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Pore characteristics of chemically activated carbons by the phosphoric acid of date stone of the south Algeria

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ABSTRACT

The present work was focused on the determination of texture, morphology, oxygenated surface groups characteristics of a two deferent activated carbon prepared from tow variety of the date stone: Ghares (ACG) and Mech Degla (ACM) given from Biskra region in south Algeria. Chemical activation of this precursor using phosphoric acid H_3PO_4 as an activation agent. The microscopic structure was examined by nitrogen adsorption at 77 K. Energy of activation was determined by Dubinin-Radushkevich(DR) model. The Results yielded a height surface area (S_{BET}) and total pore volume of 1060 m^2/g and 0.52cm^3/g for Mech Degla variety.

Keywords: activated carbon, chemical activation, adsorption isotherm, Boehm method, phosphoric acid.

INTRODUCTION

For environmental protection and economic exploitation, many researchers valorized of different organic products in the food industry by chemical.

Activated carbon, defined by its property as well as by its source, can be produced from almost any organic substance that has high carbon content as : cotton stalks [1, 2], almond shells[3], waste tea [4],coconut shell[5-7].The application of activated carbon has expanded into many fields, including water purification and pollution treatment [8]air and gas purification (motor vehicle exhaust control, cigarette filters), and the food and pharmaceutical industries[9]gas separation and storage [10, 11],etc.

The production of activated carbons with high surface area realized by different methods chemical activation with activation agent as KOH[12-14],$ZnCl_2$[1, 15-17] ,H_3PO_4[18] , or physical activation in different temperature[19, 20].

The objective of this works is prepared the activated carbon from different variety of date stone Mech Degla and Ghares variety a resource from the south of Algeria exactly Biskra region.

MATERIALS AND METHODS

2.1. Preparation of date stones porous carbon

The two kinds date stone Ghares and Mech Degla were used as precursors of activated carbon (ACG) and (ACM) respectively. This stone was imported from Biskra locality. The precursors were crushed and then sieved to reduce their particle size of 2mm after washing with distilled water to eliminate the impurities (dust and water soluble substances. The granular date stones were impregnated with a weighed amount of H_3PO_4 aqueous solution and further heat treated at 600 °C in air atmosphere.

1.2. Activated carbon characterization

1.2.1.External surfaces of resulting carbon using SEM

Microstructure of the sample was examined using a scanning electron microscopy ***(Quanta 600W environmental (ESEM))*** which is a technique of electron microscopy based on the principle of electron-matter interactions capable of producing high-resolution images of the surface of samples.

2.2.2. Adsorption of N_2 at 77 K according to the BET method

2.2.2.1. Adsorption isotherm: Such isotherms are classified into six shapes and these are as shown in Figure1 [21]: Type-I isotherms reach a maximum value of adsorption without inflections and are characteristic of carbons containing microporosity only. Type-II isotherms describe adsorption in mixed situations of micropores and open surfaces with multilayer formation (assisted condensation, and not to be considered as volume filling. Type-III isotherms are convex and are characteristic of adsorption at sites of low adsorption potential, systems. Type-IV isotherms resemble Type-II isotherms but additionally, instead of adsorption on open surfaces at high relative pressures, adsorption takes place in mesoporosity. Such isotherms may exhibit hysteresis when the mechanism of filling by capillary condensation in mesopores differs from that of mesopore emptying. Type-V isotherms are those of a low energy, homogeneous solid surface possessing mesoporosity. Type-VI isotherms are of surfaces with an extremely homogeneous structure[21, 22].

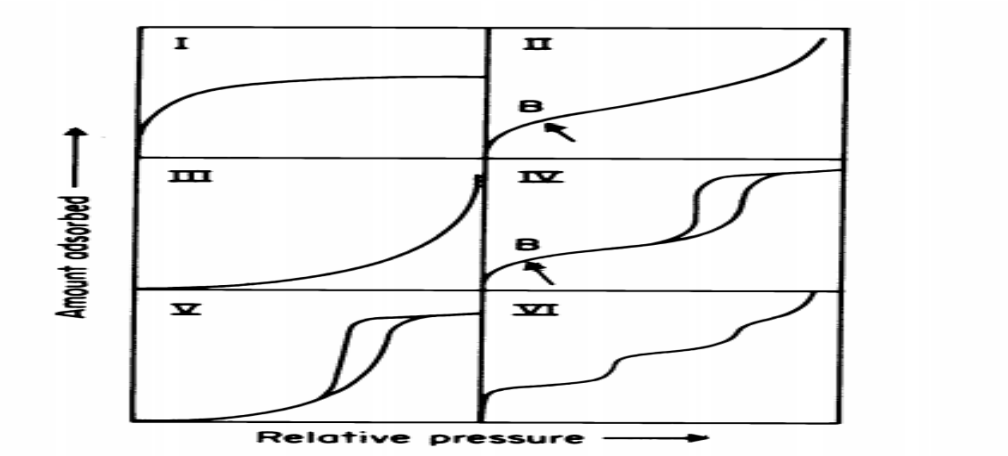

Figure 1: Type of adsorption isotherm (sing and al 1985) [23]

2.2.2.2. Activated carbon characteristic by the BET method

Pore structure of the porous carbon was characterized by adsorption N_2 at -196 C with an Quantachrome Instruments, Model NOVAWIN2 according to the classical method Brunauer,Emmet and Teller or BET [23].the activated carbons have been degassed under vacuum at 300 ◦C for 3 h prior to the measurement.N_2 adsorption isotherm was measured over a relative pressure (P/P0) range from approximately 10^{-7} to 1.

The BET surface area is calculated from the isotherms by applying the Brunauer–Emmett–Teller (BET) model tothe isotherm data points of the adsorption branch in the relative pressure range $0.05<P/P_0<0.3$ using the BET equation(1)[21, 23]. The micropore volume (Vmic); micropore area(Smicro) were determinated by the t-plot method .The pore size distribution was ascertained by Density Functional Theory (DFT) method[22, 24].

$$\frac{P}{V(P_0-P)} = \frac{1}{V_m.C} + \frac{C-1}{V_m.C} \cdot \frac{P_0}{P} \quad (1)$$

Two Constants V and C can be evaluated From the slope ($1/V_m.C$) and the intercept ($C-1/V_m.C$).C alsowas diffined as the equation (2):

$$C = e^{[\frac{\varepsilon_1-\varepsilon_L}{RT}]} \quad (2)$$

$\varepsilon_1-\varepsilon_L$: difference between adsorption molar energy for the first layer ε1 and liquefaction energyε_L[25].
The average pore diameter **Dp** was estimated by applying the following equation (3) assuming cylindrical pore geometry [26]:

$$Dp = \frac{4Vp}{S_{BET}} \quad (3)$$

2.2.2.3. Determination ofThe micropore volume (V_{DR}) and average width (L) by (DR) method

The Dubinin–Radushkevich equation for the characterization of microporous carbons determined from Equation (4)[27, 28]:

$$\mathbf{Ln(W) = ln(W_0) - \left(\frac{Rgaz.T}{E_0.B}\right).\left[ln\frac{P_0}{P}\right]^2} \quad \textbf{(4)}$$

With: $\mathbf{R_{gas}}$: the gas constant, **T**: the analysis temperature (k), **B:** the affinity coefficient (B = (E_0/E) =0.33 for nitrogen, $\mathbf{E_0}$**:** the interaction energy (characteristic adsorption energy: physisorption or chimisorption).

The limiting micropore volume $\mathbf{W_0}$was deteminated by back extrapolation of the linear section of the DR plots [**ln W= f (ln(P_0/ P)^2)**][22].

The characteristic energy E_0 (KJ/mol) related to the average width (**L** in nm) of activated carbon micropores wich determinated from the equation (5,6)[29]:

$$\mathbf{L = \frac{2(\beta k)}{E}} \qquad \textbf{(For } E_0 < \textbf{20 kJ/mol)} \quad \textbf{(5)}$$

$$\boldsymbol{L = 10,8/(E_0 - 11,4)} \qquad \textbf{(For } E_0 > \textbf{20 kJ/mol)} \quad \textbf{(6)}$$

With k(structural parameter) =12 nm kJ/mol when using nitrogen at 77K[29].

2.2.3. Determinationthe number of the sitefunction group (acid-basic) byBoehm titration

Boehm titration method [30]was applied in order to determination of the quantification of acidic and basic surface oxide groups of the adsorbents. The neutralization realized with different solutions: 0.1M of HCl solution (for basic groups) and 0.1M of NaOH solution (for acidic groups)[30, 31].

The site active of the activated carbon can be determinated by the following equation:

$$\boldsymbol{N_{site}\left(\frac{sitenumber}{nm^2}\right) = \frac{C*N_{avogadro}}{S_{BET}}} \quad \textbf{(7)}$$

RESULTS AND DISCUSSION

Observations from the scanning electron microscope (**SEM**) showing in **Figure2(a.b)** that for activated carbon studied, there is a highly developed pore over the entire sample surface with certain heterogeneity of the microporous.

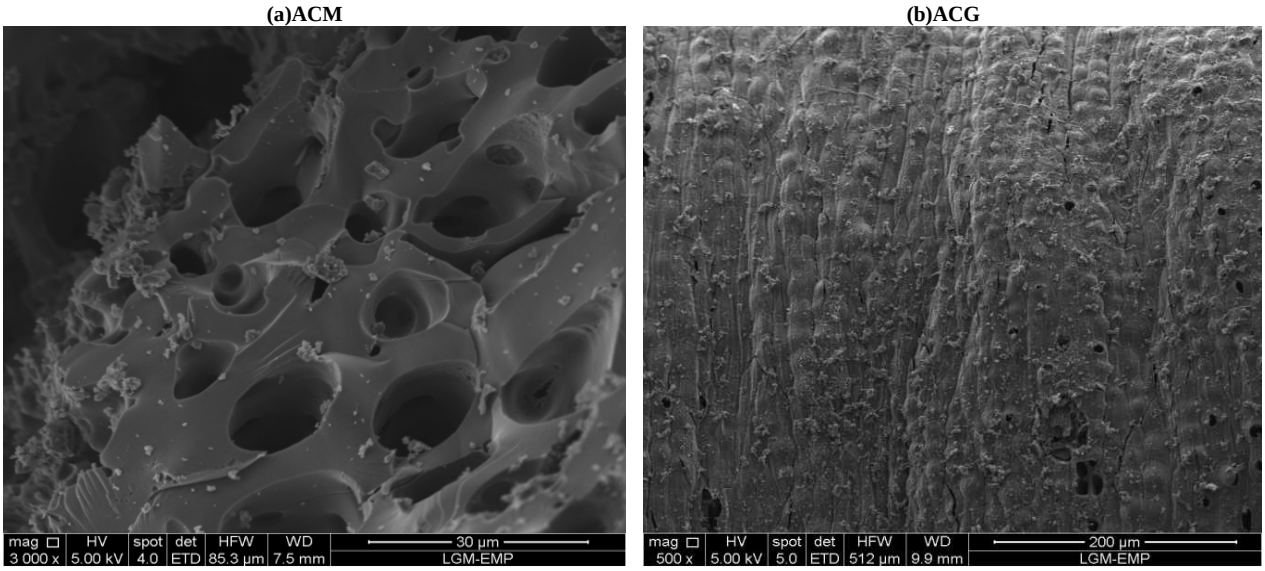

Figure 2: The SEM of different activated carbon

The results isothermal of the adsorption of nitrogen (N_2) at 77 K are presented in **Figure 3**. The isotherm of two activated carbon (and) classified as **Type I** according to the UIPAC classification with small hysteresis.

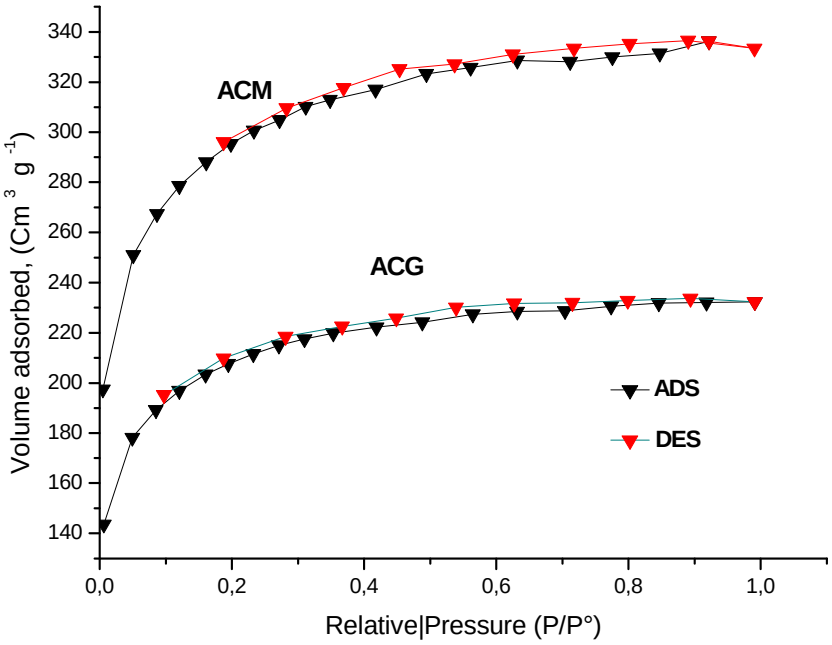

Figure 3: Isotherm adsorption desorption of tow activated carbon

The Adsorbent characteristics summarized in the table (1) and compared with some works who prepared the activated carbon from material lignocellulosic different [5, 32-35].

Table 1: Textural characteristic of activated carbon prepared ACG and ACM

Sample code	Activation process (activation agent)	Properties								Reference
		S_{BET} (m^2/g)	V_T (cm^3/g)	S_{ext} (m^2/g)	S_{micro} (m^2/g)	V_{mico} (cm^3/g)	S_{mico}/S_{BET} (%)	V_{micro}/V_T (%)	D_{moy} (nm)	
Date stone (Ghares)	Chemical (H_3PO_4)	765	0.36	5.13	759	0.35	99.33	97.66	1.71	This work
Date stone (Meh Degla)	Chemical (H_3PO_4)	1060	0.52	8.74	1050	0.50	99.17	97.43	1.77	This work
Olive stone	Chemical (H_3PO_4)	1194	0.56	-	-	0.55	-	98.4	2.08	[7]
Coconut shell	Physical 1000°c	702	0.53	-	-	0.35	-	66	3.03	[35]
Artichoke leaves	Chemical (H_3PO_4)	2038	2.47	780	1258	0.61	61.7	24.65	4.84	[36]
Tea industry	Chemical ($ZnCl_2$)	1141	0.81	-	254	0.13	22.3	16.1	2.83	[37]
Cherry stone	Chemical ($ZnCl_2$)	1971	1.15	-	-	0.74	-	64.35	2.33	[38]

Figure 4 shows the pores size distributions of the active carbon prepared who are less than 60 Å with most pores less than 20 Å, which indicates that the carbons are mainly microporous.

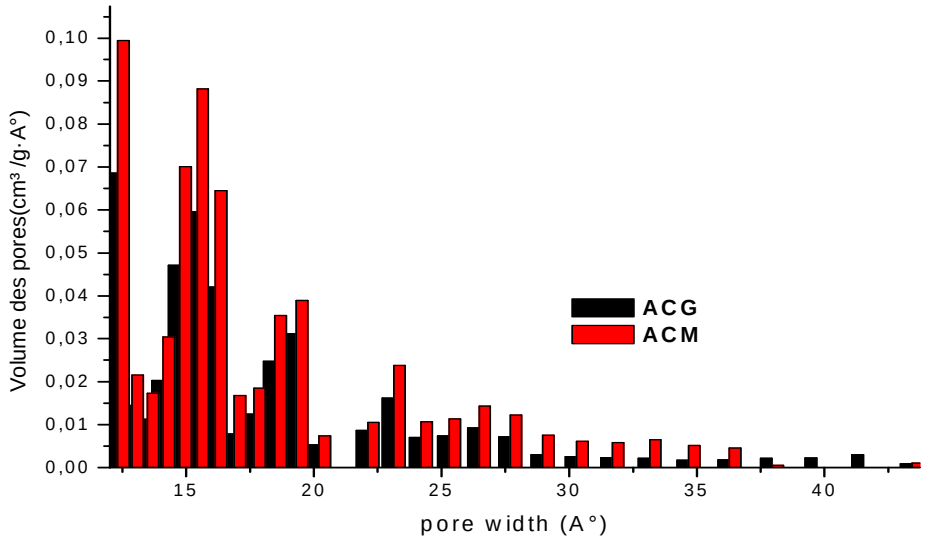

Figure 4: pore size distribution

The extrapolation of the linear section of the DR plots presented in Figure5,

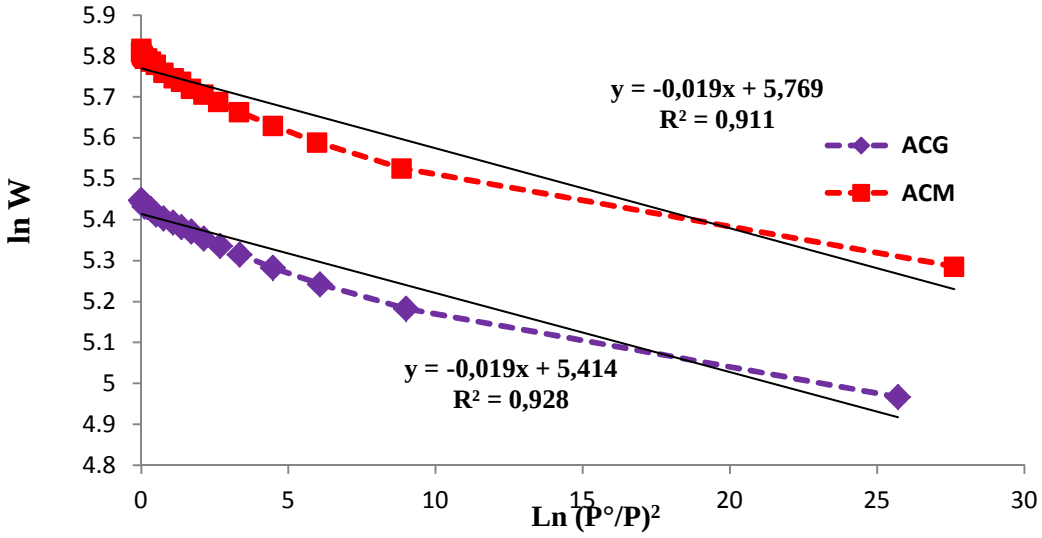

Figure 5: Plotting of Dubinin–Radushkevich model(DR) from the activated carbon

The Table02 indicated that parameter of Dubinin–Radushkevich model. From the interaction energy obtained, the type of adsorption is physisorption that based on the attraction of molecules to a surface by dispersion forces [10].

Table 02. Textural parameters of the Dubinin-Radushkevich model (DR)

	W_0 (cm^3/g)	E_0 (kJ/mol)	V_{Micro} (dr)	E (kJ/mol)	L (nm)
Mech degla activated carbon (ACM)	224,53	12983	0,29	4284,5	1,85
Ghares biskra activated carbon (ACG)	319,58	12983	0,41	4284,5	1,85

The number active sites at the surfaces of different carbon ACM and ACG in figure 6 proved that every activated carbon Takes acidic nature.

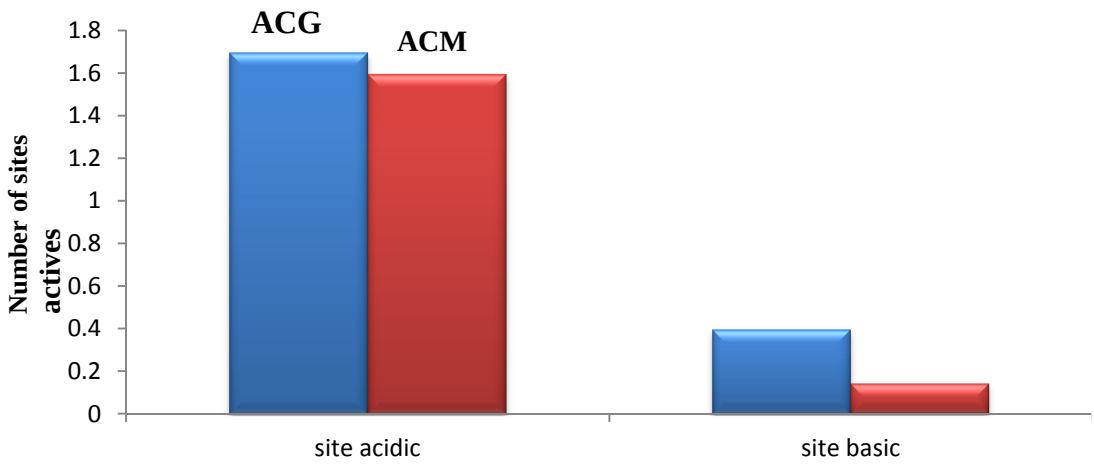

Figure 6.histogram of the number of site active

CONCLUSION

The phosphoric acid used as agent activation it was developed pore structure of the activated carbons prepared from date stone gives a high surface and high total pore volume carbons. It was found that the best specific surface area and total pore volume of the activated carbon of Mech Degla from Biskra region were 1060 m^2/g and 0.52cm^3/g.

The future study is the determination of the power adsorption of these activated carbon in the elimination of various organic pollutants to assess the chemical nature of the pollutants for which efficacy was proven.

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