108.

[50] IUPAC, IUPAC manual of symbols and terminology, Pure Appl. Chem. 31 (1972) 587–594.