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Physically activated microporous carbon from a new biomass source: Date palm petioles

Préparation de charbons actifs microporeux à partir d'une nouvelle matière première issue de la biomasse : les pétioles de palmiers dattiers

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ABSTRACT

Activated carbons were prepared from a new lignocellulosic biomass source: date palm petioles. The activation process comprise the pyrolysis to 1000 °C under nitrogen flow and then the activation at 750, 850 and 900 °C under CO_2 flow. The samples were characterized by N_2 adsorption, scanning electron microscopy and mercury porosimetry. The activated carbons exhibited a predominant microporosity with specific surface area from 225 $m^2 \cdot g^{-1}$ to 546 $m^2 \cdot g^{-1}$, and micropore volumes from 0.09 $cm^3 \cdot g^{-1}$ to 0.23 $cm^3 \cdot g^{-1}$.

Mots-clés:
Biomasse
Pétioles de palmier dattiers
Charbon actifs
Activation physique

RÉSUMÉ

Des charbons actifs ont été préparés à partir d'une nouvelle matière première issue de la biomasse : les pétioles de palmiers dattiers. Le processus d'activation comporte deux étapes. Dans un premier temps, la pyrolyse des échantillons a été conduite jusqu'à une température de 1000 °C sous flux d'azote. Les monolithes carbonés obtenus ont ensuite été activés physiquement à 750°, 850° et 900° C sous flux de CO_2. Tous les échantillons ont été caractérisés par adsorption d'azote, microscopie électronique à balayage et porosimétrie au mercure. Les charbons actifs présentent une microporosité importante, avec des surfaces spécifiques allant de 225 $m^2 \cdot g^{-1}$ à 546 $m^2 \cdot g^{-1}$, et des volumes microporeux variant entre 0,09 $cm^3 \cdot g^{-1}$ et 0,23 $cm^3 \cdot g^{-1}$.

1. Introduction

Activated carbon is a versatile material with large surface area, adequate pore size distribution, good thermal

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stability, and various functional groups at the surface [1]. In the last decade, activated carbon received considerable attention due to its attractive characteristics that promote powerful utilization for a variety of applications such as adsorption [2], energy storage [3], electrochemical application (super capacitor) [4] and catalysis [5]. The preparation of activated carbon from cheap and readily available agricultural by-products (date stone [6], rice hulls [7], olive stone [8], grape seeds [9], cassava peel [10], etc.) has lured attention from economic and environmental aspects. Activated carbon can be prepared from carbonaceous precursors by different activation methods [11]. Basically they can be activated by chemical and physical methods. Typically, when performed by chemical methods, the raw material is mixed with active agents such as (H_3PO_4 [12] $ZnCl_2$ [13] and KOH [14]) followed by heat treatment at temperatures between 400 °C and 900 °C, carbonization and activation being performed simultaneously. On the other hand, the physical procedure implies the pyrolysis of the raw material under N_2 at a higher temperature (800 −1000 °C), followed by activation under gas flow like CO_2, water vapor or a mixture of them.

The palm tree, a plant cultivated in Tunisia, is rich in by-products but it is currently poorly valued. Interestingly, the date stone, leaves, wood and petioles may serve as precursors for the preparation of activated carbon. In the present study, we focused on the preparation of activated carbons from date palm petioles using physical activation with CO_2 at different temperatures. The materials obtained were characterized by different techniques such as nitrogen sorption, scanning electron microscopy and thermal analysis to gain insights on the surface properties.

2. Experimental procedures

2.1. Raw materials and treatment

Palm wastes, namely date palm petioles (Fig. 1), were obtained from a date palm oasis in Gabès, Tunisia. Petioles were washed with distilled water to remove dust and other hydrophilic impurities, and then dried at room temperature. After being dried, they were cut into small pieces.

Fig. 1. Visual aspect of a raw date palm petiole.

2.2. Activated carbon preparation

Pyrolysis and physical activation were carried out in a horizontal tube furnace. In a typical experiment, a palm petiole sample (30 g) was placed in a furnace under N_2 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 cooling process was not controlled and therefore directed by the oven inertia.

The obtained chars were then activated under CO_2 flow (100 mL·min^{-1}) at different temperatures: 750 °C, 850 °C and 950 °C for 30 min at a heating rate of 5 °C·min^{-1}.

The different samples are referred as raw date palm petiole (**PP**), carbonized palm petiole (**CPP**) and activated palm petiole (**APP**). Samples nomenclature also includes the activation temperature; for example **APP750** refers to the carbonized palm petiole activated at 750 °C.

2.3. Samples characterizations

2.3.1. Yield and burn-off

The pyrolysis yield was defined as: $\%\,\text{Yield} = 100 \times [m_{(\text{after pyrolysis})}/m_{(\text{before pyrolysis})}]$. Burn-off is defined as the weight difference between the precursor biomass and the activated carbon. The following relationship was used: $\%\,\text{burn-off} = 100-[(m_{\text{after activation}})/m_{\text{precursor}}) \times 100]$.

2.3.2. Nitrogen sorption analysis

The specific surface area was determined by nitrogen sorption measurements in a Micromeritics ASAP 2010 analyzer. The total pore volume, V_{total}, was obtained from the amount of gas adsorbed at a relative pressure p/p_0 of 0.99. The collected data were subjected to the Brunauer, Emmett, and Teller (BET) treatment [15]. The microporous volume (V_{micro}) and the microporous specific surface area (S_{micro}) were obtained by the application of the *t*-plot method [16] to the nitrogen adsorption data. The pore size distribution of the materials was assessed by the density functional theory (DFT) [17].

2.3.3. Thermogravimetric analysis (TGA)

The weight loss studies of the materials were performed in a Netzsch STA 409 thermobalance under high purity argon flow (60 mL·min^{-1}). The TGA data were obtained at a heating rate of 5 °C·min^{-1} and the temperature ranged from 30 to 1000 °C.

2.3.4. Microscopy analysis

The morphologies of **PP**, **CPP** and **APP** samples were observed by scanning electron microscopy (SEM) using a Hitachi TM-1000 microscope. To run the analysis, pieces of samples (sections of about 0.5 cm^2) were cut from the corresponding monoliths and then 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. Micrographs were taken at several different magnifications between ×500 and ×10,000.