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

Chafia Bouchelta [a,*], Mohamed Salah Medjram [a], Odile Bertrand [b], Jean-Pierre Bellat [b]

[a] *Laboratory LARMACS, Faculty of Science and Engineering, 20 Août 55 University, El-Hadaeik Road, P.O. Box 26, Skikda 21000, Algeria*
[b] *Institut Carnot de Bourgogne, UMR 5209 CNRS, 9 avenue A. Savary, Université de Bourgogne, BP 47870, 21078 Dijon, France*

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Abstract

Activated carbons are produced from wastes of Algerian date stones by pyrolysis and physical activation in the presence of water vapor into a heated fixed-bed reactor. The effect of pyrolysis temperature and activation hold time on textural and chemical surface properties of raw date stones and carbon materials produced are studied. As expected, the percentage yield decreases with increase of activation temperature and hold time. The characterization of carbon materials is performed by scanning electron microscopy (SEM). X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and nitrogen adsorption (BET). Results show the presence of cellulose and hemicellulose in the raw material, and the predominance of carbon and graphite after pyrolysis. Different oxygen-containing functional groups are found in the raw material while aromatic structures are developed after pyrolysis and activation. The best specific surface area (635 $m^2\ g^{-1}$) and microporous volume (0.716 $cm^3\ g^{-1}$) are obtained when the date stones are grinded, pyrolysed at 700 °C under a 100 $cm^3\ min^{-1}$ nitrogen flow and then activated under water vapor at 700 °C for 6 h.

Keywords: Date stones; Activated carbon; Pyrolysis; Physical activation; Microporosity; Surface area

1. Introduction

Activated carbons are usually used worldwide for water treatment, wastewater reclamation, gas purification and also as catalyst support [1]. Adsorption capacity of activated carbons depends essentially on their preparation methods and initial structural properties. They can be prepared by physical or chemical activation. Activated carbon produced by physical activation is obtained after two steps: the first one is the carbonisation so-called pyrolysis of carbonaceous material at high temperature (500–1000 °C) in inert atmosphere in order to eliminate the maximum of oxygen and hydrogen elements. The second one is the thermal activation at the same temperature as for pyrolysis or at a higher temperature in the presence of oxidizing gas such as water, carbon dioxide or both [2]. By chemical activation it is possible to prepare activated carbon in only one step. Pyrolysis and activation are carried out simultaneously in the presence of dehydrating agents (e.g. $ZnCl_2$, H_2SO_4 and KCl) [3]. Activated carbons can be prepared from many organic materials having a high carbon content like wood [4,5], coal [6], lignite [7] and coconut shells [8–10]. In the recent years, many other agricultural by-products have been used as sources for activated carbons production such as cherry stones [11,12], olive stones [13–18], oil palm stones [19–21], apricot stones [22,23], almond shells [24], sugar cane bagasse [25,26], walnut shells [13], pecan shells [27–29], cotton stalks [30] and date stones [31–35]. World production of dates was approximately 6.7 million tonnes in 2004. The major producers in the world are: Egypt, Iran, Saudi Arabia, United Arab Emirates, Pakistan, Algeria and other mediterranean countries. Algeria produces 450,000 t/year of dates [36]. Hamada et al. [37] and Haimour and Emeish [31] found that date pits constitute approximately 10% in weight of the fruit. Adapted from a number of literature references according to FAO Agricultural Services [36] an indicative picture of the chemical composition of the date pits are given in Table 1. Carbohydrates are the major components of date pits. They are composed of cellulose (42%), hemicellulose (18%), sugar and other compounds (25%), lignin

* Corresponding author. Tel.: +213 33704319; fax: +213 33704319.
E-mail address: cbouchelta2000@yahoo.fr (C. Bouchelta).

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Table 1
Approximate chemical composition of date pits (% of dry weight)

Compound	Content (%)
Moisture	5–10
Protein	5–7
Oil	7–10
Crude fiber	10–20
Carbohydrates	55–65
Ash	1–2

(11%) and ash (4%). This lignocellulosic composition promotes the preparation of activated carbon from their precursors. With regard to the mineral content, date pits show appreciable amounts of K followed by P, Mg, Ca and a low Na content. Among the elements present as traces, Fe, Mn, Zn and Cu are the more important ones. In the Middle East this by-product is sometimes pulverized on dirt roads as a type of road base gravel. Date pits are also used in animal feed [37], as a new renewable energy source via combustion [38] and as a complementary feeding source for livestock [39]. Date stone charcoal is used as a filtering medium for automobiles exhaust gases and as an adsorbent of toxic organic and inorganic compounds. Many studies have been done for production of activated carbon from this agricultural waste by using the chemical process. Haimour and Emeish [31] and Girgis and El-Hendawy [32] have prepared activated carbon from date pits by chemical activation with phosphoric acid. In addition, Kannan et al. [33] have obtained activated carbon from date pits under chemical activation using sulphuric acid. Nevertheless, the preparation of activated carbon from date pits by physical activation has not been extensively studied [40,41]. So, it seems to us relevant to study this activation procedure in more details, which is more favourable to preserve the environment because no chemical reagents are used. The aim of this study is then to prepare an activated carbon from date pits that are abundant Algerian by-products by using the physical activation process under steam in a fixed-bed reactor. A particular attention has been paid to the effect of several parameters as the pyrolysis temperature and the activation hold-time on porosity and chemical properties of carbon materials obtained by this way.

2. Experimental

2.1. Starting material

Date stones were of different varieties produced in Algeria. They were obtained from the pastry date manufacturing. First, the pits were washed, and then dried at 120 °C for about 24 h. The clean stones were kept in a desiccator to protect them from moisture. Some initial characteristics of date pits were determined: apparent density (0.32 g cm^{-3}), moisture (9% in weight), apparent porosity measured by helium pycnometry (12% in volume) and pH (6.67).

2.2. Activation procedure

Activated carbons were prepared from date stones by pyrolysis under nitrogen flow and activation under water vapor.

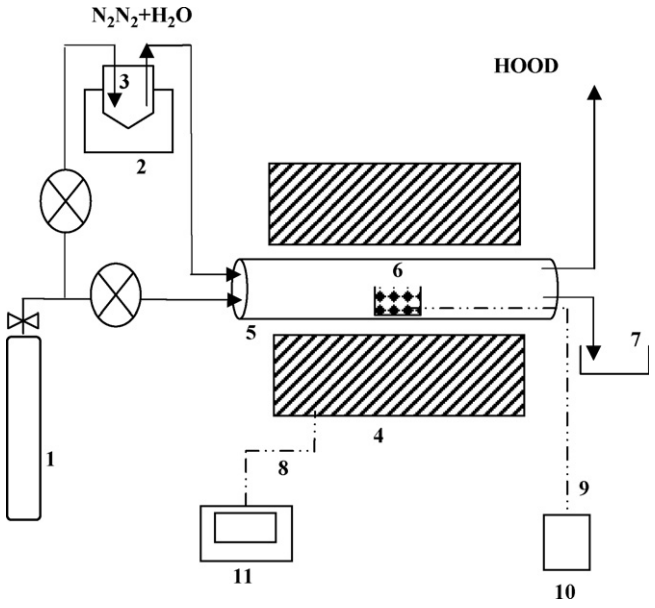

Fig. 1. Schematic diagram of the experimental setup: (1) nitrogen gas cylinder; (2) flask heater; (3) water saturator; (4) tubular furnace; (5) tubular reactor; (6) sample; (7) beaker (liquid product collectors); (8) furnace thermocouple; (9) sample thermocouple; (10) temperature recorder; (11) temperature controller.

Pyrolysis of the raw material was carried out with a horizontal tubular furnace (length of 450 mm and internal diameter of 65 mm). The reactor was a quartz tube (length of 750 mm and internal diameter of 35 mm), which was placed in the furnace as shown in Fig. 1. Two thermocouples were used to measure the temperature in the reactor and for monitoring the furnace.

For the pyrolysis step, about 20 g of date stones were placed in the middle of the reactor. Different pyrolysis temperatures of 500, 600, 650, 700 and 800 °C were used. Nitrogen flow rate was of 100 cm^3 min^{-1} and heating rate was of 10 °C min^{-1} for all the samples. Once the pyrolysis temperature was reached, sample was maintained at this one for 1 h. The resulting chars were then physically activated at 500, 600, 650, 700 or 800 °C for 0.5,1, 2, 3 or 6 h under a nitrogen flow (100 cm^3 min^{-1}) saturated in steam after passing trough the water saturator heated at 80 °C. Thus, the water partial pressure was of 474 hPa. During pyrolysis and activation treatments, gaseous by-products such as CO, CO_2, H_2 and H_2O were evacuated by an extractor hood and the liquid by-products were collected in a flask. After activation, the sample was cooled to ambient temperature under N_2 flow rate.

Pyrolysis was performed on raw date pits and on granular and powdered samples obtained by grinding the pits. The particle size was between 1 and 3 mm and lower than 0.5 mm for the granular and powdered forms, respectively.

The nomenclature used to denote the date stones treated under different conditions is given in Table 2.

2.3. Characterization

The morphology of raw material, pyrolysed material and activated carbons produced from date pits were examined using scanning electron microscopy (JEOL 6400F OXFORD).