

Preparation and characterization of activated carbon monoliths from date stones by physical activation

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(Received: 07 March 2016, accepted: 17 May 2016)

Abstract: Binderless activated carbon monoliths have been prepared from date stone of the south of Tunisia (Kébili). The activation process involved two steps. First, pyrolysis of the samples was conducted up to a temperature of 1000°C under nitrogen flow. The obtained carbon monoliths were then physically activated at 500 - 900°C under CO₂ flow. All samples have been characterized by N₂ adsorption, scanning electron microscopy and mercury porosimetry. The activated carbons exhibited a predominant microporosity with specific surface area from 476 m² g⁻¹ to 877 m² g⁻¹, and microporous volumes from 0.19 cm³ g⁻¹ to 0.33 cm³ g⁻¹.

Key-words: Date stones; Binderless Carbon Monoliths; Physical Activation

Résumé: Des monolithes de charbon actif ont été préparés sans liants à partir de noyaux de datte du sud de la Tunisie (Kébili). Le processus d'activation comporte deux étapes. Tout d'abord, une pyrolyse des échantillons est réalisée sous courant d'azote jusqu'à une température de 1000°C. Les monolithes de carbone obtenus ont ensuite été activés physiquement à 500°C ou 900°C sous un courant de CO₂. Tous les échantillons préparés ont été caractérisés par adsorption d'azote, par microscopie électronique à balayage et par porosimétrie par intrusion de mercure. Les monolithes carbonés obtenus présentent une microporosité prédominante avec une surface spécifique entre 476 m² g⁻¹ et 877 m² g⁻¹, et des volumes microporeux situés entre 0,19 cm³ g⁻¹ à 0,33 cm³ g⁻¹.

Mots-Clés : Noyaux de datte, monolithes carbonés sans liant, activation physique

INTRODUCTION

The growing demand for adsorbent materials for environmental protection processes raises further research in the manufacture of activated carbon from renewable sources such as plant wastes. A major part of these wastes are fruit stones (apricot, peach, cherry, olive and date stones), nutshells (almond, walnut, and pecan), rice hulls, bagasse, grape seeds [1]. In Tunisia and some other countries, a large quantity of date stones is generated every year and is a significant source of agricultural waste. Such by-products are nevertheless likely to have a significant economic interest. It turns out important to value such wastes.

Chemical activation with KOH or NaOH is the most common methods to produce activated carbons [2], usually as fine powder [3], thus making its shaping to monoliths an important area of research. The manufacture of monoliths normally involves the use of a binder, which implies a reduction of porosity due to partial blocking, the extent of which depends on the kind and proportion of binder used [4].

The aim of this work is the preparation of activated carbon monoliths of high surface area from date stone by physical activation without using a binder. CO₂ was selected as the activation gas as it is clean and easy to handle. Furthermore, it facilitates

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control of the activation process due to the slow reaction rate at temperature around 800°C [5].

MATERIALS AND METHODS

1. Materials

Date stone were acquired from Kebelli (Tunisia). The pits were scratched with a knife to deprive any present fiber from the surface and then dried at 120°C for about 24 h. A solid powder was obtained after grinding and sieving in the desired size grade, then washed with distilled water and dried in an oven at 50°C for 48 h.

2. Activated carbon monolith preparation

Date stone powder was first dried at 110°C for 2 h then shaped into cylindrical monoliths (10 mm × 13 mm) by uniaxial pressing at room temperature under 500 MPa. Carbonization of monoliths was carried out in an horizontal tube furnace under N₂ flow (100 mL min⁻¹). The thermal program was as follows: heating from room temperature to 1000°C at a 1°C min⁻¹ rate, including a first plateau at 300°C for 4 h, then a second one at 700°C for 2 h and a final maintenance at 1000°C for 2 h. The obtained carbon monoliths were then activated at 500 or 900°C for 30 min using a CO₂ flow of 100 mL min⁻¹ (heating rate 5°C min⁻¹).

The nomenclature of raw date stone monoliths (DSM), carbonized monoliths (CM1000) and activated carbon monoliths (ACM) samples includes also the temperature; for example the carbon monolith activated at 500°C will be labeled ACM500.

3. Characterizations

3.1. Porosity determination

The porosity of a porous material is given by the relation: $\Phi = 1 - \rho_a/\rho_s$ where ρ_a is the apparent (bulk) density and ρ_s the skeletal density. The experimental porosity Φ_{exp} and pore size distribution of each sample were determined by mercury intrusion porosimetry in a Micromeritics Autopore IV 9500 porosimeter with the following parameters: contact angle = 130°, mercury surface tension = 485 mN m⁻¹, maximum intrusion pressure = 124 MPa.

3.2. Skeletal density

The skeletal density ρ_s of the materials was determined using a Micromeritics Accupyc II 1340 helium pycnometer.

3.3. Specific surface area determination

The specific surface area was determined by

nitrogen sorption measurements on a Micromeritics ASAP 2010 analyzer. The collected data were subjected to the Brunauer, Emmett and Teller (BET) treatment [6]. The mesopore and micropore volumes were obtained by application of the α_s method [7]. The total pore volume V_t was obtained from the amount adsorbed at a relative pressure p/p_0 of 0.99, while the mesopore volume V_{meso} was obtained from the difference between the total pore volume and the microporous volume.

3.4. Scanning electron microscopy investigation

The morphology of the monoliths was observed by scanning electron microscopy (SEM) in a Hitachi TM-1000 microscope. Photographs were taken at several different magnifications between ×500 and ×10,000. Pieces of sample (section of about 0.5 cm²) cut from the corresponding monoliths were mounted on a carbon tab, which ensured a good conductivity. A thin layer of gold-palladium was sputtered on the sample fragment prior to analysis.

3.5. Thermogravimetric analysis (TGA)

Materials weight loss studies were performed on a Netzsch STA 409 thermobalance under high purity argon atmosphere. TGA and DTG data were obtained under argon flow (60 mL min⁻¹) at a heating rate of 5°C min⁻¹ and the temperature ranged from 30 to 1000°C

3.6 Elemental analysis

The C, H, N and O elemental analyses were carried out in a Thermo Fisher Flash 2000 analyzer ensuring a precision of ± 0.3%.

RESULTS AND DISCUSSION

1. Thermogravimetric analysis of date stone powder

The thermogravimetric curve of date stone powder under inert atmosphere is shown in Figure 1.

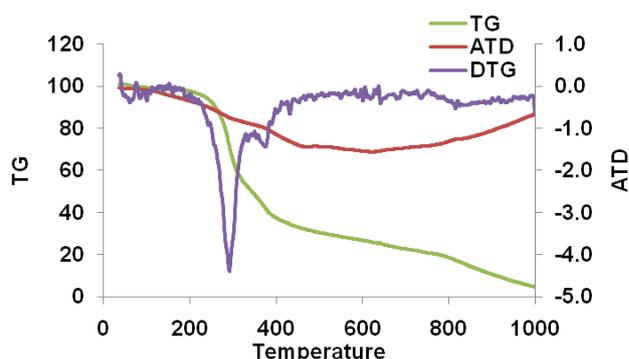


Fig. 1. Thermogravimetric analysis of date stone powder.

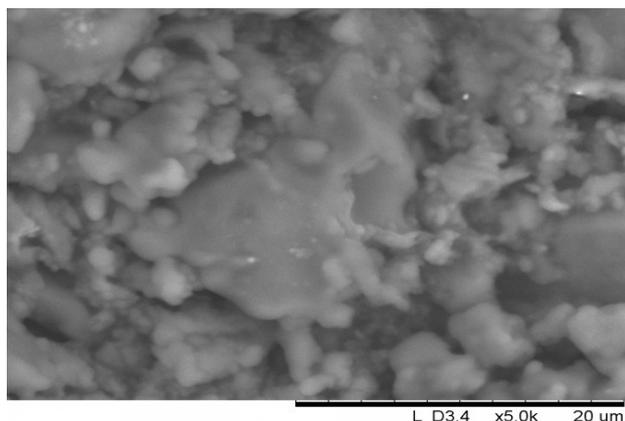


Fig. 2. SEM micrograph of date stone monolith (DSM)

Three stages of evolution can be observed during pyrolysis of the sample: dehydration, decomposition of polymers and carbonization. Carbonization program of the samples was then established according to these results.

The TG curve shows a first weight loss (2.5%) up to 155°C due to moisture elimination. The second weight loss (73%) arising between 155°C and 550°C, corresponds to the carbonization step. This major weight loss is due to the elimination of volatile matters and tars. Carbonization proceeds in two steps: a first range from 250°C to 350°C and a second one from 250°C to 500°C attributed to cellulose and lignin decomposition, respectively [8]. Above 550°C the weight loss is small indicating that the basic structure of the char has been formed.

2. Visual aspect of the different samples

SEM image of date stone monolith (DSM) (Figure 2) shows that this material has a very rough surface, an intact external structure where

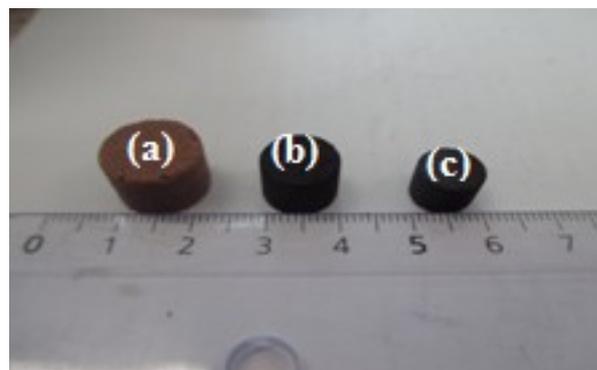


Fig.3. Visual aspect of date stone monoliths: a) compressed date stone monolith DSM, b) Carbonized monolith CM1000, c) Activated monolith ACM900.

the caking agglomeration of the carbonaceous aggregates was not observed.

The shape of the samples is preserved during the carbonization but a shrinking in volume was observed. This behavior can be visualized by comparing: a) Compressed date stone monolith DSM, b) Carbonized monolith CM1000, and, c) Activated monolith ACM900 (Figure 3). Volumetric shrinkage is associated to a weight loss during carbonization.

3. Elemental analysis of samples

The result of elemental analysis of the different samples is reported in Table I.

Data reported indicates a strong increase in C/H and C/O ratios during the carbonization step as expected. The pyrolysis stage under neutral atmosphere allows to obtain a carbonaceous product by the volatilization of hydrogen, oxygen and nitrogen traces. In this process, hydrogen and oxygen elimination occurs in the form of CO, CO₂ and H₂O. The release of monoxide and carbon

Table I: Elemental analysis of the different samples.

Sample	Elemental analysis (%)				Atomic ratio	
	C	H	N	O	C/H	C/O
DSM	46.83	6.66	0.74	40.55	0.59	1.54
CM1000	78.17	0.99	0.58	8.48	6.58	12.29
ACM500	78.07	0.93	0.39	11.16	6.99	9.33
ACM900	73.41	1.45	0.53	12.41	4.22	7.89

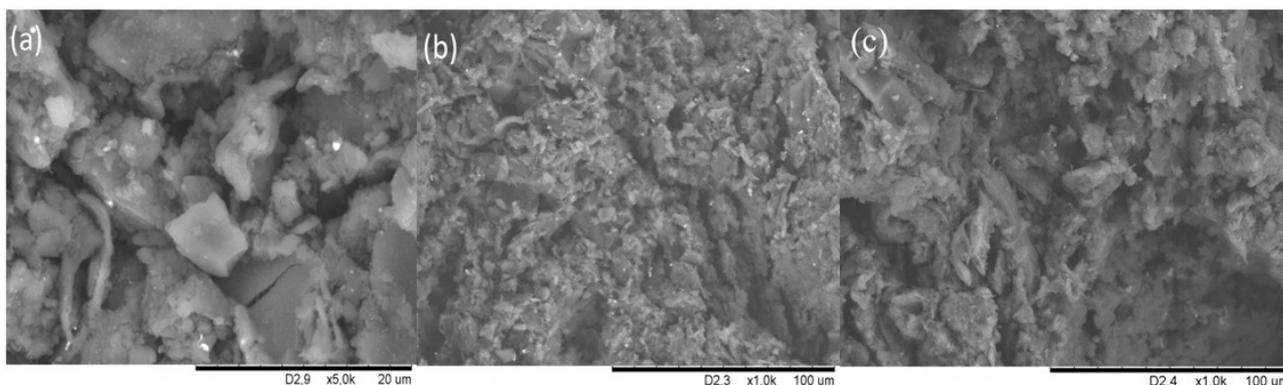


Fig. 4. SEM micrograph of CM1000 (a), ACM500 (b), ACM900 (c)

dioxide is generally observed between 200 and 300°C. The cellulose is degraded between 240°C and 360°C. At 300 and 400°C, the production of hydrocarbons occurs, between 400 and 500°C, there is a release of a large quantity of gas hydrocarbons and thick tar. From 500 to 700°C, the production of gas refers mainly to hydrogen, carbon monoxide and hydrocarbons. From 700 with 1000°C, the major remaining product is carbon residue [9]. Activation under CO₂ at 500°C or 900°C do not modify significantly these data, but allows the formation of micropores during activation when the temperature exceeds 700°C.

4. Morphology analysis of the pyrolysed and activated carbons

SEM images of pyrolysed (CM1000) and activated (ACM500, ACM900) carbon monoliths are presented in Figure 4.

As can be seen from these clichés, pyrolysis creates some porosity (Fig. 4a). After activation, the porosity is more developed. By comparing Fig. 4b and Fig. 4c, we can notice that the porosity is more developed with an activation temperature of 900°C than with 500°C, which indicates clearly that a regular macroporosity and a rather homogeneous surface are obtained by activation at 900°C under CO₂ for 30 min (Fig. 4c) [10].

5. Porous morphology of pyrolyzed and activated carbons

The experimental porosity Φ_{exp} of the different samples was estimated by mercury intrusion porosimetry. The obtained values are: $\Phi_{\text{exp}} = <0.01, 0.23, 0.40$ and 0.52 for DSM, CM1000, AC500, and AC900 respectively. Raw date stone powder monolith (DSM) is, as expected, almost

non-porous: porosity is generated by pyrolysis. Skeletal density of DSM was found to be $\rho_s = 1.47 \pm 0.01 \text{ g cm}^{-3}$. This value is consistent with that of other lignocellulosic materials [11]. The skeletal density of the carbon monoliths was found to be $\rho_s = 1.79 \pm 0.01 \text{ g cm}^{-3}, 1.91 \pm 0.01 \text{ g cm}^{-3}$ and $1.83 \pm 0.01 \text{ g cm}^{-3}$ for CM1000, AC500, and AC900 respectively. These values are consistent with that of amorphous carbons [12], indicating an efficient carbonization process.

Nitrogen adsorption-desorption isotherms of samples CM1000, ACM500 and ACM900 are reported in Figure 5.

Isotherm profiles are type I-IV composites. The volume adsorbed at low p/p_0 value is indicative of the presence of micropores, the hysteresis observed over $p/p_0 = 0.4$ indicates the presence of mesopores.

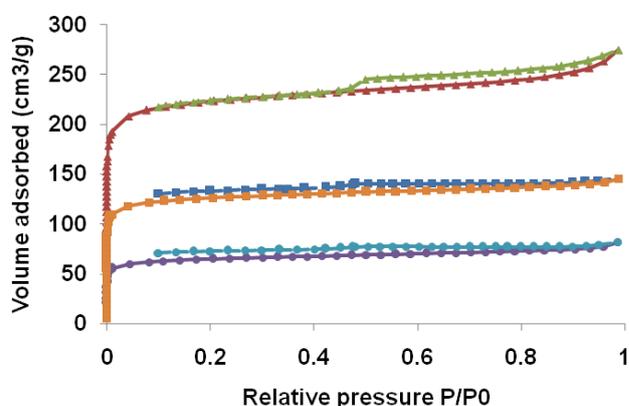


Fig. 5. N₂ Adsorption-desorption isotherms of pyrolyzed (CM1000) and activated (ACM500, ACM900) date stone monoliths.

**Table II:** Porous morphology analysis of carbons monoliths.

Sample	BET specific surface area (m ² g ⁻¹)	α_s -method					
		S_{meso} (m ² g ⁻¹)	S_{super} (m ² g ⁻¹)	S_{ultra} (m ² g ⁻¹)	V_{meso} (cm ³ g ⁻¹)	V_{super} (cm ³ g ⁻¹)	V_{ultra} (cm ³ g ⁻¹)
CM1000	248	32	137	78	0.033	0.052	0.040
ACM500	496	47	138	311	0.039	0.074	0.112
ACM900	877	87	250	540	0.100	0.126	0.199

Different pore volumes and specific surface areas were then determined from the data collected from the isotherms using specific methods (Table II).

The Brunauer-Emmett-Teller theory gives the BET specific surface area (S_{BET}) [6]. The α_s method allows the determination of pore volumes and specific surface areas of mesopores (pores with diameter between 2 and 50 nm), supermicropores (pores with diameter between 0.7 and 2 nm) and ultramicropores (pores with diameter < 0.7 nm) [7]. Specific surface areas (S_{BET}) values of pyrolysed (CM1000) and activated (ACM500, ACM900) samples are considerably higher than that of the monolith precursors prepared from date stone powder ($S_{\text{BET}} \sim 2 \text{ m}^2 \text{ g}^{-1}$). This result is in agreement with the formation of a fine structure essentially micro-mesoporous during

carbonization. S_{BET} value is significantly higher for activated samples (ACM900 and ACM500) than for CM1000, indicating the efficient role of physical activation by CO₂ on the micropores generation. The BET specific surface area value is generally considered as including the surface contribution of all kind of pores size from small macropores (< 200 nm) to ultramicropores. Therefore, it can be expected that ACM900 sample contains a larger micropore volume than the other samples do. Indeed, the total pore volume is: $V_t = 0.125, 0.225$ and $0.425 \text{ cm}^3 \text{ g}^{-1}$ for CM1000, ACM500 and ACM900 respectively. The α_s method confirms that hypothesis.

A tentative repartition of pore volumes and specific surface areas according to pore class using the α_s method results is reported in Table III.

For each sample prepared, the porous volume determined by the α_s method is distributed between mesopores, supermicropores and ultramicropores with a preference toward the latter, excepted for sample ACM500. This behavior is in good agreement with the specific surface area evolution, giving the higher value to the ACM900 sample.

Table III - Percent repartition of the specific pore volumes and surface areas extracted from α_s method

	CM1000	ACM500	ACM900
$S_{\text{meso}} \%$	13	9	10
$S_{\text{super}} \%$	55	28	28
$S_{\text{ultra}} \%$	32	63	62
$V_{\text{meso}} \%$	26	17	23
$V_{\text{super}} \%$	41	33	30
$V_{\text{ultra}} \%$	32	50	47

CONCLUSION

In this study we have succeeded in preparing a series of binderless activated carbon monoliths from date stone powder. This work shows that date stone can be used as precursor to produce activated carbons with a rather well-developed microporosity by pyrolysis followed by physical activation with CO₂. Porosity analysis shows that the monoliths obtained are essentially microporous

with a specific BET surface area increasing with the activation temperature. Specific surface area reaches $877 \text{ m}^2 \text{ g}^{-1}$ after physical activation at 900°C . This value competes very well with data reported in the literature about similar materials [13,14].

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