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Preparation and Characterization of Activated Carbon from Residues of Oregano

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Abstract — The objective of this study is to value the residues of oregano by an evaluation of the performances of the activated carbon elaborated from this precursor based on the phenomenon of adsorption described in the bibliographical studies. After the process of chemical activation of oregano marc by the phosphoric acid 80 % (1/1) at 350°C during 60 min, the specificity of obtained material is defined from two parameters. The first one is related to the existence of surface chemical functional groups, the second parameter concerns the porous texture defined by the specific surface area according to the Brunauer, Emmet and Teller method (B.E.T), the microporous surface according to the thickness method, the pore size distribution and the structural morphology of the material. The adsorption study of the activated carbon from residues of oregano hence provides evidence for better activity and surface area than commercial activated carbons and could be tried in water treatment process.

Keywords : *Activated carbon, BET surface area, micropore area, surface chemical functional groups.*

INTRODUCTION

The growing global interest focused on the sustainable development requires extensive studies of waste recovery by developing new materials derived “green materials”. The production of activated carbon from the lingo-cellulosic residues is a beneficial ecological solution combines low cost and performance [1, 2]. Generally, the raw materials for the production of activated carbon are those with high carbon but low

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inorganic contents such as wood, lignite, peat and coal. Beside that, lot of agricultural waste and by product have successfully converted to activated carbon for examples bagasse, scrap tires, saw dust, almond, pecan, olive stones, black walnut, hazelnut shells, rice husk ... etc. In Morocco, there are potential raw materials resources for the production of the activated carbon. In this research, the local agricultural waste of oregano was used to produce an activated carbon due to the availability and inexpensive material with high carbon and low inorganic content. By now, a lot of research has been done on activated carbon to improve its applications in gas purification, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and respirators, filters in compressed air and many other applications [3, 4]. The uses of these adsorbents materials in the fields cited above requires knowledge of the structure and texture of the elaborated material namely its specific surface area, porous texture, external morphology, thickness of the adsorbed layer and pore size distribution. These characterization parameters allow explaining the phenomenon that governs the efficiency and sustainability of the activated carbon [5, 6]. The aim of this research is to characterize the optimal activated carbon prepared from the local agricultural waste which is oregano. The optimum operating conditions of obtaining this activated carbon, namely the temperature (350°C), activation time (60 min) and phosphoric acid 80% (1/1) as an impregnation agent, have been study by using the method of the experimental designs [7].

EXPERIMENTAL

Preparation of activated carbon

Oregano marc is milled in the hammer mill "CONDUX D 6451" and sieved to reduce the size. The sample was mixed with the equal mass of phosphoric acid 80% for half an hour in the ambient temperature. The impregnated sample was dried in an oven at 120°C overnight. The carbonization and activation were carried out at 350°C for 60 min in a leading electric thermolyne oven to self-regulation provided with a programmer of temperature, connected with the oven by a thermocouple and a special steel reactor. The system was then purged with 100 mL/min of N₂ for 15 min to ensure inert conditions. The reactor was heated at a rate of 20°C/min to a final temperature of 360°C. The resulting activated carbon was washed by distilled water until all acid was eliminated, dried, ground and sifted to obtain a powder with a particle size between 100 and 400 µm.

Characterization of activated carbon

The BET surface area and porous properties of activated carbon was determined from N₂ adsorption experiments. The activated carbon was characterized by N₂ adsorption

at 77 K using a Micromeritics model ASAP-2010 analyzer. The carbon sample was outgassed for 24 h at 573 K to remove any moisture or adsorbed contaminants that may have been present on their surface. The manufacturer's software can provide BET surface area (S_{BET}) of the carbon by applying the BET equation to the adsorption data. The microporous surface (S_{micro}) and external surface (S_{ext}), as well as the micropore volume (V_{mi}) were evaluated by the t-plot method. The pore size distribution in the micropore range was determined by mercury intrusion porosimetry using a Micromeritics Autopore IV 9500. The cumulative pore volume distribution was first calculated using points from the isotherm at relative pressures corresponding to previously calculated pore sizes. Then, the cumulative distribution was differentiated to give the pore size distributions (PSDs). Meanwhile, PSD was computed by the DFT method by minimizing the grand potential as a function of the fluid density profile [8].

Chemical composition analysis

Elemental analysis was determined by the X-ray fluorescence (XRF) using an X-ray diffractometer Advance/Discover Bruker AXS with 0.1% as the limit of elements detection.

The determination of surface functions was made by chemical titration method, such as proposed by the Boehm method [7]. The acidic groups are determined in turn by basic solutions: the acidic functions relatively strong (carboxylic acids) were measured by neutralization with NaHCO_3 , lactones (condensed structure between an hydroxyl group and a carboxyl group) are given by the difference between neutralization by Na_2CO_3 and NaHCO_3 and phenol functions (or enol) which give non hydrolyzable ethers are obtained by the difference between neutralization by NaOH and Na_2CO_3 .

SEM observation

The texture and pore structure were visualized under a Hitachi TM scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Isotherm of adsorption

Volumetric adsorption isotherm of N_2 on activated carbon is shown in Fig. 1. The basic character of this isotherm is type I in BDDT (Brunauer, Deming, Deming and Teller) with a well-developed sharp "knee" at the low relative pressure that tend to become almost a plateau at higher relative pressure. The shape of this isotherm. Indicates that the activated carbon is very easily saturated with N_2 molecules at low relative pressure. The direct observation of this isotherm can provide qualitative

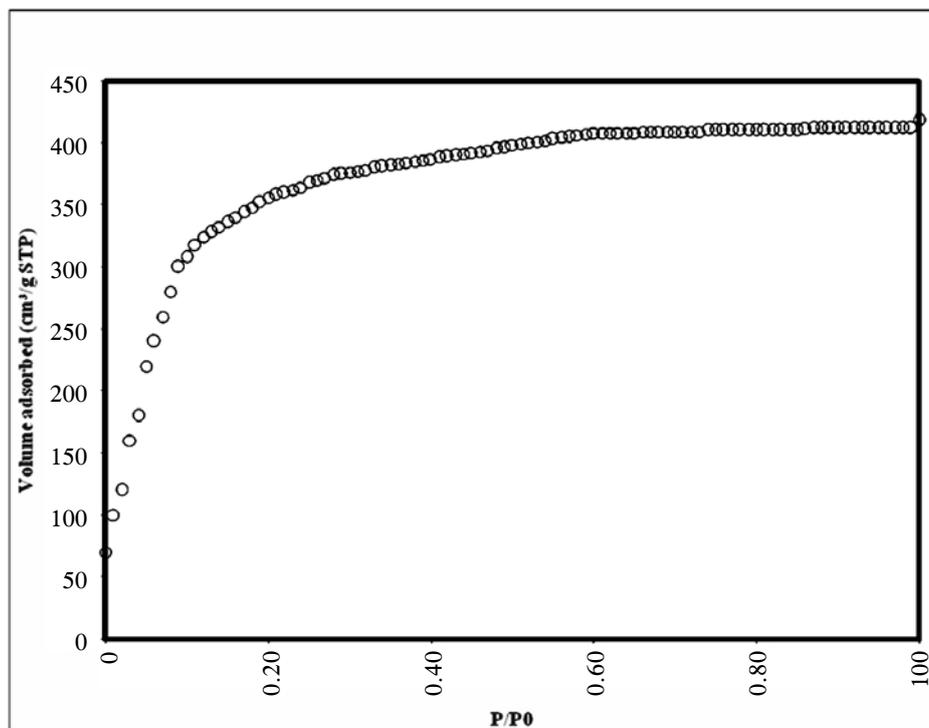


Fig. 1. N_2 (77k) adsorption isotherm on activated carbon.

information about the approximate pore structure of the activated carbon having predominantly narrow and uniform microporosity, with a very low value of external surface area (Table 2). Consequently, the interaction between the activated carbon (adsorbent) and nitrogen (adsorbate) are greater than those between the molecules of nitrogen.

Specific surface area

Smoothing of adsorption isotherm data by the BET equation in the relative pressure range of 0.05–0.35 allowed us to calculate the specific surface area of the activated carbon (S_{BET}), the constant C of the BET equation (C_{BET}) and the monolayer capacity (V_m) (Table 1).

The specific surface area is calculated from the following equation [10] :

$$S_{BET} \text{ (m}^2\text{/g)} = \frac{V_m \text{ (STP cm}^3 \text{ g}^{-1}) \cdot \sigma \cdot 10^{-20} \text{ (m}^2) \cdot N_A \text{ (mol}^{-1})}{22415 \text{ (STP cm}^3 \text{ mol}^{-1})} \quad (1)$$

TABLE 1.

Porous characteristics of the activated carbon and Oregano

Sample	V _m (cm ³ /g)	C BET	SBET (m ² /g)	Correlation Coefficient (R ²)
Activated carbon	233.48	118	1020.22	0.999
Activated carbon from the shell of the coconut [11]	263	761	975	-

where σ is the cross-sectional area occupied by a molecule of adsorbate (16.27Å for N₂ at 77 K) and N_A is the Avogadro's constant.

The BET constant is related to the enthalpy of adsorption in the first layer adsorbed. Although it does not give a quantitative measure of the adsorption enthalpy, it is an indication of the magnitude of the interaction energy between adsorbate and adsorbent. Thus, the value obtained (C_{BET} = 118) indicates that the interactions between nitrogen molecules and activated carbon sites are strong. On the other hand, the obtained specific surface area of 1020.22 m²/g enabled us to deduce that the pyrolysis temperature of 350°C enhanced the removal of molecular weight volatile compounds and further created new pores, resulting in the acceleration of porosity development of the activated carbon. The presence of H₃PO₄ as an impregnation agent would increase the heat energy on the pyrolysis process, and thus initiate to develop the porosity of activated carbon [12].

Thickness of the adsorbed layer « t-plot method »

According to Boer, Linsen and Osinga, if we assume that the adsorbed layers are composed of a compact assembly of nitrogen molecules, we can express the statistical thickness "t" of the adsorbed layer in the material as a function of V_a (volume adsorbed) at a given relative pressure and V_m (monolayer capacity).

For better characterization, a t-plot of activated carbon was derived. The curve shape in Fig. 2 shows similarity to the adsorption isotherm (Fig. 1); it characterizes the existence of smallest pores that fill by multilayer adsorption at low relative pressure, which reduces the area available for subsequent adsorption. The approximately linear section at greater layer thickness was used to calculate the micropore volume (V_{mi}), the micropore surface (S_{micro}) and the other surface. Indeed, the t-plot was used to compare the BET surface area (S_{BET}) and the external surface area on which can form a multimolecular layer. The difference of these two values

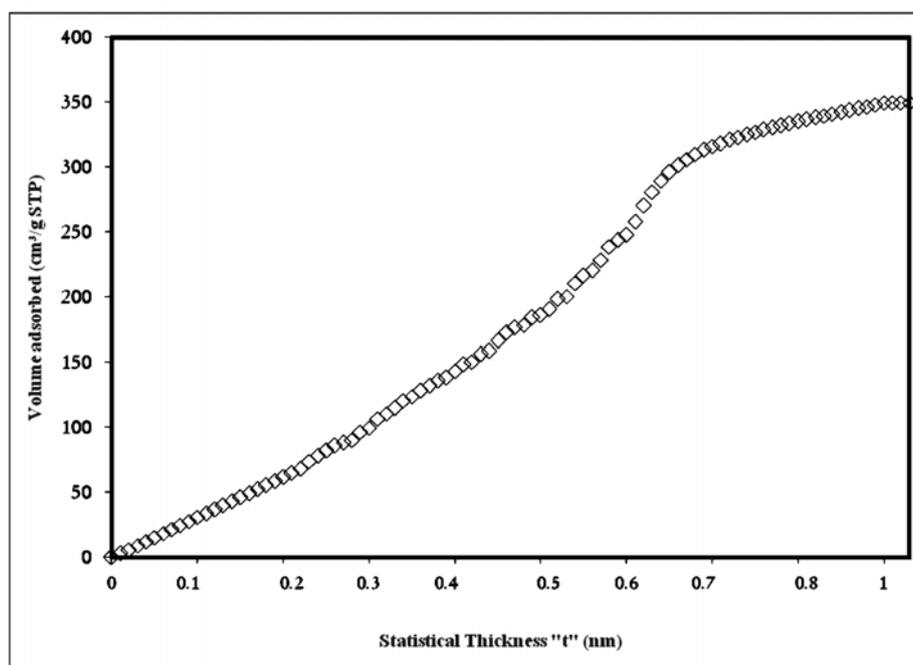


Fig. 2. t-plot of activated carbon.

confirms the existence of microporosity (Table 2).

As it is seen, the activated carbon prepared from the oregano marc by chemical activation has a greater surface area with a microporous trend [13]. The result was comparable and even better with commercial activated carbons [14] as shown in Table 2. The BET surface area obtained in this study showed the activated carbon

TABLE 2.

Porous characteristics of commercial and elaborated activated carbon

Echantillon	S_{BET} (m ² /g)	S_{EXT} (m ² /g)	S_{micro} (cm ³ /g)	Total pore volume	Micropore volume (cm ³ /g)
Activated carbon	1020.22	29.8	990.42	0.93	0.50
Chemviron	951	–	–	0.49	0.36
Norit	1058	–	–	0.96	0.55

synthesized was good which offered shorter activation time and simpler process.

Pores sizes distribution

It is necessary and important to analyze the whole pore size distribution of adsorbent because the difference in the pore size affects the adsorption capacity for molecules of different sizes and shapes, and also this is one of the criteria by which carbon adsorbents are selected for a particular application. Hence, porosity distribution of activated carbons was calculated using Density Functional Theory method (DFT) based on nitrogen adsorption assuming slit pore geometry. DFT describes the thermodynamic grand potential as a function of the single particle density distribution and therefore calculates the density profile that minimizes the grand potential energy and yields the equilibrium density profile. Using the DFT model, pore size distribution was obtained by deconvolution from experimental data. The pore size distribution obtained by DFT analysis of nitrogen adsorption isotherm was shown in Fig. 3 and the results were consistent with the isotherm trend discussed earlier. The pore size distribution curve suggested a predominant micropore owing to the sharp increase of pore size distribution curve to pore diameter less than 20 Å [15] with 53.30% of total porosity

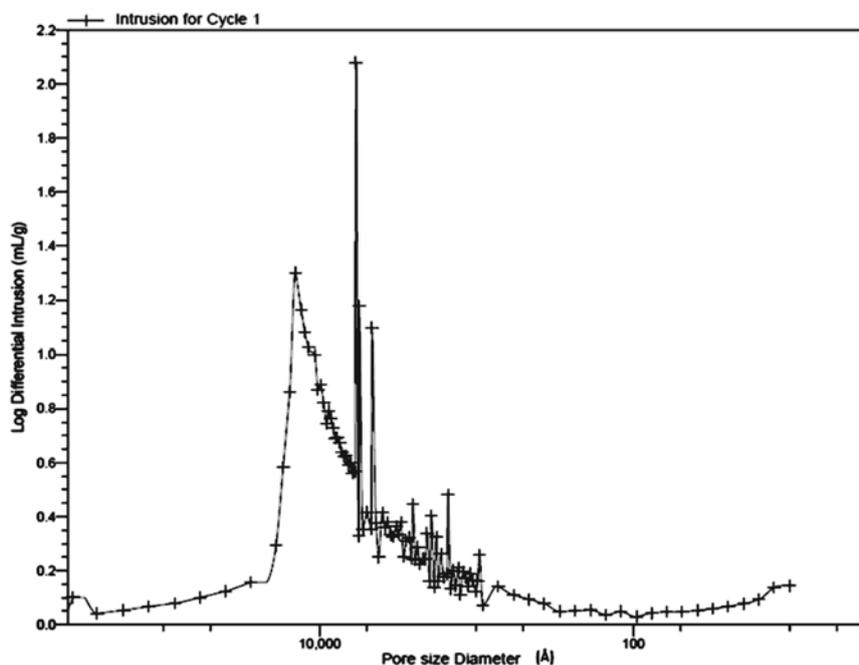


Fig. 3. Pore sizes distribution of activated carbon by DFT method.

percentage.

External morphology

The Scanning Electron Micrograph shows a maximum porosity developed and well distributed throughout the material (Fig. 4.b). The higher surface area of activated carbon could be related to the fact that heating at 350°C destroys the tiny pores structure and therefore reduces the available surface area. This indicates the chemical effects on the sample or physical washing of organic matter from the surface.

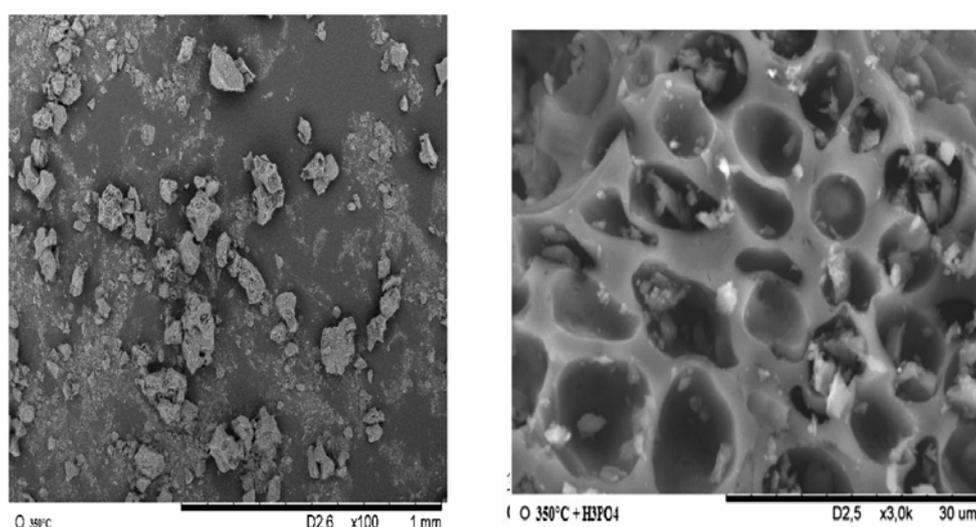


Fig. 4. SEM of (a) precursor and (b) activated by H_3PO_4 at 350°C.

Chemical composition

Chemical composition of activated carbon obtained in this work by impregnation with H_3PO_4 is shown in Table 3 along with its raw material. As expected, the processed sample has much higher contents of carbon and lower percentages of oxygen and hydrogen compared to the initial biomass. As a matter of fact, the chemical activation, during the heat treatment, may accelerate the chemical changes in material and enable the removal of hydrogen and oxygen, resulting in supplemented carbon content.

As we can see (Table 4), the nature and concentration of surface functional groups were modified by chemical treatment. The determination of surface functional groups shows that the chemical activation at 350 °C promotes the departure of the carboxylic acid in the form of carbonic acid [16] and the recombination of organic matter probably accompanied by insertions of the oxygen atom, which explains the

TABLE 3.

Elemental composition of oregano and activated carbon

Sample	Carbon (%)	Oxygen (%)	Hydrogen (%)
Origan	39	5.44	38.59
Activated carbon	65.48	2.44	15.69

TABLE 4.

Surface chemical functional groups of oregano and activated carbon

Sample	Carboxyls (meq/g)	Lactones (meq/g)	Hydroxyls (meq/g)	Basic functions (meq/g)
Origan	1	0.3	0.9	0.4
Activated carbon	0.4	1.5	0.3	0

increase in lactones for the activated carbon at the expense of carboxyls. The hydroxyls are also low and the total basic sites of the activated carbon have disappeared.

CONCLUSION

We have demonstrated in this study that we can make an activated carbon with very interesting structural characteristics from the residues of Oregano.

The overall results show that with optimized conditions and the use of phosphoric acid as activating agent, we obtained an activated carbon essentially microporous and competitive. It has a higher specific surface area ($S_{\text{BET}} = 1173.24 \text{ m}^2/\text{g}$), a micropore volume calculated using the “t-plot” of $0.50 \text{ cm}^3/\text{g}$ and a pore sizes of 2 nm with a total porosity percentage of 53.30%.

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