Optimization of Preparation Conditions of Activated Carbons Based on the Shells of *Ricinodendron heudoltii*

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Abstract

The purpose of this work is to prepare better activated carbons from the shells of Ricinodendron Heudelotii by chemical activation with sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH). The process was optimized by a full factorial design (2^K) based on the analysis of the external specific surface area of sixteen (16) activated carbons prepared according to the parameters of the preparation. This active analysis reveals that under the preparation conditions, good carbons are obtained for a sodium hydroxide concentration equal to 1 M, an impregnation time of 24 h and carbonization at 500°C for 1 h. The external specific surface of this carbon is 358 $m^2 \cdot g^{-1}$. The characteristics of this prepared carbon are as follows: a pH at zero point charge (pHpzc) of 8.2, a predominantly amorphous structure, a basic character and a low ash content (4.2%). It also has surface functions; the lactonic and carbonyl groups (C=O) at 1600 cm^{-1} and the carboxylate groups (O-H or C-O) at 1340 cm^{-1}.

Keywords

Activated Carbons, Ricinodendron Heudelotii, Chemical Activation, Optimization, Specific Surface

1. Introduction

Activated carbon is widely used in environmental protection. Evidence for the

use of activated carbon dates back to antiquity with its medical use by Hippocrates around 400BC or for water purification by the Egyptians around 1500BC [1]. In the 21st century, production and manufacturing processes are improved to allow industrial production of activated carbon for various applications such as the capture of gaseous or aqueous phase pollutants and separation processes [2] [3]. Activated carbons are relatively expensive materials. They can be obtained by carbonization and activation of a precursor already containing a large part of carbon and a low percentage of inorganic matter. Enough plant debris and animal bones have been used to produce activated charcoal [4]-[9]. Thus, coconut shells [4], cocoa pods [5], peanut shells [6], rice bran [7], chicken bones [8] and corn cobs [9] were used to produce activated carbon. Manufacturing can be done in two ways: either by physical activation or by chemical activation. Physical activation consists of carbonization of the precursor followed by activation of the carbonization product in the presence of activating agents under an oxidizing atmosphere such as carbon dioxide or water vapor at very high temperatures (between 800°C and 1000°C) [10] [11]. As for chemical activation, it takes place at relatively low temperatures, which justifies its choice by many researchers. It consists of impregnating the precursor by activating agents such as Lewis acids ($ZnCl_2$ $AlCl_3$, etc.), phosphoric acid, soda, etc., and then calcining it [12] [13] [14]. This activation process has the additional advantage of a high specific surface and a well-developed microporosity of the prepared carbons, in addition to the simplicity of the method and the high activation rate [15] [16]. However, the chemicals used in this process are harmful and are mostly more expensive and more corrosive than the oxidants used in physical activation. The production of activated carbon by chemical activation should be optimized in order to minimize the quantity and concentration of activating agent used in order to reduce the environmental consequences during the production of activated carbon.

In this work, particular attention is paid to the production of activated carbons based on Ricinodendron Heudelotii shells. Indeed, previous work has proven that these shells are excellent precursors for producing activated carbon [17].

The Ricinodendron Heudelotii plants give fruits whose kernels are widely used in cooking in Africa and for cosmetics. After extraction of the almond, the shells are thrown away becoming domestic waste which piles up because it is difficult to biodegrade. Using this abundant waste material could help reduce the cost of producing activated carbons.

The optimization of the production of activated carbon based on this precursor having never been the subject of study, we undertook to carry out this research work.

The objective of this work is to optimize the production of activated carbon based on Ricinodendron Heudelotii shells in order to have carbons with excellent adsorbent properties and able to adsorb a varied number of pollutants con-

tained in water.

To achieve this, we first evaluated the effect of the different variables: the activating agent, the impregnation ratio, the impregnation time and the carbonization temperature on the preparation of the carbons. Subsequently, methylene blue being used as a model pollutant to determine the external specific surface, an experimental plan was applied to the various carbons applied to determine the optimal parameters. Finally, the best activated carbon is characterized.

2. Materials and Methods

2.1. Precursor

The shells of Ricinodendron Heudelotii used in this work were obtained from peasant women in the town of Bangolo in western Côte d'Ivoire after extraction of the kernel. Indeed after extraction of the almonds, these shells are abandoned in nature and constitute abundant waste there. The shells were first washed with distilled water to remove all impurities, then dried in an oven at 105°C for 24 hours. The shells were subsequently crushed to have diameters between 1 and 2 mm.

2.2. Chemical Agents and Apparatus

All the chemicalsreagents used in this study are analytical grade. These are sulfuric acid (H_2SO_4, 96%) supplied by CARLO ERBA (France), sodium hydroxide (NaOH, 99.1%) manufactured by VWR CHEMICALS (Czech Republic), methylene blue ($C_{16}H_{18}ClN_3S$) 100 g STDC38022 and distilled water.

A Nerbatherm muffle furnace, a UV-30 SCAN absorption spectrophotometer, a Mega Star 600 centrifuge, a GBC Emma XRD device with a copper anticathode and Raman spectrometer are the main devices used.

2.3. Choice of Factors

The operating conditions of impregnation and pyrolysis significantly influence the adsorbent power of an activated carbon [18].

In the present work, four (4) factors were considered within the framework of the design of experiments because of the importance of their influence on the adsorption capacity during the preparation of an activated carbon. These are the activating agent (oxidant), the initial concentration of the activating agent, the soaking time and the carbonization temperature.

Thus with these four (4) factors, the experimental domain (Table 1) for the preparation of the different carbons was defined. U_1, U_2, U_3 and U_4 are the real variables.

2.4. Method of Preparation of Carbons

The prepared activated carbons were chemically activated with sulfuric acid (H_2SO_4) or soda (NaOH). The previously cleaned hulls were impregnated with either H_2SO_4 or NaOH (1 M or 2 M). Some mixtures were kept for 24 hours and

Table 1. Experimental field.

Factors	Names	Min level (−1)	Max level (+1)
U_1	Initial concentration	1.00	2.00
U_2	Impregnation time	24.00	48.00
U_3	Carbonization temperature	400.00	500.00
U_4	Activating agent	NaOH	H_2SO_4

others 48 hours with stirring (1500 rpm). Once the activation step was completed, each mixture was filtered and oven-dried at 105˚C for 4 hours. The impregnated shells were placed in a quartz crucible to be calcined in a Nerbatherm muffle furnace under an inert atmosphere for one hour. The carbonization temperatures are 400˚C and 500˚C. The carbon obtained is cooled, washed to neutral pH, then dried and weighed. Sixteen (16) activated carbons were thus prepared.

2.5. Construction of the Matrix of Experiences

The experiment matrix is the table that indicates the number of experiments to be carried out with the way to vary the factors and the order in which to carry out the experiments. For k variables (factors), the experiment matrix has k columns and 2^k rows. All columns start with −1. We alternate the −1 and the +1 every row for the first column, every two rows for the second column, every four rows for the third and more generally, every 2^{j-1} rows for the jth column

In this work, with four (4) factors, the complete factorial experience matrix is formed of $2^4 = 16$ combinations described in **Table 2**. X_1, X_2, X_3 and X_4 are coded variables.

2.6. Elaboration of the Mathematical Model

We can write a mathematical model of the response studied Y as a function of all the factors X_i according to the formula:

$$Y = a_0 + \sum a_i X_i + \sum a_{ij} X_i X_j + \sum a_{ijk} X_i X_j X_k + \cdots \qquad (1)$$

where a_0: the medium effect, a_i: the main effects, a_{ij}: the second-order interaction effects, a_{ijk}: the third-order interaction effects and X_i: the coded variables.

The effect of a factor i is the change in the response when the corresponding coded variable X_i increases by one unit. Its estimate b_i is determined by taking the difference between the arithmetic mean of the results obtained when X_i is at the upper level +1 and the mean of the results obtained when X_i is at the lower level −1 (multiple linear regression). The various coefficients are calculated using the following formulas:

$$a_0 = \frac{\sum Y}{n} \qquad (2)$$

$$a_i = \frac{\sum Y_{i+} - \sum Y_{i-}}{n} \qquad (3)$$

Table 2. Matrix of factorial experiences 2^4.

Experience	X_1	X_2	X_3	X_4
1	−1	−1	−1	−1
2	+1	−1	−1	−1
3	−1	+1	−1	−1
4	+1	+1	−1	−1
5	−1	−1	+1	−1
6	+1	−1	+1	−1
7	−1	+1	+1	−1
8	+1	+1	+1	−1
9	−1	−1	−1	+1
10	+1	−1	−1	+1
11	−1	+1	−1	+1
12	+1	+1	−1	+1
13	−1	−1	+1	+1
14	+1	−1	+1	+1
15	−1	+1	+1	+1
16	+1	+1	+1	+1

With: Y_{i+}: the yield of factor i at the upper level (+1), Y_{i-}: the yield of factor i at the lower level (−1), a_0: the average coefficient and a_i: the main coefficient of factor i.

The interaction coefficients were calculated from the model matrix for a full factorial design 2^4. The coefficients were then calculated using the same formula as the calculation of the main coefficients. The significant coefficients are determined by comparing the calculated coefficients to twice the experimental standard deviation (σ_e). These coefficients are interpreted as follows:

- A confusion coefficient is statistically nil and is not taken into account in the model $S_i |a_i| < 2 \times \sigma_e$,
- A confusion coefficient is statistically different from zero and is taken into account in the model $S_i |a_i| > 2 \times \sigma_e$.

The experimental data were analyzed using the software NEMROD (new efficient methodology of research using optimal design).

3. Results and Discussion

The two parameters used to optimize the preparation of the activated carbon are the yield of activated carbon and the external specific surface. The results obtained for the various activated carbons prepared are given in **Table 3**.

3.1. Analysis of the Results of the Yields Obtained from the Prepared Activated Carbons

Yield is an important quantitative characteristic for activated carbons. It reflects

Table 3. Experimental plan and results obtained for yields (%) and specific surfaces (m²·g⁻¹) of the various activated carbons (ACi) prepared.

N°Exp	Initial Concentration (M)	Impregnation time (Hour)	Carbonization temperature (˚C)	Activatingagent (g)	Y_1: Yield of carbon (%)	Y_2: External specific surface (m²·g⁻¹)
1	1.00	24	400	NaOH	58.20 (CA1)	316.69 (CA1)
2	2.00	24	400	NaOH	58.60 (CA2)	201.98 (CA2)
3	1.00	48	400	NaOH	59.20 (CA3)	143.84 (CA3)
4	2.00	48	400	NaOH	62.07 (CA4)	119.33 (CA4)
5	1.00	24	500	NaOH	53.00 (CA5)	357.99 (CA5)
6	2.00	24	500	NaOH	49.20 (CA6)	199.63 (CA6)
7	1.00	48	500	NaOH	51.20 (CA7)	231.94 (CA7)
8	2.00	48	500	NaOH	53.40 (CA8)	89.75 (CA8)
9	1.00	24	400	H_2SO_4	55.80 (CA9)	112.02 (CA9)
10	2.00	24	400	H_2SO_4	56.40 (CA10)	103.26 (CA10)
11	1.00	48	400	H_2SO_4	57.20 (CA11)	103.70 (CA11)
12	2.00	48	400	H_2SO_4	56.20 (CA12)	81.72 (CA12)
13	1.00	24	500	H_2SO_4	51.60 (CA13)	119.76 (CA13)
14	2.00	24	500	H_2SO_4	50.60 (CA14)	138.96 (CA14)
15	1.00	48	500	H_2SO_4	49.80 (CA15)	114.62 (CA15)
16	2.00	48	500	H_2SO_4	50.20 (CA16)	140.15 (CA16)

the mass loss of the biomass during its pyrolysis. It is expressed by the following formula where m_1 is the mass before calcination and m_2 that after calcination.

$$\text{Yield}(\%) = \frac{m_1 - m_2}{m_1} \times 100 \qquad (4)$$

The results of **Table 4** show a low variability at the level of the different yields (Y_1) of the activated carbons prepared, because these vary from 49.80% to 62.07%, with an average of 54.54% (value of a_0 in **Table 4**). Authors have obtained yields of 49% to 52% during the preparation of activated carbon by orthophosphoric acid using coconut shells as a precursor [19].

3.1.1. Estimates and Statistics of the Coefficients Linked to the Various Factors Acting on the Yield of Prepared Activated Carbons

The experimental error (standard deviation) obtained is 17. The significant coefficients (those whose absolute value of their coefficient is greater than 2*σ = 0.666) are the main effects a_3 and a_4 respectively linked to the time variables d stirring (X_3) and activating agent (X_4) (**Table 2**). As for the interaction effects, none of them has a significant effect on the different yields of the activated carbons obtained (**Table 4**). The importance of the factors is also highlighted by using Equation (5). Indeed, it is possible to give more significant information by

Table 4. Statistics and estimates of coefficients related to factors acting on the yield of prepared activated carbons.

Name	Coefficient	Stand Deviat	Signif. %
a_0	**54.542**	**0.333**	**<0.01*****
a_1	0.042	0.333	90.5
a_2	0.367	0.333	32.0
a_3	**−3.417**	**0.333**	**0.0150*****
a_4	**−1.067**	**0.333**	**2.38***
a_{12}	0.517	0.333	18.1
a_{13}	−0.317	0.333	38.5
a_{23}	−0.342	0.333	35.1
a_{14}	−0.167	0.333	63.7
a_{24}	−0.492	0.333	19.9
a_{34}	0.492	0.333	19.9

calculating the contribution of each factor to each response. The diagram obtained is that of Pareto.

$$P_i = \frac{a_i^2}{\sum a_i^2} * 100 \quad (i \neq 0) \tag{5}$$

where b_i represents the different estimates the main effect of the factors.

These observations elucidated previously are confirmed by the analysis of the Pareto diagram (**Figure 1**) which effectively shows a significant contribution of the factors U_3 and U_4 on the yield of the activated carbons prepared. These contributions are 83.71% and 8.16% (**Figure 1**) respectively for the carbonization time factors and the type of activating agent. This Pareto diagram also confirms very low contribution rates (**Figure 1**) in general from the different interactions existing between the different factors.

3.1.2. Influencing Preparation Factors on Mass Yield
- Influence of the initial concentration (M)

The coefficient a_1 = +0.042 (**Table 4**) linked to the initial concentration factor (M) indicates that the different yields of these prepared activated carbons undergo an increase of 0.042 × 2 = 0.084%, when this goes from 1 to 2 M. There is an increase negligible on these yields. This could be explained by the fact that at 1 M and 2 M we could get good returns. This very small increase in the various yields was confirmed previously by the low rate of contribution of this factor (Pareto diagram). The positive sign of the coefficient linked to this factor being positive indicates that for better yields of these prepared activated carbons, it will be necessary to use initial concentrations greater than or equal to 2 M. However, given the fact that this increase is negligible, the Initial concentration of 1 M can be used to obtain large yields.
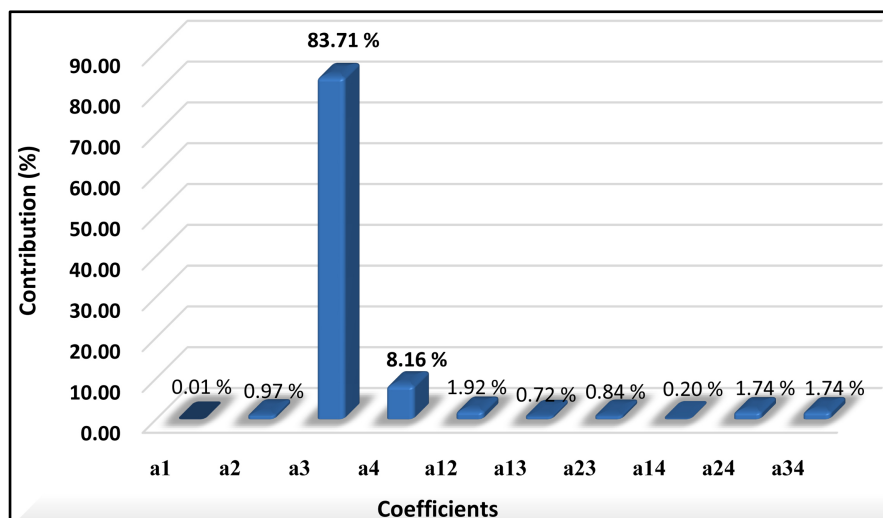- Influence of soaking time (Hour)

Figure 1. Pareto chart of main coefficients and related interactions to the factors of the yields obtained from the activated carbons prepared.

The impregnation time has a lesser influence on the mass yield while the concentration has a significant influence on the mass yield. This is explained by a continuous release of tars inside the pores. Some authors have obtained similar results [20] [21]. They respectively activated date pits and coconut shells with phosphoric acid. Thus, the coefficient a_2 = +0.367 (**Table 4**) linked to the impregnation time factor (hour) indicates that the different yields of these prepared activated carbons undergo an increase of $0.367 \times 2 = 0.734\%$, when this goes from 24 to 48 hours. There is also an insignificant increase in these yields. This could be explained by the fact that with 24 hours, we can obtain good returns. This very small increase in the various yields was confirmed previously by the low rate of contribution of this factor (Pareto diagram). The positive sign of the coefficient related to this factor that for better yields of these prepared activated carbons, it will be necessary to use times equal to 48 hours. However, given this insignificant increase, we could obtain good yields also with an impregnation time of 24 hours.

- Influence of temperature carbonization (˚C)

The coefficient a_3 = −3.417 (**Table 4**) related to the carbonization temperature factor (˚C) indicates that the various yields of these prepared activated carbons undergo a reduction of $3.417 \times 2 = 6.834\%$, when this goes from 400˚C to 500˚C. There is also a significant decrease in these yields. This consequent decrease in the different yields was previously confirmed a very high contribution of 83.71% of this factor this response (Pareto diagram). However, the coefficient linked to this factor being negative, this clearly indicates that for better yields of these prepared activated carbons, it will be necessary to use temperatures equal to 400˚C since there is a reduction (6.834%) in the yield rates.

- Influence of the activating agent (NaOH or H_2SO_4)

The coefficient a_4 = −1.067 (**Table 4**) linked to the activating agent type factor indicates that the different yields of these prepared activated carbons undergo a

reduction of $1.067 \times 2 = 2.134\%$, when it passes from the NaOH activating agent to the H_2SO_4 activating agent. There is also a slight decrease in these yields. This slight decrease in the various yields was previously confirmed with an average contribution of 8.71% of this factor to this response (Pareto chart). However, the coefficient linked to this factor being negative, this clearly indicates that for better yields of these prepared activated carbons, it will be necessary to use the activator NaOH since there is a reduction (2.134%) in the yield rates. In short, to obtain a good yield rate from the activated carbon prepared in this study, the following levels must be used: 1 M for the initial concentration (X_1), 24 hours as the impregnation time (X_2), 400 as the carbonization temperature (X_3) and NaOH as activating agent (X_4). With these levels the yield obtained is 58.20%.

3.2. Analysis of the Results of the Specific Surfaces Obtained from the Prepared Activated Carbons

The specific surface is one of the important characteristics for obtaining a good activated carbon. Methylene blue (MB) is used to determine the external surface area of carbons. Indeed, this molecule can only enter the macropores. Thus, the MB is used as a probe to evaluate the adsorption capacity of the adsorbent for solutes of molecule sizes >15 Å [22] [23].

The concentration of methylene blue was determined by a UV-30 SCAN absorption spectrophotometer. The amount of methylene blue adsorbed is determined by the following equation:

$$Q_{ads} = \frac{C_0 - C_e}{m} \times V \qquad (6)$$

where Q_{ads} (mg·g^{-1}) is the quantity of MB adsorbed per gram of carbon, C_0 (mg·L^{-1}) is the initial concentration of MB, C_e (mg·L^{-1}) is the concentration of MB at the balance and V (L), the volume of MB.

The application of the Langmuir model in its linear form given by Equation (7), made it possible to determine the external specific surface using Equation (8).

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m K_L} \times \frac{1}{C_e} \qquad (7)$$

$$S_{BM} = \frac{Q_m \cdot S \cdot N}{1000 \cdot M} \qquad (8)$$

where Q_e (mg·g^{-1}) is the quantity of MB adsorbed per unit mass of carbon at equilibrium; Q_m (mg·g^{-1}), the maximum amount of MB adsorbed per unit mass of carbon; C_e (mg·L^{-1}) is the concentration of MB at equilibrium; K_L is the Langmuir constant, S_{BM} (m^2·g^{-1}) is the external specific surface; S is the area occupied by a molecule of MB (175 Å^2); N (6.02 × 10^{23} mol^{-1}) is Avogadro's constant and M (319.85 g·mol^{-1}), the molar mass of MB.

The specific surface areas of the prepared carbons (Y_2) are listed in **Table 3**. The values vary between 14.62 m^2·g^{-1} and 357.99 m^2·g^{-1}, with an average of 160.959 m^2·g^{-1} (value of b$_0$ in the **Table 5**). A great variability of these specific

Table 5. Statistics and estimates of coefficients related to factors acting on the specific surface of prepared activated carbons.

Name	Coefficient	Stand Deviat	Signif. %
b_0	160.959	7.939	<0.01***
b_1	−26.611	7.939	2.03*
b_2	−32.828	7.939	0.904**
b_3	13.141	7.939	15.9
b_4	−46.685	7.939	0.202**
b_{12}	6.217	7.939	46.9
b_{13}	−5.366	7.939	52.9
b_{23}	2.842	7.939	73.5
b_{14}	28.360	7.939	1.60*
b_{24}	28.601	7.939	1.55*
b_{34}	0.958	7.939	90.9

surfaces of the activated carbons prepared is noted.

3.2.1. Estimates and Statistics of the Coefficients Related to the Various Factors Acting on the Specific Surface of Prepared Activated Carbons

The experimental error (standard deviation) obtained is 7.989 (Table 5). The significant coefficients are the main effects b_1, b_2 and b_4 respectively linked to the variables; initial concentration (X_1), impregnation time (X_2) and activating agent (X_4) (Table 2). As for the effects of interactions, only b_{14} (existing interaction between the factors: Initial concentration and Activating agent) and b_{24} (existing interaction between the factors: Impregnation time and Activating agent) have a significant effect on the different specific surface of activated carbons obtained (Table 5).

These observations elucidated previously are confirmed by the analysis of the Pareto diagram (Figure 2) which effectively shows a significant contribution of the factors U_1, U_2 and U_4 on the specific surface of the activated carbons prepared. These contributions are 12.13%; 18.46% and 37.34% (Figure 2) respectively for the factors: Initial concentration (U_1), impregnation time (U_2) and Activating agent (U_4). This Pareto diagram also confirms considerable contribution rates of the interactions between the factors: initial concentration and activating agent and between the factors: impregnation time and activating agent (Figure 2). However, the interactions between the factors: initial concentration and impregnation time (b_{12}), impregnation time and carbonization time (b_{23}) and impregnation time and type of activating agent (b_{34}) have a very insignificant effect on the specific surface (Y_2) of these carbons obtained.

3.2.2. Influencing Preparation Factors on the Specific Surface of the Prepared Activated Carbons
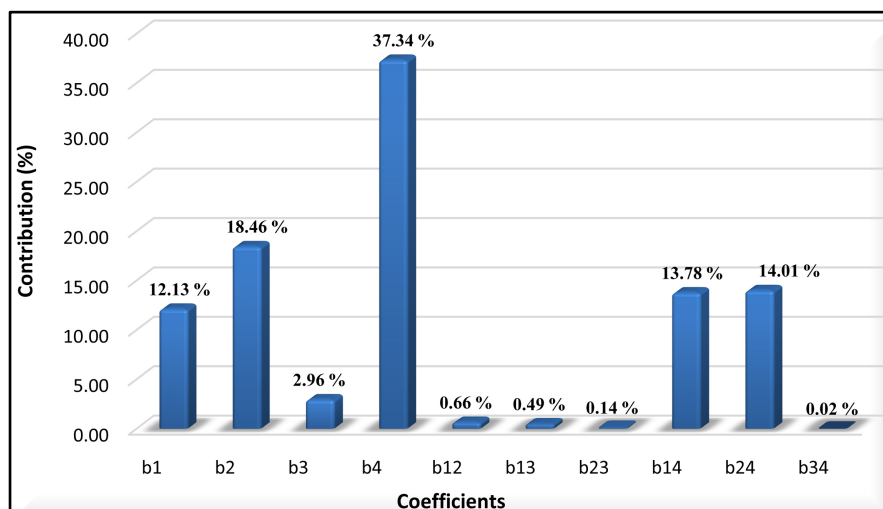- Influence of the initial concentration (M)

Figure 2. Pareto diagram of the main coefficients and interactions related to the factors of the specific surfaces obtained from the prepared activated carbons.

The coefficient $b_1 = -26.611$ (Table 5) linked to the initial concentration factor (M) indicates that the different specific surfaces of these prepared activated carbons undergo a considerable loss of $26.611 \times 2 = 53.222$ $m^2 \cdot g^{-1}$, when this goes from 1 to 2 M. There is a significant loss on these specific surfaces. This consequent loss in $m^2 \cdot g^{-1}$ of the specific surfaces was previously confirmed by a high rate of contribution (12.13%) of this factor on the preparation of the activated carbons (Pareto diagram). However, the negative sign of this coefficient related to this factor clearly indicates that to obtain better specific surfaces of these coals, it will be necessary to use initial concentrations equal to 1 M.

- Influence of impregnation time (Hours)

Thus, the coefficient $b_2 = -32.828$ (Table 5) linked to the impregnation time factor (Hour) indicates that the various specific surfaces obtained from these prepared activated carbons undergo a significant reduction of $32.828 \times 2 = 65.665$ $m^2 \cdot g^{-1}$, when this goes from 24 to 48 hours. There is also an insignificant increase in these specific surfaces. This consequent loss of specific surfaces has been confirmed previously by an important contribution of this factor (Pareto diagram). However, the negative coefficient sign related to this factor clearly indicates that, to obtain better specific surfaces of these prepared activated carbons, times equal to 24 hours should be used.

- Influence of carbonization temperature (°C)

The coefficient $b_3 = 13.141$ (Table 5) related to the carbonization temperature factor (°C) indicates that the different specific surfaces of these prepared activated carbons undergo an average increase of $13.141 \times 2 = 26.282$ $m^2 \cdot g^{-1}$, when this increases from 400°C to 500°C. There is also a significant decrease in these specific surfaces. This small decrease in specific surface areas in $m^2 \cdot g^{-1}$ was previously confirmed as a small contribution of 2.96% of this factor to this response (Figure 2: Pareto diagram). However, the coefficient linked to this factor being negative, this clearly indicates that for better specific surfaces of these prepared

activated carbons, it will be necessary to use temperatures greater than or equal to 500˚C since there is an increase (26.282 $m^2 \cdot g^{-1}$) on them.

- Influence of the activating agent (NaOH or H_2SO_4)

The coefficient $b_4 = -46.685$ (Table 5) related to the activating agent type factor indicates that the various specific surfaces of these prepared activated carbons undergo a reduction of $46.685 \times 2 = 93.37$ $m^2 \cdot g^{-1}$, when this passes from the activating agent NaOH to activating it H_2SO_4. There is also a slight decrease in these specific surfaces. This slight decrease in the various specific surfaces was previously confirmed as a very high contribution of 37.34%, of this factor this response (Pareto diagram). However, the coefficient linked to this factor being negative, this clearly indicates that for better specific surfaces of these prepared activated carbons, it will be necessary to use the activator NaOH since there is a significant reduction (93.37 $m^2 \cdot g^{-1}$) of these. NaOH appears in this study as the best activating agent for obtaining good specific surfaces [24].

3.2.3. Influence of Interactions between Preparation Factors on the Specific Surface of Prepared Activated Carbons

With regard to the values recorded in Table 5 the interactions X_{14} and X_{24} have a more significant interaction effect according to the rule of significance of the coefficients.

- Influence of the interaction between the initial concentration and the type of activating agent (X_{14})

Using the axis of the activating agent, it appears that the value of the specific surface decreases from 150 $m^2 \cdot g^{-1}$ at 1 M and from 36.65 $m^2 \cdot g^{-1}$ at 2 M, when changes from the activating agent (X_4) NaOH to the activating agent H_2SO_4. In both cases there is a reduction, but the most important is that of 1 M. Besides this fact, the best specific surface is observed at 1 M and with the activating agent NaOH. According to Figure 3, this specific surface is 262.62 $m^2 \cdot g^{-1}$. It also emerges from the analysis of the interaction between the initial concentration and the type of activator that 1 M and NaOH are the best levels for obtaining high specific surface areas. These observations were also observed previously during the analysis of the influence of the type of activating agent (X_4) and the initial concentration (X_1).

Influence of the interaction between the impregnation time and the type of activating agent (X_{24})

Also using the axis of the activating agent, it appears that the value of the specific surface decreases by 170.57 $m^2 \cdot g^{-1}$ at 24 hours and by 36.17 $m^2 \cdot g^{-1}$ at 48 hours, when we pass from the activating agent (X_4) NaOH to the activating agent H_2SO_4. In both cases there is also a decrease, but the most important is that of 24 hours. Besides this fact, the best specific surface is observed at 24 hours and with the activating agent NaOH. According to Figure 4, this specific surface is 289.07 $m^2 \cdot g^{-1}$. It also emerges from the analysis of the interaction between the impregnation time (X_2) and the type of activator (X_4) that 24 hours and NaOH are once again the best levels for obtaining high specific surface areas.
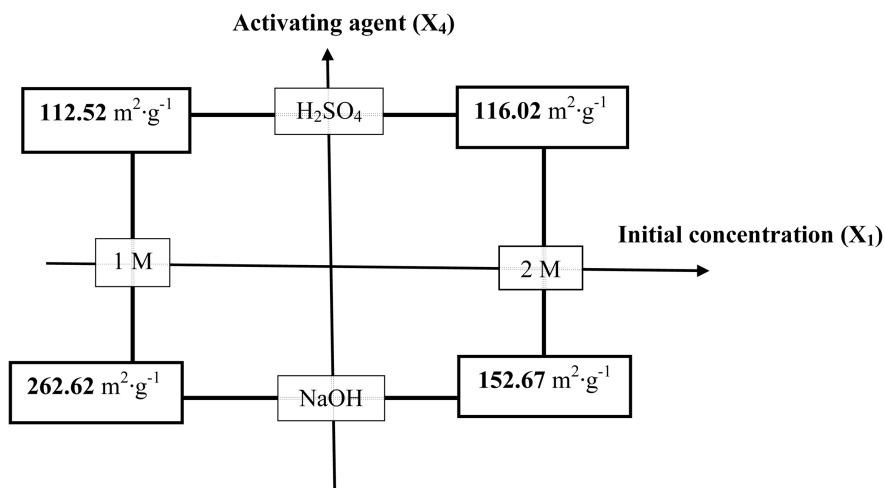
Figure 3. Interaction diagram between the initial concentration and the carbon impregnation time (X_{14}).
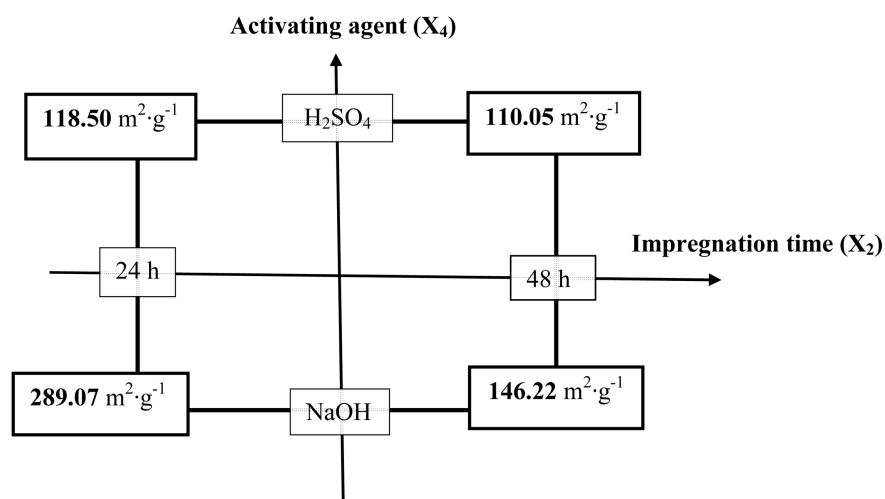

Figure 4. Interaction diagram between impregnation time and carbonization temperature (X_{24}).

In short, the analysis of the influence of factors and interactions show that to obtain high specific surfaces, it will be necessary to use as levels: 1 M for the initial concentration (X_1), 24 hours for the impregnation time (X_2), 500°C for the carbonization temperature (X_3) and NaOH as the best activating agent (X_4) to obtain good specific surface areas. These best levels were confirmed because the highest specific surface obtained is 357.99 $m^2 \cdot g^{-1}$ using these levels (Experiment 5 of **Table 3**).

3.3 Modeling of the Responses Studied

In this study, yield Y_1 (%) and specific surface Y_2 ($m^2 \cdot g^{-1}$) were investigated as responses. However, the specific surface area being one of the best characteristics for a good activated carbon, it will be the response that will be modeled.

Indeed, the mathematical model that emerges from this experimental plan is a

1st degree model, whose equation is:

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 + b_{12}(X_1 X_2) + b_{13}(X_1 X_3)$$
$$+ b_{23}(X_2 X_3) + b_{14}(X_1 X_4) + b_{24}(X_2 X_4) + b_{34}(X_3 X_4)$$

(9)

where, b_i is the effect of factor (X_i) and b_{ij} that of the interactions between factors *i* and *j*.

According to the estimates and statistics of the coefficients, b_1, b_2, b_4, b_{14} and b_{24} are the most significant than the others. Thus, the mathematical model of the response Y_2 is in the form:

$$Y = 160959 - 26611 X_1 - 32828 X_2 - 46685 X_4 + 28360 X_1 X_4 + 28601 X_2 X_4 \quad (10)$$

The statistical analysis of this model first leads to the analysis of variance table (ANOVA) (Table 6). It mainly indicates that the model used is well adjusted since the sum of the squares of the residuals is (5.04172×10^3) is large compared to the total sum of the squares (9.84298×10^4). A more detailed analysis of the correlation coefficient which is 0.946 (Table 6) confirms that the model is well adjusted because it tends towards 1 ($R^2 = 0.946$). The model obtained explains the phenomenon (Y_2) to more than 94.6%. All these findings confirm the fact that the linear model (Equation (8)) is best suited to explain this phenomenon. The correlation coefficient obtained confirmed not only that our experimental field was well chosen but also and above all that 94.6% of our specific surfaces obtained would be good. Indeed, a prepared activated carbon is of good quality when it has a specific surface area above 100 m²·g⁻¹ [25].

3.4. Characterization of the Best Activated Carbon

3.4.1. Surface Functions

Raman spectroscopy used in substitution of the Fourier transform by infrared was used for the qualitative determination of the surface functions. Indeed, the Raman vibrations which depend on the molecular polarizabilities are more easily transposable from one molecule to another than the intensities of the infrared spectrum which depend on the dipole moments and are more sensitive to the presence of the other groups in the molecule. Raman spectra can therefore also be used to identify organic and inorganic species in solution. The curve obtained is that of Figure 5. Two narrow peaks are observed at 1340 and 1600 cm⁻¹. The peak at 1600 cm⁻¹ is characteristic of a C=O bond of lactonic and carbonyl groups as well as C=C bonds in the aromatic nucleus [26]. That of 1340 cm⁻¹ is characteristic of an O-H or C-O bond of a carboxylate group [27]. There would

Table 6. Analysis of variance (ANOVA).

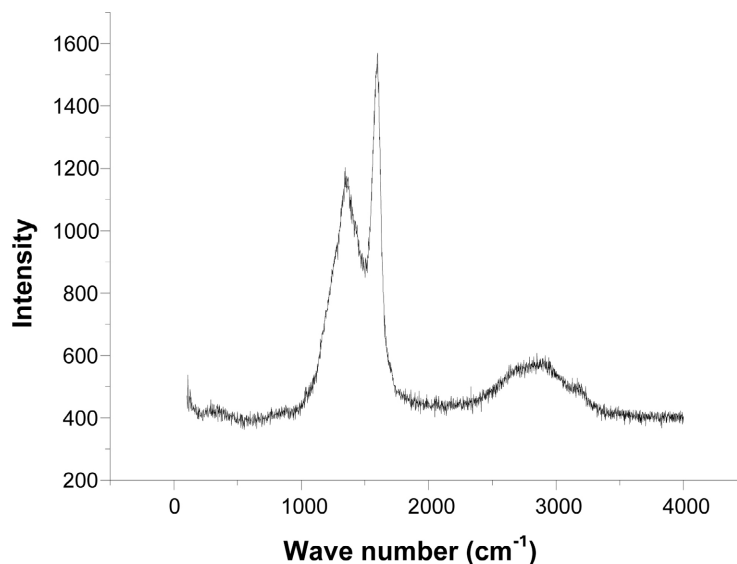| Source of Variation	sum of squares	Deviation	Correlation coefficient (R^2)
Regression	9.33881×10^4	31.754	0.949
Residues	5.04172×10^3		
Total	9.84298×10^4		

Figure 5. Raman spectrum of activated Carbon.

therefore be the presence of acid (carboxylic, lactonic and phenolic) and basic functions at the surface of the activated carbon.

3.4.2. pH at Zero Point Charge (pHpzc)

pHpzc is a good indicator of the chemical and electronic properties of functional groups. Thus, when pHpzc > pH, the AC surface is positively charged, while when pHpzc < pH, the AC surface is negatively charged [28]. The result of pHpzc is given in Figure 6. The value of pHpzc is 8.2, suggesting that the character of carbon is basic. If the pH of the solution is lower than the pHpzc, the surface functional groups of the carbon will be protonated by an excess of H⁺ protons in the solution, the adsorbent attracting negatively charged adsorbate. On the other hand, if the pH of the solution is higher than the pHpzc the surface functional groups will be deprotonated by the presence of the OH⁻ ions of the solution. Consequently, the support attracts any positively charged adsorbate and promotes the adsorption of cationic dyes, by increasing the electrostatic forces between the negative charge of the adsorbent and the positive charge of the dye [29]. Thus the adsorption of cationic molecules on this carbon in aqueous medium would be favored if the pH is higher than 8.2.

3.4.3. X-Ray Diffraction (XRD)

The XRD profile of the Ricinondendron Heudelotiioptimun Activated Carbon is shown in Figure 7. The X-ray diffraction pattern did not show well-defined peaks in any region, indicating that no discrete mineral phase was detected. Thus, activated carbon has a predominantly amorphous structure.

3.4.4. Ash Content of Activated Carbon

Through the ash content, it is the quality of the preparation of the carbon that is highlighted. The presence of ash in activated carbon is undesirable for its quality and is considered an impurity [21]. When the ash content is greater than 20%, it
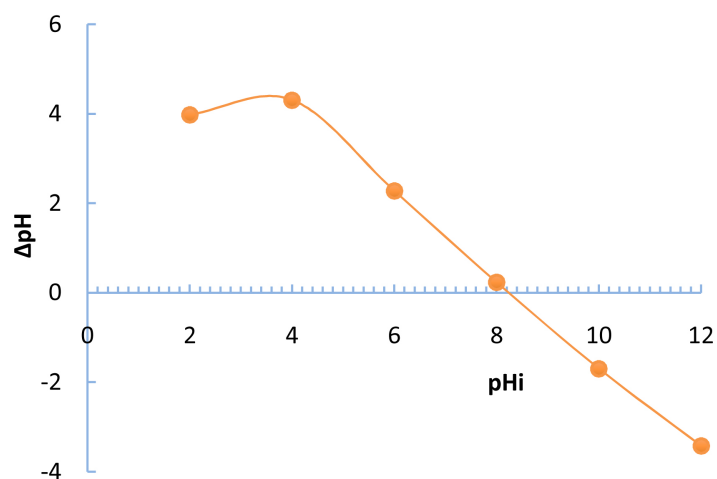
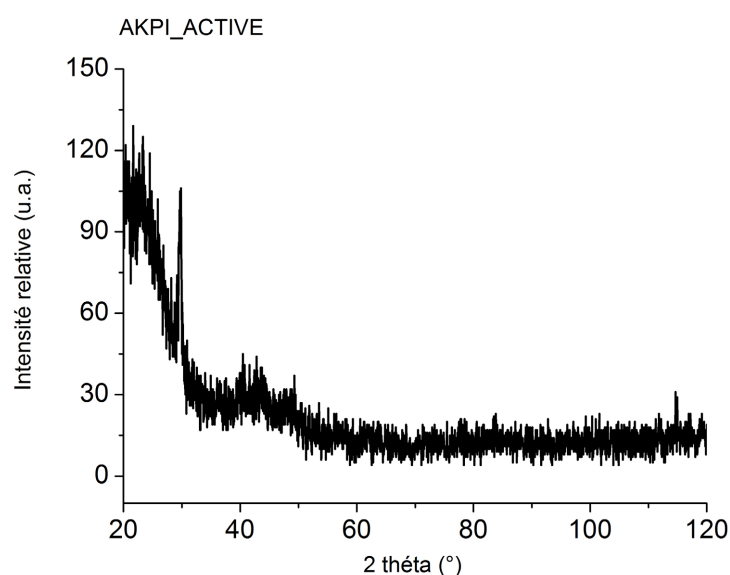**Figure 6.** Curve for activated Carbon pHpzc determination.

Figure 7. XRD spectrum of activated Carbon.

is considered too high. The consequence is a decrease in the adsorption capacity of the carbon. The ash content obtained for this charcoal is 4.2%, therefore less than 10%, thus showing that the charcoal has been well prepared. This low value of the ash content is due on the one hand to the fact that the precursor of this carbon is the vegetable matter therefore less rich in mineral matter and on the other hand to the washing of the carbon after preparation which eliminated the ashes possibly available.

4. Conclusion

In this work, the complete factorial plan (2^K) was used as an experimental methodology, for the preparation of activated carbons based on the shells of Ricinodendron Heudelotii by chemical activation. The parameters evaluated were the activating agent (oxidant), the initial concentration of the activating agent,

the impregnation time and the carbonization temperature. The results showed that a significant synergy of action between the activating agents and their concentrations was the factor that most influenced the adsorption capacity of methylene blue by these carbons as well as the production yield. The activated carbon having the greatest specific surface (358 $m^2 \cdot g^{-1}$) with a satisfactory mass yield (58.2%) is obtained by impregnating the shells for 24 hours with 1 M NaOH and carbonizing them at a temperature of 500˚C. The characterization of this coal showed its predominantly amorphous structure and its low ash content (4.2%). The pHpzc is 8.2, suggesting its basic character. The adsorption of cationic molecules on this carbon in an aqueous medium would therefore be favored if the pH is greater than 8.2. This carbon can be used in the depollution of water loaded with dyes and metallic salts.

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Author Contributions

Kouakou Yao Urbain and Trokourey Albertdefined and designed the work and the experiment. Kouakou Yao Urbain and Karidioula Daouda prepared the materials. ZranVanh Eric-Simon and Yao Kouassi Benjamincarried out the study of modeling by experimental plans. Kouakou Yao Urbain and ZranVanh Eric-Simonwrote the manuscript. Trokourey Albert and Drogui Patrickrevised the manuscriptcritically. All authors read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Sadashiv, B. and Shivashankar, M. (2017) History, Method of Production, Structure and Applications of Activated Carbon. *International Journal of Engineering Research & Technology*, **6**, 495-498. https://doi.org/10.17577/IJERTV6IS060277

[2] Kouakou, U., Ello, A.S., Yapo, J.A. and Trokourey, A. (2013) Adsorption of Iron and Zinc on Commercial Activated Carbon. *Journal of Environmental Chemistry and Ecotoxicology*, **5**, 168-171.

[3] Puccini, M., Stefanelli, E., Tasca, A.L. and Vitolo, S. (2018) Pollutant Removal from Gaseous and Aqueous Phases Using Hydrochar-Based Activated Carbon. *Chemical Engineering Transactions*, **67**, 637-642.

[4] Urbain, Y.K., Ardjouma, D., Augustin, Y.Y. and Albert, T. (2016) Removal of Imidacloprid using Activated Carbon from Coconut Shells. *International Journal of Advanced Research in Science, Engineering and Technology*, **3**, 2573-2581.

[5] Olugbenga, S.B., Tan, T.S. and Mohd, A.A. (2011) Adsorption of Remazol Brilliant Violet-5R Reactive Dye from Aqueous Solution by Cocoa Pod Husk-Based Activated Carbon: Kinetic, Equilibrium and Thermodynamic Studies. *Asia-Pacific Journal of*

Chemical Engineering, **7**, 378-388. https://doi.org/10.1002/apj.557

[6] Paul, H.K.O., Marc, I.G.B., Urbain, K., Ardjouma, D., Aboua, J.Y. and Albert, T. (2014) Preparation and Characterization of Activated Carbons Based on Peanut Shell (Arachis Hypogea) Green Soya Shell (VignaRadiata). *International Journal of Scientific Research*, **3**, 933-937.

[7] Suzuki, R.M., And rade, A.D. and Sousa, J.C. (2007) Preparation and Characterization of Activated Carbon from Rice Bran. *Bioresource Technology*, **98**, 1985-1991. https://doi.org/10.1016/j.biortech.2006.08.001

[8] Letícia, N.C., Susanne, P.D., Angélica, F.M.S., Tito, R.S.C.J., Gabriela, C.C. and Guilherme, L.D. (2019) Preparation of Carbonaceous Materials from Pyrolysis of Chicken Bones and Its Application for Fuchsine Adsorption. *Environmental Science and Pollution Research*, **26**, 28574-28583. https://doi.org/10.1007/s11356-018-3679-2

[9] Kambiré, O., Kouakou, Y.U., Kouyaté, A. and Sadia, S.P. (2021) Removal of Rhodamine B from Aqueous Solution by Adsorption on Corn Cobs Activated Carbon. *Mediterranean Journal of Chemistry*, **11**, 271-281.

[10] Ahmad, A., Hameed, B. and Ahmad, A. (2009) Removal of Disperse Dye from Aqueous Solution Using Waste-Derived Activated Carbon: Optimization Study. *Journal of Hazardous Materials*, **170**, 612-619. https://doi.org/10.1016/j.jhazmat.2009.05.021

[11] Aber, S., Khataee, A. and Sheydaei, M. (2009) Optimization of Activated Carbon Fiber Preparation from Kenaf Using K_2HPO_4 as Chemical Activator for Adsorption of Phenolic Compounds. *Bioresource Technology*, **100**, 6586-6591. https://doi.org/10.1016/j.biortech.2009.07.074

[12] Rinita, R.J. (2015). Optimization of Conditions for the Preparation of Activated Carbon from Lapsi (*Choerospondias axillaris*) Seed Stone Using $ZnCl_2$. *Journal of the Institute of Engineering*, **11**, 128-139. https://doi.org/10.3126/jie.v11i1.14707

[13] Deng, H., *et al.* (2010) Optimization of Preparation of Activated Carbon from Cotton Stalk by Microwave Assisted Phosphoric Acid-Chemical Activation. *Journal of Hazardous Materials*, **182**, 217-224. https://doi.org/10.1016/j.jhazmat.2010.06.018

[14] André, L.C., Alexandro, M.M.V. and Eurica, M.N. (2011) NaOH-Activated Carbon of High Surface Area Produced from Coconut Shell: Kinetics and Equilibrium Studies from the Methylene Blue Adsorption. *Chemical Engineering Journal*, **174**, 117-125. https://doi.org/10.1016/j.cej.2011.08.058

[15] Angin, D., Köse, T.E. and Selengil, U.G. (2013) Production and Characterization of Activated Carbon from Sour Cherry Stones by Zinc Chloride. *Fuel*, **115**, 804-811. https://doi.org/10.1016/j.fuel.2013.04.060

[16] Blazquez, G., Hernainz, F., Calero, M. and Ruiz-Nunez, L.F. (2005) Removal of Cadmium Ions with Olive Stone: The Effect of Some Parameters. *Process Biochemistry*, **40**, 2649-2655. https://doi.org/10.1016/j.procbio.2004.11.007

[17] Kouakou, Y.U., Essy, K.F., Dembélé, A., Brou, Y.S., Ello, S.A., Gouli, B.I.M. and Trokourey, A. (2017) Removal of Imidacloprid Using Activated Carbon Produced from *Ricinodendron heudelotii* Shells. *Bulletin of the Chemical Society of Ethiopia*, **31**, 397-409. https://doi.org/10.4314/bcse.v31i3.4

[18] Diao, Y., Walawender, W.P. and Fan, L.T. (2002) Activated Carbons Prepared from Phosphoric Acid Activation of Grain Sorghum. *Bioresource Technology*, **81**, 45-52. https://doi.org/10.1016/S0960-8524(01)00100-6

[19] Gratuito, M.K.B., Panyathanmaporn, T., Chumnanklang, R.A., Sirinuntawittaya, N. and Dutta, A. (2008) Production of Activated Carbon from Coconut Shell: Optimization Using Response Surface Methodology. *Bioresource Technology*, **99**, 4887-4895.

https://doi.org/10.1016/j.biortech.2007.09.042

[20] Haimour, N.M. and Emeish, S. (2006) Utilization of Date Stones for Production of Activated Carbon Using Phosphoric Acid. *Waste Management*, **26**, 651-660. https://doi.org/10.1016/j.wasman.2005.08.004

[21] Tan,I.A.W., Ahmad, A.L. and Hameed, B.H. (2008) Preparation of Activated Carbon from Coconut Husk: Optimization Study on Removal of 2,4,6-Trichlorophenol Using Response Surface Methodology. *Journal of Hazardous Materials*, **153**, 709-717. https://doi.org/10.1016/j.jhazmat.2007.09.014

[22] Brij, B.T. and Clint, O.T. (2010) Use of Basic Methylene Blue Dye for Specific Surface Area Measurement of Metal Hexacyanoferrate(II) Complexes. *Revista de la Sociedad Químicadel Perú*, **76**, 330-335.

[23] Daouda, K., Horace, N.M., Abdelaziz, B., Abdelrani, Y. and Joseph, K.M. (2013) Optimization of Activated Carbons Prepared by H_3PO_4 and Steam Activation of Oil Palm Shells. *Journal of Chemistry*, **2013**, Article ID: 654343.

[24] Nurul, S.S., Rokiah, H., Mohd, H.M.A., Mohammed, D. and Othman, S. (2018) Optimization of Activated Carbon Preparation from Cassava Stem Using Response Surface Methodology on Surface Area and Yield. *Journal of Cleaner Production*, **198**, 1422-1430. https://doi.org/10.1016/j.jclepro.2018.07.061

[25] Deepak, P., Shikha, S. and Pardeep, S. (2017) Removal of Methylene Blue by Adsorption onto Activated Carbon Developed from *Ficus carica* Bast. *Arabian Journal of Chemistry*, **10**, S1445-S1451. https://doi.org/10.1016/j.arabjc.2013.04.021

[26] Wimonrat, T., Manop, S. and Phunsiri, H. (2011) Preparation of Activated Carbon Derived from *Jatropha curcas* Fruit Shell by Simple Thermo-Chemical Activation and Characterization of Their Physico-Chemical Properties. *Chemical Engineering Research and Design*, **89**, 335-340. https://doi.org/10.1016/j.cherd.2010.06.012

[27] Qing, S.L., Tong, Z. and Peng, W. (2010) Preparation and Characterization of Activated Carbon from Bamboo by Microwave-Induced Phosphoric Acid Activation. *Industrial Crops and Products*, **31**, 233-238. https://doi.org/10.1016/j.indcrop.2009.10.011

[28] Wibowo, N., Setyadhi, L., Wibowo, D., Setiawan, J. and Ismadji, S. (2007) Adsorption of Benzene and Toluene from Aqueous Solution onto Activated Carbon and Its Acid Heat Treated Forms: Influence of Surface Chemistry on Adsorption. *Journal of Hazardous Materials*, **146**, 237-242. https://doi.org/10.1016/j.jhazmat.2006.12.011

[29] Wang, S., Zhu, Z.H., Coomes, A. and Haghseresht, F. (2005) The Physical and Surface Chemical Characteristics of Activated Carbons and the Adsorption of Methylene Blue from Wastewater. *Journal of Colloid Interface Science*, **284**, 440-446. https://doi.org/10.1016/j.jcis.2004.10.050