



## Characterization and evaluation performance of activated carbon prepared from coconut shell argan

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### ABSTRACT

The objective of this study is the valorization of a sub-product of the fruit of the argan tree; it is the shell of argan nuts which represents about 50% of fresh fruit. It is a natural lino-cellulosic residue that we could turn into charcoal under the effect of chemical activation with phosphoric acid which allows the development of a large pore in the activated material. We studied the effect of the activation temperature, activation time and the amount of acid added to the char yield and the adsorption capacity of the material developed in response to the experimental determination of the kinetics of adsorption of an organic molecule: the methylene blue. The results showed that the temperature of 400 °C, the processing time of one hour and the mass ratio (precursor/phosphoric acid) equal to one, are optimal conditions for development of the adsorbent material. The product obtained under these conditions has good textural and structural properties; a specific surface area  $S_{BET}$  reached 1105 m<sup>2</sup>/g and development of surface functions.

**Keywords:** Coconut Shell Argan; Activation; Adsorbents; MEB; BET.

### INTRODUCTION

Currently, the growing demand for adsorbent materials processes for environmental cause pushes further research in the field of manufacturing adsorbents from materials that are not traditional; concretely from byproducts waste or industrial plants, clays and other abundant materials.

Activated carbon is considered the most efficient adsorbent whose use for remediation of waste waters is of great interest for researchers. Therefore, several studies have focused on the development of active carbons from industrial or agricultural waste such as peat [1], bagasse [2], sawdust [3], desert plants [4], olive stones [5], rice bran [6] and husk [7], fruit peel [8], tea waste [9], and coffee grounds [10], microwave heating [11], globe artichoke leaves [12], bark of pomegranate [13], molasses [14], and coconut [15].

In this context, we conducted research to explore the possibility of producing activated carbon from a byproduct of the fruit of the argan tree; it is the nutshell argan represents about 50% of fresh fruit. We chose this natural precursor because of its composition lino-cellulose as a source of carbon.

This study has two objectives:

a- Optimization of the experimental conditions for the preparation of activated carbon, with significant textural and structural properties from the nut shell argan by chemical activation using phosphoric acid.

b- Highlight the effectiveness of activated carbon prepared by testing the adsorption of the molecule of methylene blue (MB), the molecule recognized as a model organic pollutant to evaluate the performance of activated carbon adsorbents in particular [16-17].

## EXPERIMENTAL SECTION

### *Method of chemical activation of the nut shell argan*

The chemical activation of the argan nut shell, agricultural waste southwestern Moroccan average particle diameter equal to 1 mm, is effected by phosphoric acid dilute at 80%; chemical activate known by its role crosslinking and protective of carbon skeleton and its participation in the creation and expansion of the pores [18-19]. A mass of the shell is mixed with phosphoric acid ( $H_3PO_4$ ) with mass ratios ( $m_{acid} / m_{precursor}$ ) determined after manual mixing of the mixture precursor-phosphoric acid at room temperature, the resulting slurry is introduced into the oven for 24 hours at 120 °C. Carbonated product obtained after this operation is called CAP.

### *Thermal activation*

The CAP is heated in oxidant atmosphere (air) in a muffle furnace at different temperatures with the set values between 250 and 500 °C, the treatment time is between 0.5 h and 2 h. The samples were then washed with distilled water in a Soxhlet apparatus for 72 hours, to remove excess acid and soluble matter, and then dried in an oven at 120 °C. The products are ground (particle size less than 100 $\mu$ m), and stored in a desiccator for eventual use.

### *Evaluation of the performance of prepared activated carbons*

#### *Determination of yield-char*

The yield-char of the prepared activated carbon (CAP) is determined from the mass of the hull argan initially used. It is given by the following formula:

$$R = (m_{CAP} / m_i) * 100$$

With

$m_{CAP}$  : mass of activated carbon prepared

$m_i$  : is the mass of the hull argan initially used.

### *Adsorption tests of methylene blue molecule*

The evaluation of the performance of activated carbons prepared is achieved by monitoring the adsorption of the molecule of methylene blue (MB) considered organic pollutant model. Indeed, the study of the kinetics of adsorption of the molecule of the BM is performed at room temperature using a given volume of solution containing the adsorbate in an initial concentration ( $C_0 = 20$  mg / L) and in the presence of a given mass of adsorbent ( $m = 50$  mg / L). The mixture is kept under constant agitation and samples are taken at the end of each time interval. MB concentration is determined by UV-visible spectrophotometry at  $\lambda_{max} = 664$  nm.

### *Characterization of activated carbon prepared*

#### *Surface area*

The measurement of the specific surface area is determined based on the BET method [20]. The device used is a Micromeritics ASAP 2010. The adsorption isotherms are obtained by nitrogen adsorption at the temperature of liquid nitrogen (78K).

#### *Morphology analysis by SEM*

The morphology, of prepared activated carbon (CAP) and the gross shell, was examined by Scanning Electron Microscope (SEM). The SEM photographs are made on the samples (Gross and CAP) of size less than 100  $\mu$ m, with a device type JED JSM 840A LGS at Thermostructural Composites Laboratory in Bordeaux.

#### *Function surface*

To highlight the effect of chemical activation with phosphoric acid on the surface chemistry, we performed quantitative functional groups of the activated carbon prepared and raw shell according to the protocol established by Boehm [21]. This technique allowed the identification of different functional groups that play a very important role in the adsorption process and therefore inform about on the quality of activated carbon studied.

## RESULTS AND DISCUSSION

### *Effect of the activation temperature*

#### *On the yield of activated carbon*

The products obtained after thermal activation at different temperatures CAP will eventually called CAP(T) or T is the temperature of activation. The histogram below (Fig. 1) shows the variation in the yield of activated carbon obtained at different temperatures.

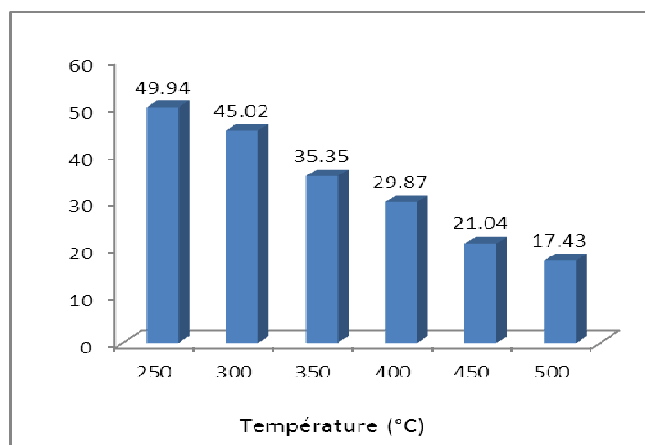


Figure 1. The variation in the yield of activated carbon obtained at different temperatures.

From the histogram in Figure 1, we see that the yield depends greatly on the activation temperature. Indeed, when the temperature increases from 250 to 500 °C, the yield increased from 49.94% to 17.43%. This can be explained by the oxidation reactions of organic matter that can be held in an oxygenated environment and the amount of phosphoric acid is in sufficient to play its role crosslinking carbon chains and consequently the protection of the carbon skeleton of the precursor from oxidation.

*On the adsorption capacity of methylene blue (MB) molecule.*

The kinetic curves of adsorption of MB by CAPT samples are shown in Figure 2. The examination of these adsorption kinetics curves (Fig. 2) allowed subdivision into three classes according to the performance of adsorption:

- The first contains those obtained by activation at temperatures below 400 °C; they are characterized by a low adsorption BM (not exceeding 20%) and remain unchanged since the first minutes of contact between the adsorbent and the adsorbate. This inefficiency prepared samples seems to come from the absence of internal porosity when the temperature is inferior to 400 °C.

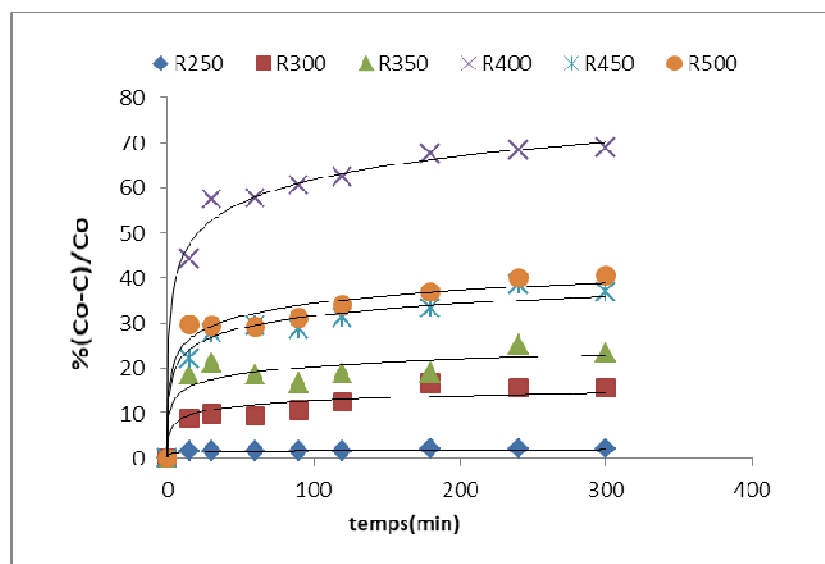


Figure 2. Kinetics adsorption of methylene blue by CAPT.

- The second class is the temperatures 450 °C and 500 °C; the adsorption process is slow compared to other temperatures. This appears to be from slow phenomena transfer between the aqueous phase and the solid phase with the release of intra-granular BM that appear in pores. These pores seem inaccessible to such molecule or closed by full oxidation of the precursor at these temperatures.

- Between the two classes, we find the curve corresponds to the product obtained by the CAP activation temperature 400 °C, which shows the best adsorption capacity of which exceeds 68% MB. This increase in the amount adsorbed is certainly due to the development of the porosity of the adsorbent CAP(400) created by the gasification reactions that can be held between the carbon matrix and the activating agent and the departure of volatile products which block pores.

In view of these results, the temperature 400 °C is chosen as the optimal temperature in the study of the effect of other parameters involved in the activation process.

### *Effect of activation time*

#### *On the yield of activated carbon*

We studied the influence of activation time on the performance of activated carbon prepared. CAP pulp was treated at the temperature 400 °C for times between 0.5 and 2 hours. Products obtained, referenced by CAP (400, t) where t denotes the length of time expressed in hours, washed, dried and balanced to determine the yield of activated carbon. The results are shown in Figure 3.

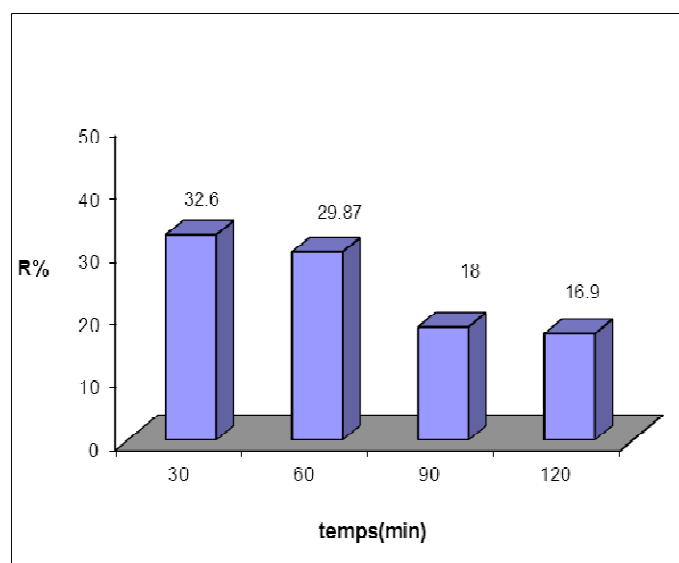


Figure 3. Effect of activation time on the yield of activation.

The histogram shows that the yield of char decreases and as the activation time increases. This loss is mainly due to degassing during activation.

#### *On the adsorption capacity of MB*

The adsorption tests of MB are performed under the same conditions mentioned before. In Figure 4, we have plotted the curves representing the adsorption kinetics of methylene blue.

The review of the curves shows that the product (CAP 400) treated for 1 hour presented the best performance followed by that obtained by activation for 0.5 h. While the increase of the activation period beyond 1h intensive causes a reduction in the adsorption of MB.

These findings can be explained as follows:

- The processing time less than 1 hour is insufficient for the completion of the reactions between the shell of argan nuts and phosphoric acid.
- One hour heat treatment seems to be the time required for the completion of dehydration reactions that allow the creation of porosity by venting that result.
- The firing time over 1h promotes oxidation of the carbon skeleton mass and thus the solidification of the products obtained and clogging of the pores.

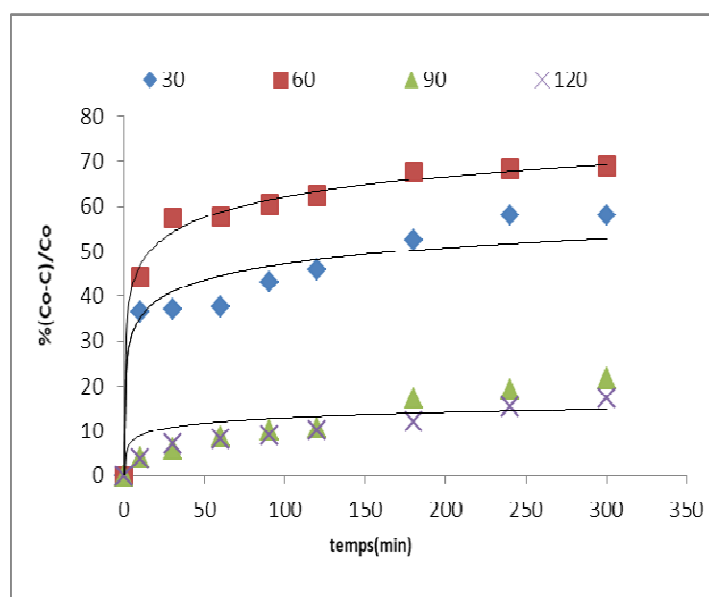


Figure 4. Kinetics adsorption of methylene blue by CAP (400, t).

#### Effect of the amount of phosphoric acid

In view of the above results, it therefore seemed important to study the effect of the amount of phosphoric acid added to the raw shell. Therefore, we varied the mass ratio ( $m_{\text{acid}} / m_{\text{precursor}}$ ) CAP prepared samples were introduced in an oven at 110 °C and then treated in an oven at temperature 400 °C for 1h. The samples referenced by CAP (400, 60, R) where R is the mass ratio of phosphoric acid and the precursor are then washed and dried and then weighed to determine the performance of each one.

#### On the yield of activation carbon

The evolution of the yield of prepared products is given in Figure 5. From the histogram, it appears that the past performance of 3.95% to 63% when the mass ratio  $m_{\text{acid}}/m_{\text{precursor}}$  increases from 0 to 2, which explains well the role crosslinking phosphoric acid which protects the carbon skeleton [13].

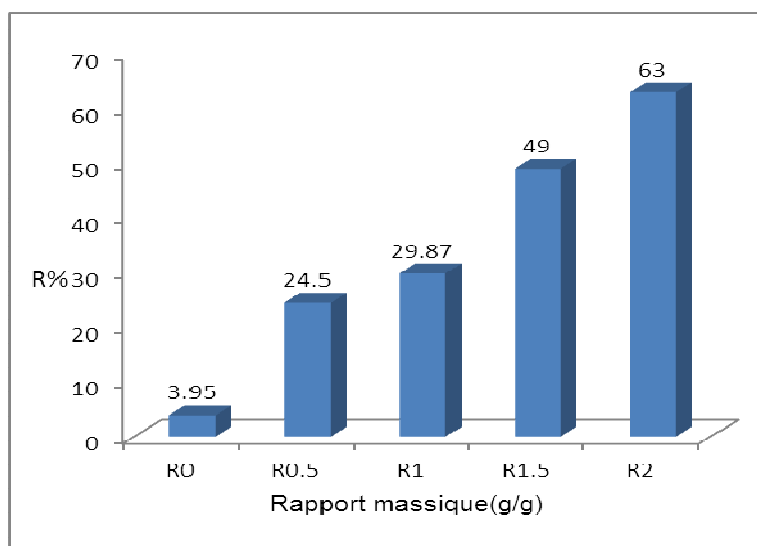


Figure 5. Effect of the amount of phosphoric acid on the yield of activated carbon.

#### On the adsorption capacity of MB

We studied the influence of the amount of  $\text{H}_3\text{PO}_4$  activation on the adsorption capacity of MB. The adsorption tests of the latter are performed under the same conditions mentioned before. The kinetic curves resulting from these tests are shown in Figure 6.

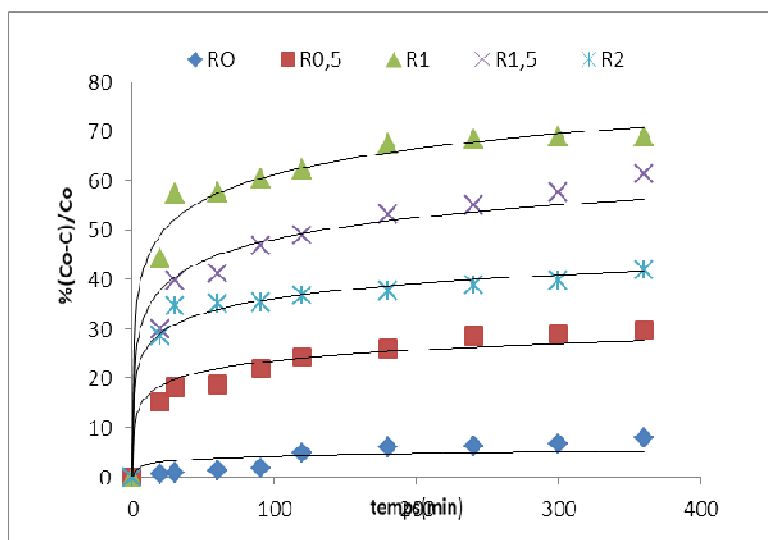


Figure 6. Kinetics adsorption of methylene blue by CAP (400, 1h, R)

Examination of Figure 6 shows the effect of the amount of phosphoric acid on the adsorption capacity of MB. The absence of phosphoric acid ( $R = 0$ ) causes the complete oxidation of organic matter, justified by the low yield of char, and therefore a low adsorption capacity of MB. The introduction of phosphoric acid leads to increasing the efficiency of adsorption MB to reach a maximum of 68% for the ratio 1.

For  $R = 0.5$ , the amount of acid seems insufficient to catalyze the dehydration reactions of the precursor and thus creating a small pore. However, the increase in the mass of  $H_3PO_4$  from 1 to 2 causes a decrease in the adsorption capacity of MB. This decrease seems highly due to excess acid in the mixture causing the incorporation of phosphorus in the structure that led to the closure of the pores created and deteriorating of textural properties of coal that is obtained.

#### Characterization of CAP (400, 1h, 1)

After getting a activated carbon, CAP (400, 1h, 1), which has a better yield char and the best adsorption capacity of MB compared to other products prepared, we proceeded to its characterization by various physic-chemical techniques.

The Table below contains the values of the quantity of functional groups existing in the surface of the activated carbon comparing them with its precursor and the specific surface area determined by the BET method.

	Functional groups in surface (meq/g)		
	Carboxylic	lactone	hydroxyl
CAP	1.05	0.48	0.37
Brute	0.6	0.65	0.65
	Total surface acidity (meq/g)	Total surface basic (meq/g)	$S_{BET}$ ( $m^2.g^{-1}$ )
CAP	1.9	0.18	1105
Brute	1.9	0.18	0.0523

The results depicted in the table, it appears that the chemical activation with phosphoric acid allows a rearrangement of the surface chemistry of activated carbon obtained, transforming lactones and hydroxyl groups of carboxylic groups that play a very important role, in the process of selective adsorption. In addition, the improvement of the quality of the surface chemistry, the value of the specific surface area (BET) obtained is very high ( $1105 m^2.g^{-1}$ ) which leads to the conclusion that the activation process was adopted led to the development of porosity. This hypothesis is confirmed by the morphology of the product obtained by scanning electron microscope.

The SEM photographs of activated carbon prepared and raw shell (Figure 8), demonstrate the catalytic role of phosphoric acid in the chemical activation on the development of microstructure. Indeed, on these pictures, we see that the CAP (400, 1h, 1) has a very compact structure with an external porosity much more developed and well distributed throughout the material compared to the precursor of departure where the grains are not consistent with the virtual absence of porosity.

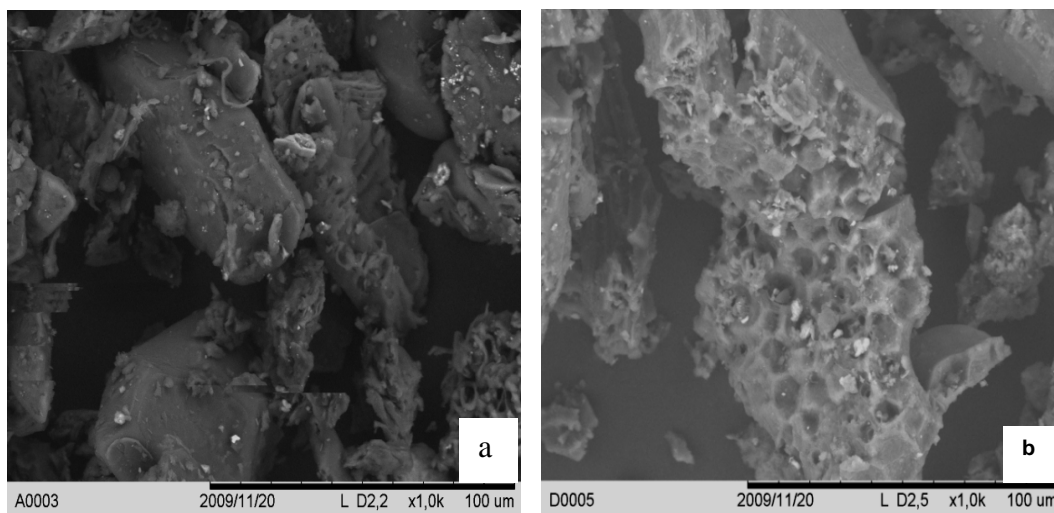


Figure 7. SEM micrographs of: a- raw shell of argan – b- CAP(400, 1h, 1)

### CONCLUSION

In this study, we developed a charcoal from the shell of the nut of the argan tree by chemical activation in the presence of phosphoric acid. The properties of this carbon depend on the amount of phosphoric acid, the activation temperature and residence time.

The characterizations of product developed, have enabled us to determine the activation parameters as follows: Heat treatment in air at 400 °C for one hour, the amount of phosphoric acid (concentration 80%) added has a weight ratio ( $H_3PO_4$ /Precursor) equal to 1.

The CAP (400, 1h, 1) obtained in powder form has a high specific surface area (1105 m<sup>2</sup>/g) which confirms its great character adsorbent. In addition, the determination of surface chemistry by Bohem method showed the strong presence of acidic groups (carboxylic function) which play a very important role in the adsorption process.

It therefore appears that the manufacturing process used in this study, chemical activation with phosphoric acid, can produce an activated carbon with textural and structural properties well developed.

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