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Optimizing the preparation conditions of activated carbon from coconut shells using a full factorial design

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ABSTRACT: Coconut shells have been used as a precursor for the preparation of activated carbon by the chemical activation method. The full factorial design was applied to determine the optimum conditions for preparing the activated carbon. The factors studied were the carbonization temperature, the carbonization time and the concentration of the activating agent. Phosphoric acid was the activating agent, used for chemical activation. Planning of the experiments using the three-level full factorial design method resulted in eight trials with the iodine number as the answer to each trial. The various results obtained were analyzed using Nemrow software in order to highlight the influence of factors and their interaction. The results reveal that carbonization temperature, the carbonization time and the concentration exert a significant influence on the iodine number, when they are at their high level, respectively 600 ° C, 4h, 30% for the value of the iodine index of 445.44mg/g.

KEYWORDS: Experimental design, Optimization, Coconut shells, Activated carbon.

1 INTRODUCTION

Special attention is paid to environmental protection processes in the search for adsorbent material such as activated carbon. Activated carbons (ACs) are the end products obtained after a physical or chemical activation process of any material containing a high percentage of carbon to make them extremely porous. These porous structures result in a large adsorption surface area available for adsorption or chemical reactions. They have proven to be efficient and economical materials to remove organic and mineral micropollutants in solution [1], [2].

Different types of carbon-rich materials have been used as precursors for the preparation of ACs by physical or chemical activation. They are agricultural wastes such as apricot kernels, sugar cane bagasse, shells, coffee grounds, cotton cake, bamboo, rice husk, maize stalks and tobacco stems [3], [4], wood residues [5]. The physical activation involves the step of the carbonization of the precursor followed by the activation of the resulting material in an oxidizing atmosphere such as carbon dioxide, steam, or a combination of both at high temperatures from 800°C to 1100°C [6]. For the chemical activation one step of preparation is necessary. This requires an impregnation of the raw material with an activating agent like $ZnCl_2$, H_3PO_4, and KOH following by the carbonization of the impregnated material at the temperature ranging from 400°C to 800°C and washing [7], [8]. The chemical activation offers several advantages: one step process, low energy cost, high yield in carbon, and efficient activated carbon with mixed porosity [9], [10].

The production of high-quality activated carbons with satisfactory physicochemical properties is at the heart of research because it depends on several factors which must be taken into account. Experimental design methods based on mathematical models are increasingly developed and implemented for this purpose [11], [12]. The preparation of activated carbon can be influenced by many factors. So, the factorial designs are widely used to study the effects of experimental factors and the interactions between those factors, that is, how the effect of one factor varies with the level of the other factors in a response.

The full factorial design consists of a 2k experiment (k factors, each experiment at two levels), which is very useful for either preliminary studies or in initial optimization steps, while fractional designs are almost mandatory when the problem involves a large number of factors [9].

In this work, activated carbon was prepared from coconut shells by phosphoric acid (H_3PO_4) activation. A lot of waste from coconut shells are found around the coastal towns of the country (Côte d'Ivoire) [13]. The preparation conditions were optimized using a factorial experimental design. The factors considered in the experimental design were the carbonization temperature, carbonization time and acid concentration. The iodine number (IN) was chosen as the response value.

2 MATERIALS AND METHODS

2.1 MATERIALS

Orthophosphoric acid (H_3PO_4) (85%), iodine (I_2) (95%), sodium thiosulfate ($Na_2S_2O_3.5H_2O$) (98%) are the main chemicals used. They are of analytical quality and were provided by Schariab S.L, Panareac Quimica and Prolabo, respectively. The coconut shells, precursors of activated carbon, come from agricultural waste from Côte d'Ivoire. Deionized water was used for solutions preparation.

2.2 PREPARATION OF ACTIVATED CARBONS

The coconut shells were collected from the region of Abidjan, Côte d'Ivoire. The row material (coconut shell) was washed with deionized water, and then dried in an oven at 110°C for three (3) days. The dried material was crushed using a grinder and then sieved to obtain the desired particle size (500 µm ≤ size ≤ 1mm). The biomass was impregnated by a solution of H_3PO_4 as activating agent at a concentration of 10 or 30% in weight, at the rate of 200 g of biomass for 200 mL of phosphoric acid. The mixture was stirred at room temperature for 24 h and dried at 105°C to remove the residual water. After impregnation comes the carbonization step [10]. The dried impregnated mixture was put in a muffle furnace (Nabertherm) and heated at a rate of 10°C.min^{-1} and held at different carbonization temperatures (400 or 600°C) during desired carbonization time (2 h or 4 h). After cooling at room temperature, the solids obtained were washed with distilled water several times, to remove any remaining acid, until the pH of the washing solution reached a constant value (between 6.5 and 7). They were finally dried in an oven at 110 °C for 24 hours and stored in glass jars for later experimental uses.

2.3 EXPERIMENTAL DESIGN METHODOLOGY

The full factorial 2^3 factorial design with three operational parameters was employed. It was used to optimize the carbonization temperature, the carbonization time and the acid concentration. Each factor was used in two levels as described in Table 1.

The carbonization time is one of the most influential parameters on the properties (specific surface area and porosity) and on the amount produced (pyrolysis yield) of activated carbon. It should generally be at least 400°C to ensure the removal of most of the volatiles and allow the phenomenon of activation [14]. According to [15], [16] the temperatures for chemical activation are between 400°C and 600°C for various plant materials.

The carbonization time is defined as the time during which the sample is kept in the oven after reaching the final pyrolysis temperature. This parameter must be optimized to obtain the development of the porosity while minimizing the decrease in the yield. Literature works have shown that a fairly long residence time (greater than two hours) can promote the increase in total pore volume and the development of the exchange surface [12], [17], [18].

The low and high levels for the factors were selected according to some preliminary experiments. The concentration of the activating agent has a very remarkable influence on the specific surface and on the pore volume of the activated carbon prepared. According to El maguana *et al [10].*, the concentration of the activating agent influences positively. The balance of absorption of the pollutant. In the present study, two activating agents were investigated with low and high levels set at 10% and 30% of orthophosphoric acid solution (85%).

Table 1. Factors and levels used in the factorial design

Factors	Coded variable	Low level (-1)	High level (+1)
Carbonization temperature (°C), F1	X1	400	600
Carbonization time (h), F2	X2	2	4
Acid concentration (%), F3	X3	10	30

2.3.1 Construction Of The Experiment Matrix

Regarding the full factorial design, for k factors at two (2) levels, the number of experiments to be performed by combining the different levels of the factors is 2^k. Thus, the experiment matrix has for k factors k columns and 2^k rows. All the columns start with -1 and for all the lines we alternate the -1 and the +1 for the first column, every two lines for the second column and generally every 2^{d-1} line for the j^{th} column. So, the number of experiments in this study for three factors is 2^3, or 8 experiments. The factorial design matrix is shown in Table 2.

Table 2. Experimentation matrix

Experiment No	X1	X2	X3
1	-1	-1	-1
2	+1	-1	-1
3	-1	+1	-1
4	+1	+1	-1
5	-1	-1	+1
6	+1	-1	+1
7	-1	+1	+1
8	+1	+1	+1

2.3.2 Response

The answer is the result of the interactions of the factors studied on the adsorbing power of activated carbon, the main property of activated carbon [8]. Indeed, there are several methods of determining the adsorption capacity. The iodine number was chosen as response value in this work. The determination of the iodine number is a simple and fast test giving a good indication to the internal surface area of the activated carbons. In many of them the iodine number is closed to the surface area measured based on Brunauer–Emmet–Teller (BET) method [19]. It was calculated based on the following equation [20]:

$$\text{Iodine number} = \frac{\left[C_0 - \frac{C_n \times V_n}{2V_{12}}\right] \times M_{12} \times V_{ads}}{m_{CA}} \quad (1)$$

where C_0 and Cn (mol. L^{-1}) are the initial concentration of the iodine solution and the concentration of the sodium thiosulfate solution, respectively; Vn (mL) is the equilibrium volume of the sodium thiosulfate solution; V_{I2} and Vads (mL) are the dosed iodine solution and the adsorption volumes; M_{I2} (g/mol) is the molar mass of iodine; and m_{CA} (g) is the mass of activated carbon.

2.3.3 Development Of The Mathematical Model

The response designated by Y was related to the coded variables X through a mathematical model as follows (2):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (2)$$

where Y is the response (iodine number). X1, X2, and X3 are the coded variables related to the carbonization temperature, carbonization time, and acid concentration, respectively. b_0 is a constant, b_1 represents the weight of carbonization temperature, b_2 represents the weight carbonization time, and b_3 represents the weight of acid concentration. b_{12} is the interaction effect between the carbonization temperature and the carbonization time, b_{13} is the interaction effect between the carbonization temperature and the acid concentration, and b_{23} is the interaction effect between the carbonization time and the acid concentration.

The NEMRODW Software (New Efficient Methodology for Research using Optimal Design, LPRAI – Marseille, France) [21] was used for generating the experimental design, estimating the coefficients, and analyzing the results.

3 RESULTS AND DISCUSSION

3.1 EXPERIMENTAL PLAN AND FACTOR COEFFICIENT

The Table 3 describes the experimental plan and the experimental responses in relation to the three factors studied. The examination of the results shows that the iodine number varies between 406.096 and 446.706 mg/g. The iodine number is a performance parameter of activated carbon. It gives a good idea of the total surface area available for adsorption of low molecular weight compounds. Our results are confirmed with those of [22] and [14] who obtained values of 482 to 852 mg/g and 550 mg/g, respectively with *Zizyphus Mauritiana* and on coconut shells.

Table 3. Factorial experimental design, experimental conditions and experimental responses

Experiment No	Experimental design			Experimental conditions			Experimental responses
	X1	X2	X3	F1 (°C)	F2 (h)	F3 (%)	Y (mg/g)
1	-1	-1	-1	400	2	10	416.248
2	+1	-1	-1	600	2	10	431.477
3	-1	+1	-1	400	4	10	406.096
4	+1	+1	-1	600	4	10	418.787
5	-1	-1	+1	400	2	30	436.553
6	+1	-1	+1	600	2	30	439.091
7	-1	+1	+1	400	4	30	444.168
8	+1	+1	+1	600	4	30	446.706

3.2 ESTIMATION AND STATISTICS OF COEFFICIENTS

The estimates and statistics of the different coefficients are presented in Table 4. The significance of the different coefficients of the model was evaluated by comparing double the standard deviation to the absolute value of the coefficient. Thus, the coefficient is said to be significant if its absolute value is greater than twice the standard deviation (0.634).

Table 4. Estimated values of coefficients for the response (iodine number, Y)

Experiment No	Coefficient	Standard deviation	Significant. %
b0	429.89	0.317	0.0470**
b1	4.12	0.317	4.89*
b2	-0.95	0.317	20.5*
b3	11.74	0.317	1.72*
b12	-0.32	0.317	50.0
b13	-2.85	0.317	7.0*
b23	4.76	0.317	4.24*

These results show that all three factors have a significant influence on the adsorption capacity of activated carbon (iodine number) and only two of their interactions are significant. The importance of factor effects and their interaction is illustrated in Figure 1.

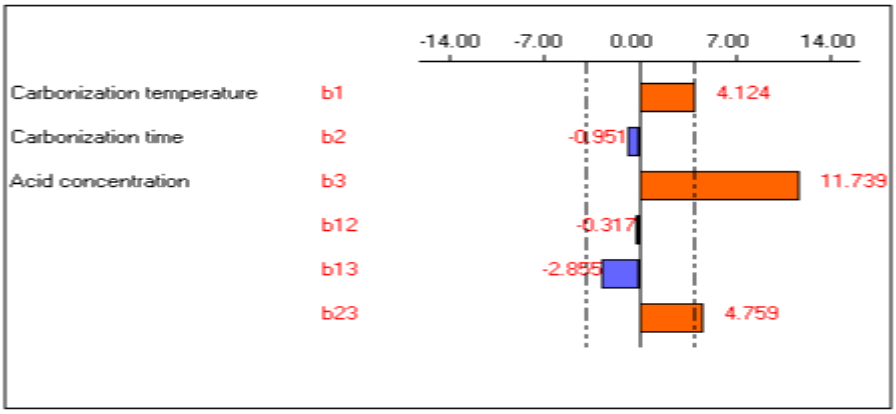

Fig. 1. Significance of factor effects diagram

In addition, depending on the importance; the main effects are due to the temperature (Variable X1), the calcination time (variable X2) and the concentration of the activating agent (variable X3). Ultimately, the equation of the adsorption capacity of carbon according to the different parameters is presented by the following mathematical model:

$$\mathbf{Y = 429.89 + 4.12X_1 - 0.95X_2 + 11.74X_3 - 2.85X_1X_3 + 4.76X_2X_3} \quad (3)$$

The detailed examination of the different coefficients of the factors having a significant influence on the adsorption of activated carbon (iodine number) allows us to understand the effect of these factors and their interactions.

3.3 Study Of The Influence Of Different Factors

3.3.1 Influence Of The Carbonization Temperature

When the temperature rises from 400°C to 600 °C, the average carbon absorption capacity increases by an average of 8.2 % (b_1 value = 4.124). We can then say that a change in temperature significantly influences the adsorption capacity of activated carbon. Thus, increasing the carbonization temperature in the area studied could promote the adsorption capacity of carbon, ie the development of microporosity. According to Gueye [14], the increase in adsorption capacity when the temperature is high can be explained by the fact that coconuts are very hard materials, so to develop porosity by creating new pores they must be charred from high temperatures.

3.3.2 Influence Of The Acid Concentration

As the concentration of the activating agent increases from 10 % to 30 %, the adsorption capacity increases by an average of 23.6 %. From this analysis, it is clear that the adsorption capacity is sensitive to a variation in the acid concentration (H_3PO_4). These results are consistent with those of authors supported by Aravindhan *et al [23].* who studied the effect of the acid concentration on the index of the activating agent is a function of the impregnation ratio and the nature of the biomass.

3.3.3 Influence Of The Carbonization Time

The value of the carbon adsorption capacity decreases on average 1.9 % (value of b_2 = -0.951) when the carbonization time goes from 2 hours to 4 hours. Therefore, a variation in this factor influences the adsorption capacity of the carbon. Indeed, the increase of the iodine number with the increase in the carbonization time could be due to the fact the coconut shells being hard, a long activation time allows a good development of the porosity of the carbon. These results agree with those found by Adinata *et al* [7].

3.3.4 Influence Of Carbonization Temperature/Acid Concentration Interaction

The shows the carbonization temperature/acid concentration interaction. The values in each small square represent the combinations of the levels of the two factors.

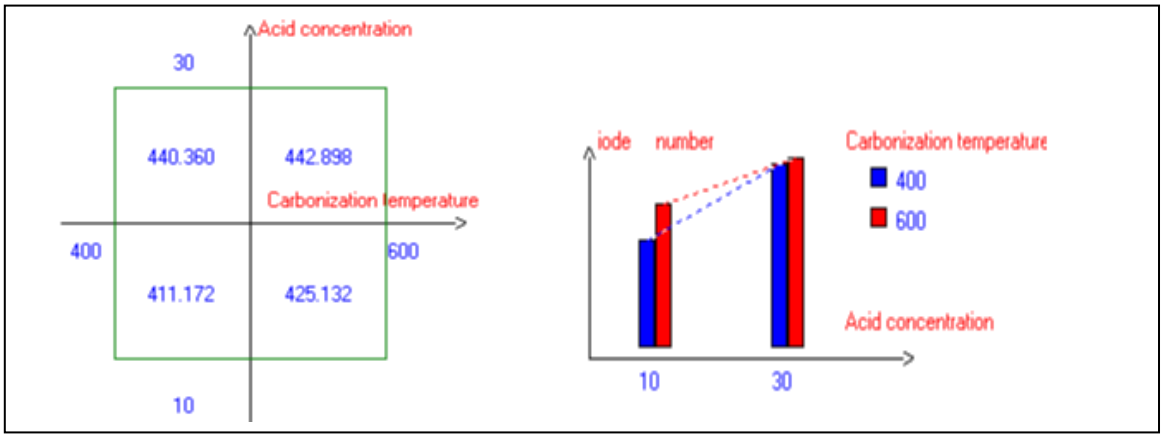

Fig. 2. Graphic study of the carbonization temperature/carbonization time interaction

Thus, when the carbonization temperature goes from 400 °C to 600 °C and the acid concentration is at its low level (H_3PO_4, 10%), the adsorption capacity of the carbon varies from 411.17 to 425.13 mg/g, i.e. a growth of 13.96 %. On the other hand, when the acid concentration is at its high level (H_3PO_4, 30%) at the same variation in the carbonization temperature, the adsorption capacity of the carbon rises slightly from 440.36 to 442.90 mg/g, an increase of 2.54 %. In this area, the effect of the carbonization temperature depends on the variation of the acid concentration and this reciprocally. The best carbon adsorption capacity is 442.90 mg/g corresponding to the high levels of the calcination temperature (600°C) and acid concentration (30 %).

These results show that increasing the carbonization temperature improves the adsorption capacity of activated carbon.

3.3.5 Influence Of Carbonization Time/Acid Concentration Interaction

The shows the interaction between the carbonization time and the acid concentration. The values in each small square represent the combinations of the levels of the two factors.

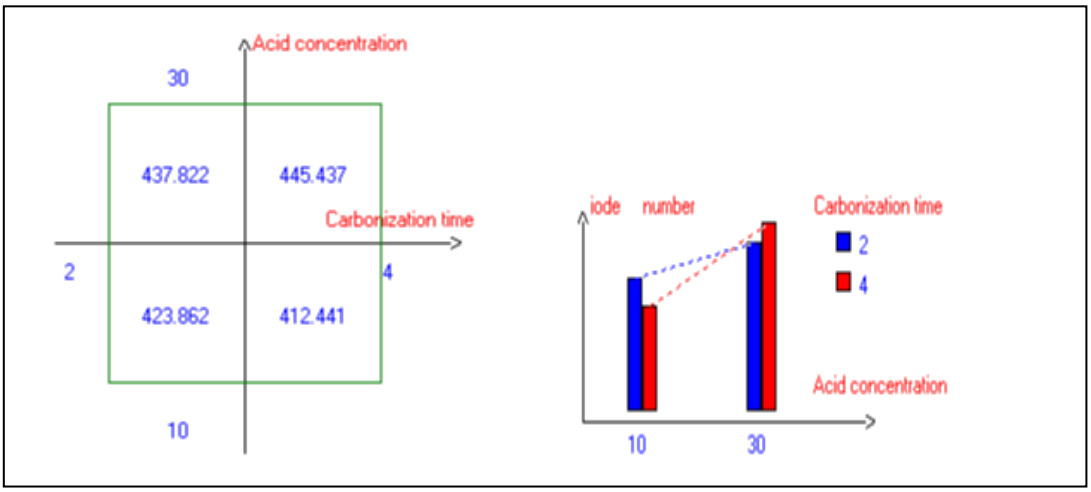

Fig. 3. Graphic study of the carbonization time/acid concentration interaction

It is observed that when the acid concentration goes from 10 to 30 %, and when the carbonization time is at its low level (2 hours), the adsorption capacity (iodine number) of the carbon increases from 423.86 to 437.82 mg/g (an increase of 13.96 %). When the carbonization is elevated (4 hours), the response changes from 412.44 to 445.44 mg/g, i.e. a gain of 33%. It is clear that in this area, the effect of the acid concentration on the adsorption capacity of the carbon is a function of the variation in the carbonization time effect and vice versa. The best carbon absorption capacity (iodine number) is 445.44 mg/g corresponding to the high level of the acid concentration (H_3PO_4, 30%) and carbonization time (4h). Thus, these results show that to have a better iodine number (adsorption capacity) of the activated carbon, the most important factors are the high acid concentration and high carbonization time.

The analysis of these results shows that the optimal experimental conditions to have an activated carbon with a better iodine number (adsorption capacity) are 600°C for carbonization temperature, 30 % for the acid concentration and 4 hours for the carbonization time.

4 CONCLUSION

The full experimental design method was used in this work to determine the optimal conditions of activated carbon preparation from coconut shell by chemical activation. Phosphoric acid (H_3PO_4) was use as the activating agent. The considered factors were the carbonization temperature, the carbonization time and the acid concentration. The results indicate that these factors positively influenced he adsorption capacity when the preparation is carried out at the high level of each factor. Thus, in our experimental field, the optimal conditions necessary for the elaboration of an activated carbon with a good adsorption capacity (better iodine number) are 600°C for the carbonization temperature, 30 % for the acid concentration when the preparation is operating for 4 hours.

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