



## Evidence for the effect of the cooling down step on activated carbon adsorption properties



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### ABSTRACT

Two activated carbons are prepared by chemical activation of olive residue using zinc chloride. The first sample is cooled down slowly after the carbonization in the furnace under a flow of nitrogen, while the second is directly removed from the furnace just after the carbonization and put at ambient temperature and pressure. The textural and structural characteristics of the two samples are determined by nitrogen adsorption and X-ray diffraction (XRD). The oxygen functional groups are characterized via Boehm's titration and Fourier transformed infrared spectroscopy (FTIR). The cooling down step at different rates is followed by thermogravimetry–mass spectroscopy analysis (TG/MS). Slow cooling down of the sample after carbonization leads to CO<sub>2</sub>, O<sub>2</sub>, and CO consumption creating more active sites, which are responsible of the formation of surface oxygen groups, and especially carboxylic groups. The latter dramatically enhance water vapor adsorption at low relative humidity. The cyclohexane adsorption on activated carbons, which is carried out by thermogravimetric analysis (TGA), shows that the cooling down step has an effect on both the initial rate of adsorption and the adsorption uptake at equilibrium.

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### 1. Introduction

It is well known that both physical and chemical properties of activated carbon affect its adsorption capacity [1]. In recent years, many authors studied the effect of surface functional groups on the adsorption phenomenon [2–5]. In the liquid phase, the surface chemical structure plays a dominant role [6]. It has been shown that these functions affect dye removal from wastewater. For example, the presence of oxygen functional groups on the surface of activated carbon materials enhances methylene blue adsorption [7].

The effect of oxygen functional groups is even more complex when the activated carbon is used in gas or vapor phase. In fact, these functions are the first responsible for humidity uptake. In particular, the carboxylic groups act as primary adsorption centers for water vapor [8]. Consequently, the presence of these functions on the carbon surface affects the adsorption process and particularly when this material is used against volatile organic compounds

(VOCs) [9]. In the case of sulfur compounds, it was shown that the presence of the same functions can significantly improve the adsorption of various volatile sulfur molecules [1].

Enhancing the adsorption capacity of activated carbons toward special adsorbents has gained great interest in the recent years. For that purpose, and in order to study the effect of the functional groups on the adsorption performance of the materials, researchers modify their surface structure by introducing [10–12] or removing [13–15] some functions. These studies are justified by the fact that the creation of surface functional groups on the activated carbon is complex, and thus the control of their creation becomes difficult.

It is not sufficient to study the effect of the activated carbon surface functional groups; particular attention should be given to understand the origin of these functions and the parameters which control their creation.

The aim of the present work is to illustrate the importance of the cooling down step after carbonization on the formation of oxygen surface groups. For this purpose, two activated carbons are elaborated with different cooling down steps. The textural and structural characterization of the two samples is performed by nitrogen adsorption isotherms and XRD analysis. The TG/MS analysis is used to understand phenomena occurring during the cooling down step.

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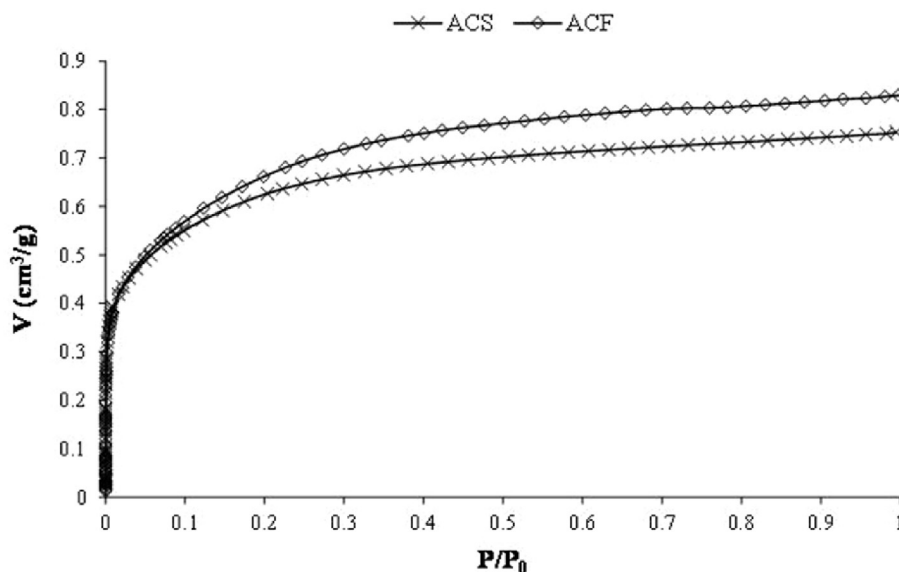


Fig. 1. Nitrogen adsorption isotherms of activated carbons at  $-196\text{ }^{\circ}\text{C}$ .

Finally, the effect of this step on the cyclohexane adsorption is studied.

## 2. Experimental

### 2.1. Activated carbon preparation

Olive waste is used as a precursor for the preparation of two activated carbons: ACS and ACF. The first step of this preparation consists in cleaning the precursor using boiling water and then distilled water. Thereafter, the olive waste is dried and sieved to a particle diameter ranging from 0.62 to 1.2 mm. A chemical activation is carried out by the addition of  $\text{ZnCl}_2$  (purity > 99%, from Biochem Chemopharma) in the ratio of 0.49 g of Zn per gram of precursor. The mixture precursor/ $\text{ZnCl}_2$  is carbonized in a tubular furnace under a controlled flow of nitrogen at  $500\text{ }^{\circ}\text{C}$  for 1 h ( $V = 10\text{ }^{\circ}\text{C}/\text{min}$ ).

The cooling down step is done differently: (i) the first sample (ACS) is slowly cooled down with a controlled rate of  $1\text{ }^{\circ}\text{C}/\text{min}$  in the same inert atmosphere until ambient temperature, (ii) the second sample (ACF) is removed from the furnace just after the carbonization and immediately set at room temperature. To ensure that the oxidation of ACF is avoided, we take care of comparing the surface properties of the so prepared sample with that cooled down by immersing the crucible in liquid nitrogen ( $\text{ACF}_{\text{LN}}$ ).

Subsequently, all samples are washed with a hydrochloric acid (HCl) solution and then with distilled water until the filtrate does not react with  $\text{AgNO}_3$ . The obtained activated carbons are dried overnight at  $105\text{ }^{\circ}\text{C}$ .

### 2.2. Experiments

#### 2.2.1. Textural characterization

Adsorption–desorption isotherms of  $\text{N}_2$  at  $-196\text{ }^{\circ}\text{C}$  are determined using an Autosorb Nova surface analyzer. Before each adsorption experiment, the samples are outgassed at  $120\text{ }^{\circ}\text{C}$  under vacuum for 24 h. The surface area is determined using the BET equation, and the total volume of pores ( $V_t$ ) is calculated at a relative pressure ( $P/P_0$ ) of 0.99. The microporous volume ( $V_{\mu}$ ) is determined using the Dubinin–Radushkevich (DR) method. The mesoporous volume ( $V_{\text{mes}}$ ) is obtained by deducing the

microporous volume from the total pore volume. The pore size distribution is calculated with the adsorption data based on the non local density functional theory (NLDFT) method using the slit shaped pore model.

#### 2.2.2. XRD analysis

The X-ray patterns of the synthesized activated carbons are recorded on a XRD diffractometer (PANalytical X'Pert PRO) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54060\text{ \AA}$ ). An X'Celerator detector is used to collect data over an angular range of  $5\text{--}60^{\circ}/2\theta$  with a step size of  $0.0170/2\theta$  and a count time of 50.1650 s for each step. The voltage is chosen to be 45 kV with a current of 40 mA. The obtained XRD patterns are analyzed to investigate the crystallographic structural changes during the cooling down step.

#### 2.2.3. FTIR spectroscopy

FTIR spectra are obtained with a FTIR-8400S Shimadzu spectrometer by averaging 60 scans in the  $4000\text{--}400\text{ cm}^{-1}$  spectral range with a resolution of  $1\text{ cm}^{-1}$ . The preparation of pressed KBr pellets is done at a sample/KBr weight ratio of 1:300. The KBr is dried overnight at  $105\text{ }^{\circ}\text{C}$ , but the two samples are analyzed without drying. The same sample weight is used in the preparation of pellets.

#### 2.2.4. Boehm's titration

Boehm's method is used to evaluate the quality and the quantity of the acidic surface groups as well as the amount of basic groups. Since the selectivity of this method is based on the value of pKa of the surface species, it is assumed that sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) neutralizes carboxylic acids, while sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) reacts with carboxylic acids and lactones, and sodium hydroxide (NaOH) reacts with all of carboxylic acids, lactones and phenols. It is also known that HCl neutralizes all surface basic groups.

**Table 1**  
Pore volumes and BET-equivalent areas of the activated carbons.

Sample	$V_t$ ( $\text{cm}^3/\text{g}$ )	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_{\mu}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{mes}}$ ( $\text{cm}^3/\text{g}$ )	Microporosity (%)
ACS	0.75	1492	0.51	0.24	68
ACF	0.83	1583	0.49	0.34	59

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