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Application of an Experimental Design Methodology to Optimize the Synthesis Conditions of an Activated Carbon from Palm Kernel Shells

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ABSTRACT

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Activated carbons from palm kernel shells were produced using the 2³ full factorial design method. The effect of some parameters such as the nature of the activating agent, the calcination temperature and the calcination time on the microporosity activated carbons were followed during their preparation. Thus, the microporosity of the eight (8) activated carbons prepared were determined by the iodine number method. Statistical analysis of the results by Nemrodw (new efficient methodology of research using optimal design) version 2000 software revealed that the activated carbon synthesized at 800 °C for one (1) hour with orthophosphoric acid has the best value of iodine number (500.006 mg.g⁻¹).

Introduction

The production of activated carbon from lignocellulosic material has been recurrent in recent decades, because of the availability of this resource and its low cost (Gomez *et al.*, 2016; Kouotou *et al.*, 2013). In addition, they are efficient adsorbents due to their large specific surface area and relatively high adsorption capacity for a wide variety of

applications (Mahmood *et al.*, 2016). One of the most widely used techniques for the synthesis of these carbon material is chemical activation. Indeed, this has the advantage of being less energy consuming because it is done at low temperature and also helps to preserve the carbonaceous matrix (Lim *et al.*, 2010). The major challenge of such process is to produce good quality activated carbons with microporous properties favorable to their

utilization in wastewater treatment. The control of the porosity of activated carbons requires a good control of the preparation conditions (Ennaciri *et al.*, 2014). This could be achieved through the use of experimental designs, which are methods for quantifying the effects of different factors on a response in well-defined experimental fields in order to optimize them. Factorial design is a very convenient statistical method for planning experiments where several factors are controlled and their effects on each other are investigated at two or more levels (Montgomery, 2010). A full factorial designed experiment consists of all possible combinations of levels for all factors. The total number of experiments for studying k factors at 2-levels is 2^k (Jiju, 2014).

The objective of this study is to determine the optimal conditions for the synthesis of activated carbons from low-coast palm kernel shells by applying a full factorial design based on activating agent, calcination temperature and calcination time.

Material and Methods

Reagents and solvents

Orthophosphoric acid (Scharlab S.L., purity 85%), sodium thiosulfate (Sigma aldrich, purity $\geq 99.5\%$), potassium hydroxide (Scharlab S.L., purity 95%), iodine (Panreac, purity 100%) and potassium iodide (Scharlab S.L., purity 85%) were used for the preparation of solutions. Deionized water was used for solutions preparation.

Procedure for the preparation of activated carbons

Pre-treatment of raw material

The biological material used for the preparation of activated carbons consists of

the shells of the African palm tree *Elaeisguineensis*. The palm kernel shells have undergone a pre-treatment before being transformed into activated carbon.

The purpose of this is to remove impurities such as dust and sand that could influence the yield or ash content of the prepared carbons. First, the raw material was washed with deionized water followed by drying at room temperature (25°C) for 24 hours. Finally, the material was crushed and sieved on a sieve column of the ANALYSENSIEB RETSCH - AS 200 type to obtain a grind with a size between 1 mm and 500 μm .

Chemical activation

The chemical activation is a two-step process, the impregnation followed by the carbonization.

Impregnation

This process was carried out with two activating agents independently. The impregnation of the biological material with KOH (0.13 mol.L⁻¹) or orthophosphoric acid (4.26 mol.L⁻¹) consisted of bringing a 200 g mass of pretreated palm kernel shell into contact with a 400 mL volume of KOH or H₃PO₄ solution (a mass-to-volume ratio of 1/2) for 24 hours, with stirring.

At the end of this time, the impregnate was removed and dried in a muffle oven for 24 hours at 120°C so that almost all the solvent (water) evaporated.

Carbonization process

The design of experiments methodology was applied to the carbonization stage in order to optimize certain activated carbon synthesis parameters. For this purpose, a full factorial design was applied.

Microporosity of activated carbons by the iodine number method

The microporosity of activated carbons was assessed by the iodine number method according to the protocol described by Abuiboto *et al.*, (2016). According to this protocol, a mass of 0.2 g of activated carbon is brought into contact under agitation in an Erlenmeyer flask with a volume of 20 mL (V_{ads}) of an iodine solution ($C_0 = 0.02 \text{ mol.L}^{-1}$). The mixture is stirred for 10 minutes. At the end of the specified time, the solution is filtered and 10 mL of the filtrate is taken for determination with sodium thiosulfate solution ($C_{th} = 0.1 \text{ mol.L}^{-1}$) in the presence of starches. The following relationship is used to calculate the iodine value.

Iodine number (mg/g)

$$= \frac{\left(C_0 - \frac{C_{th} \times V_{th}}{2 \times V_{I_2}}\right) \times M_{I_2} \times V_{ads}}{m_{CA}}$$

With V_{th} the volume of the sodium thiosulphate solution at equivalence (in mL) and M_{I_2} the molecular weight of iodine (254 g.mol^{-1}).

Design of experiment

The design of the experiment was performed with factors likely to have an influence on the development of the microporosity of activated carbon during its manufacture. These are the nature of the activating agent, the calcination temperature and the calcination time. The studied ranges with minimum (-1) and maximum (+1) values and corresponding coded symbol for each factor are given in table 1.

The iodine number was chosen as a response to evaluate the microporosity and thus to assess the adsorption capacity of these materials to adsorb small molecules. In

general, this parameter evolves in the same order of magnitude as the specific surface. It is therefore a good indicator for evaluating the quality of the activated carbons prepared.

Experimentation matrix of the full factorial plan

The experimentation matrix is the experimenter's dashboard. It shows the number of experiments and the conditions under which each experiment was carried out (Table 2). For a full factorial design with two (2) levels and three (3) factors, eight (8) experiments are required.

Analysis of experimental data

Within the framework of the complete factorial plan, the mathematical model postulated relating the response to the various factors is a first-order equation.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3$$

where Y is the response (iodine number). X_1 , X_2 , and X_3 are the coded variables for the activating agent, the calcination temperature and the calcination time, respectively. b_0 is a constant, b_1 represents the weight of activating agent factor, b_2 is the weight of the calcination temperature, and b_3 represents the weight of calcination time. b_{12} is the interaction effect between the activating agent and calcination temperature, b_{13} is the interaction effect between the activating agent and the calcination time, and b_{23} is the interaction effect between the calcination temperature and the calcination time.

Statistical analysis of the experimental results was carried out with the Nemrodw software (New efficient methodology for research using optimal design, LPRAI – Marseille, France) version 2000 (Mathieu *et al.*, 2000).

The Lenth method was used to evaluate the importance of the effects (Ibraheem *et al.*, 2019). This method is based on the estimation of a pseudo standard error which assumes that the variation in the smallest effects is due to random error. The first step in this method is to order the absolute values of the coefficients (b_i) in ascending order. Next, the coefficients with an absolute value greater than $2.5 \times S$ ($S = 1.5 \times \text{median } b_i$) are eliminated. This iteration continues until no coefficient is found that is greater than the condition set. The median of the last iteration is used to determine the pseudo standard error (PSE). Indeed, S of the last iteration is equal to PSE ($PSE = 1.5 \times \text{median } b_i$). In addition, the significant limits are determined by multiplying PSE by the student table value for $t_{0.05, \text{ddl}}$ (degree of freedom) (Lenth, 1989).

Results and Discussion

Statistical analysis of results

The table 3 shows the conditions under which the experiments were conducted. The results for each experimental condition are also indicated. The analysis of table 3 reveals that the values of the iodine number of the synthesized activated carbons vary according to the preparation conditions used, with an optimum in experiment 4 (iodine number = $500.006 \text{ mg.g}^{-1}$). For the same activating agent, the response increases following an increase in temperature from 400°C to 800°C .

Similarly, this parameter increases from KOH to H_3PO_4 for the same operating conditions. We also note a global decrease in microporosity from 1 h to 3 h for the same preparation conditions. Thus the increase of the calcination time has an unfavourable effect on the adsorption properties of activated carbon. This phenomenon was also observed in works from Gratuito *et al.*, (2008) and Abechi *et al.*, (2013). Indeed, during

activation and/or calcination, phosphorus or potassium, depending on the activating agent used, is incorporated into the carbon matrix to develop microporosity. By increasing the calcination time, some of the bonds formed by the phosphorus or potassium in the carbon matrix are destroyed from the surface of the activated carbon. Consequently, the iodine value of activated carbons decreases (Tchakala *et al.*, 2012).

The estimates and statistics of the main effects and interactions of different factors on the response as well as the standard deviation were calculated and presented in table 4. The results shows that the iodine number is affected by the variations in factors. All factors appear to have a significant influence on the adsorption capacity of the prepared activated carbons. Indeed, the absolute values of the main coefficients of the factors, notably b_1 (5.87); b_2 (7.46) and b_3 (1.11) are greater than twice the standard deviation (0.3172). Furthermore, all interactions seem to have a significant influence on the response as the absolute values of the coefficients of these interactions are greater than twice the standard deviation.

However, some effects and interactions could be more influential than others on the value of the iodine number. To elucidate this finding, a determination of significant effects was made by the Lenth method shown in figure 1. The limits of significance are represented in the diagram by dashed lines. All coefficients whose representation extends beyond the limits are considered significant.

The analysis of figure 1 indicates that factors activating agent and calcination temperature are significant. Similarly, the interaction between the calcination temperature and the calcination time, which extends beyond the limits of significance, is also found to be significant.

Therefore, the variations in the response observed in table 3 and the variations in the coefficients in table 4 are mostly attributable to the combined effects of the activating agent, the calcination temperature and the calcination temperature/calcination time interaction. Therefore, the equation of the response to the different factors of the experimental design is given by the following mathematical model:

$$Y = 482,71 + 5,87 X_1 + 7,46 X_2 - 5,55 X_2 X_3$$

Study of significant factors and the calcination temperature/calcination time interaction

Influence of the nature of the activating agent

The effect of the nature of the activating agent can be observed when its level is changed from (-1) to (+1). This change in the level of the activating agent leads to an increase of 11.74% in the value of the iodine number. Therefore, the nature of the activating agent can be considered as a very important parameter to take into account in the production of activated carbon. Indeed, the activating agent plays an important role in the development of the pore structure (Vargas *et al.*, 2012). In this case, orthophosphoric acid seems to be the best activating agent.

Influence of calcination temperature

The response increases by 14.91% when the temperature is increased from 400°C to 800°C. The effect of the temperature is therefore considerable on the adsorption capacity of the prepared activated carbons. According to Aboua *et al.*, (2010), the raising of the calcination temperature increases the adsorption capacity of activated carbon to adsorb small molecules. Indeed, the elevation

of the calcination temperature induces a strong release of volatile matter, thus freeing the pores. In parallel to this phenomenon, the increase in calcination temperature leads to a greater reactivity of the activating agent towards the carbon being formed. This process leads to the enlargement of existing pores and the creation of new pores (Adinata *et al.*, 2007).

Interaction between calcination temperature and calcination time

The interaction between calcination temperature and calcination time is shown in figure 2. An analysis of this figure shows that when the temperature is high, the evolution of the calcination time from one hour to three hours leads to a decrease in the value of the iodine number. The value of the iodine value decreases from 496.833 mg.g⁻¹ to 483.508 mg.g⁻¹, which represents a decrease of 2.68%. On the other hand, for a temperature of 400°C, the evolution of the calcination time leads to an increase in the iodine value. It increases from 470.817 mg.g⁻¹ to 479.701 mg.g⁻¹ (i.e. 1.85% increase).

In all cases, the analysis of this interaction and the factors shows that the highest value of the iodine value (500.006 mg.g⁻¹) is obtained for calcination at 800°C for one hour with H₃PO₄.

The aim of the study was to determine the optimal conditions for the synthesis of activated carbons from palm kernel shells. To this end, a 2³ full factorial design was applied. This design showed that the calcination temperature and the nature of the activating agent were all statistically significant. However, the factor calcination time had a negative impact on the development of the microporosity of the prepared activated carbons. This implies working at its low level during the implementation of this process.

Table.1 Experimental field

Factors	Coded variables	Levels	
Activating agent	X ₁	-1	KOH
		+1	H ₃ PO ₄
Calcination temperature	X ₂	-1	400°C
		+1	800°C
Calcination time	X ₃	-1	1 h
		+1	3 h

Table.2 Experimentation matrix

N° Experience	Activating agent	Calcination temperature	Calcination time
	No unit	°C	hour
1	KOH	400	1
2	H ₃ PO ₄	400	1
3	KOH	800	1
4	H ₃ PO ₄	800	1
5	KOH	400	3
6	H ₃ PO ₄	400	3
7	KOH	800	3
8	H ₃ PO ₄	800	3

Table.3 Results of the experimental design

N° Experience	Activating agent	Calcination temperature	Calcination time	Iodine number
	No unit	°C	Hour	mg.g ⁻¹
1	KOH	400	1	465.741
2	H ₃ PO ₄	400	1	475.894
3	KOH	800	1	493.660
4	H ₃ PO ₄	800	1	500,006
5	KOH	400	3	470.818
6	H ₃ PO ₄	400	3	488.584
7	KOH	800	3	477.163
8	H ₃ PO ₄	800	3	489.853

Table.4 Estimation and statistics of coefficients

Name	Coefficient	Standard error	Signif. %
b ₀	482.7149	0.1586	0.0209 ***
b ₁	5.8694	0.1586	1.72 *
b ₂	7.4557	0.1586	1.35 *
b ₃	-1.1103	0.1586	9.0
b ₁₂	-1.1103	0.1586	9.0
b ₁₃	1.7447	0.1586	5.8
b ₂₃	-5.5521	0.1586	1.82 *

Fig.1 Graphical study using Lenth's method

Fig.2 Interaction between temperature and calcination time

Similarly, except for the calcination temperature/calcination time interaction, this was statistically significant. The antagonistic effect of this interaction on the iodine value was noted.

Finally, the full factorial plan applied made it possible to determine the conditions leading to good development of the microporosity of activated carbons. The optimal conditions determined for best adsorption capacity are 800°C for the calcination temperature for a duration of 1 hour with H₃PO₄ as activating agent.

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