

Study of cherry stones as raw material in preparation of carbonaceous adsorbents

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Abstract

Cherry stones (CS) have been characterised in terms of chemical composition, texture, and thermal behaviour with a view to be used as a raw material in the preparation of activated carbon. Ashes obtained from CS have also been studied. CS have been heated in various atmospheres (i.e., in the atmosphere of the products released during the pyrolysis of CS, in nitrogen or in air) and the resultant products characterised as well. The study has been accomplished by means of chemical analyses, FT-IR spectroscopy, X-ray diffraction, density measurements, mercury porosimetry, scanning electron microscopy, and TG-DTG and DSC analyses. CS possess a low inorganic matter content and a high volatile matter content. Their packing density is also high. The yield of the pyrolysis process of CS in N₂ is 39.1 wt.% at 400 °C and 21.6 wt.% at 1000 °C. The chemical composition of ashes obtained from CS depends on heat treatment temperature and atmosphere. The main components are maghemite and hematites for ashes prepared at 650 °C in air and periclase for ashes heated subsequently to 950 °C in N₂. CS are an essentially macroporous material. The ash content is also relatively low in the products prepared by heat treatment of CS. Such products are microporous and macroporous solids. The surface area and microporosity develop to a larger extent in nitrogen and air. The micropores are wider in air.

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1. Introduction

Activated carbon is a porous material, widely used as adsorbent of substances from the gas and liquid phases. Since the textural properties of activated carbon depend on the starting material and the method of preparation, many natural and synthetic materials have been used as precursors of such a carbonaceous material. So far, of the raw materials used, approximately half of them are lignocellulosic ones [1]. In view of the large number of applications of activated carbon and having into account the fact that many of these applications are related to the environment, the preservation of which being of growing concern, an increase in the demand of activated carbon is predictable [2,3]. For this

reason, since a long time, new raw materials have been frequently tested for obtaining activated carbon, agricultural forest and industrial by-products being of particular interest. An agricultural residue, which is abundantly produced in Extremadura (Spain), is cherry stones (CS). These are a residual product of the industrial production of kirsch from the cherry fruit.

Cherry stones have been used previously in the preparation of activated carbon in one [4,5] or two [6] stages, which reveals the interest of this raw material to be used with such an aim. In this work, residual CS from the manufacture of kirsch are analysed from the chemical, physical, and thermal standpoints to serve as model for the study of the influence of several variables of the carbonisation and activation processes on properties of the resultant activated carbons, such as the composition and texture. Since in the physical method of preparation of activated

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carbon, the starting material is first carbonized and the product obtained is then activated in a gasifying atmosphere, usually of air, carbon dioxide or steam, the process being catalysed by inorganic impurities, ashes prepared from CS are also studied here in terms of their chemical composition and thermal behaviour. The products prepared from CS by heat treatment in the atmosphere of the pyrolysis products, N₂ or air are also characterised. The purpose of this work is to chemico-physically characterised CS and CS-derived products with a view to the use of CS as feedstock for the preparation of activated carbon.

2. Experimental

2.1. Raw material

Cherry stones were furnished by the Agrupación de Cooperativas Valle del Jerte (Valdastillas, Cáceres, Spain). The stones, as-received, were first ground and sized, the fraction of particle sizes between 1 and 2 mm being chosen. Then, the size-reduced stones were air-dried at ambient temperature.

2.2. Study of CS and ashes

2.2.1. Chemical analyses

The proximate analysis of CS was effected using a thermogravimetric method (moisture and volatile matter contents) [7], by heating at 650 °C for about 8 h until mass constancy in a muffle furnace (ash content), and by difference (carbon content). The ashing temperature was lower than the standard temperature (i.e., 815 °C for coal) as ashes obtained by burning CS at 650 °C were subsequently heated at higher temperatures in N₂, as seen below. Determinations of C, H and N were performed in a Perkin-Elmer elemental analyser, Model 240 C, and the oxygen percentage was estimated by difference.

Information on the chemical structure of CS was provided by FT-IR spectroscopy. From CS powder, a disc was prepared by mixing 0.8 mg of this material with 400 mg of KBr (Merck, for spectroscopy) in a small agate mortar, and by then pressing the resulting mixture successively at 5 and 10 tonnes cm⁻² for 5 min under vacuum. Water was removed from the disc by oven-drying at 110 °C for a longer time than 24 h. Using a Perkin-Elmer 1720 spectrometer, the FT-IR spectrum was recorded between 4000 and 450 cm⁻¹. From such a spectrum, the spectrum of a similar thickness KBr disc was subtracted.

2.2.2. Preparation and characterisation of ashes

Ashes were prepared by burning CS at 650 °C in air until mass constancy. A fraction of such ashes was subsequently heated to 950 °C in N₂ (flow rate = 200 ml min⁻¹). The elemental composition of ashes was determined using inductively coupled plasma emission spectroscopy (Mod.

Optima-3000, Perkin-Elmer). The crystalline components of CS ashes were identified by X-ray diffraction. The samples were analysed in a Philips PW-1700 powder diffractometer (40 kV, 35 mA, Cu K α). The X-ray patterns were recorded in the scan range $2\theta = 3\text{--}70^\circ$, at a scan rate of $0.2^\circ \text{ min}^{-1}$ [8].

2.2.3. Thermal characterisation

The thermal behaviours of CS to 1000 °C and of the 650 °C-ashes to 950 °C in N₂ (flow rate = 200 cm³ min⁻¹) were studied using a Mettler TA3000 system. The heating rate was 10 °C min⁻¹. Differential scanning calorimetry (DSC) was also applied to the study of CS between 30 and 600 °C. By integration of each peak in the DSC curve, the enthalpy change associated with a single stage of the pyrolysis process could be estimated.

2.2.4. Textural characterisation

Cherry stones were texturally characterised by density measurements, mercury porosimetry, and scanning electron microscopy [9]. The packing density (ρ_p), or bulk density, which is defined as the weight of one millilitre of sample, was determined by weighing a given volume of sample. The mercury density (ρ_{Hg}), or apparent density, was measured by the usual method. From a glass reservoir mercury was brought into contact with about 0.5 g of CS, after evacuation at 13.33 Pa in a Quantachrome filling apparatus. Using approximately 3 g of CS, the helium density (ρ_{He}), or true density, was determined in a Quantachrome stereopycnometer. From the values of ρ_{Hg} and ρ_{He} the total pore volume accessible to helium at room temperature (V_T) was calculated by expression $V_T = 1/\rho_{Hg} - 1/\rho_{He}$.

The mercury porosimetry experiment was performed in a Quantachrome porosimeter, Autoscan-60. The values of surface tension and contact angle used in the computational program of the porosimeter were 0.480 N m⁻¹ and 140°, respectively. The cumulative pore volume of macro- and mesopores ($V_{me + ma}$) was derived at the pore radius of ca. 1 nm. The macropore volume (V_{ma}) was regarded as being equal to the cumulative pore volume at the pore radius of 25 nm. The mesopore volume (V_{me}) was calculated by subtraction of V_{ma} from $V_{me + ma}$. Mercury porosimetry also enabled one to derive a pore size distribution of CS in the macropore and mesopore ranges.

The SEM micrograph of CS was obtained by means of a Jeol 5400 scanning microscope.

2.3. Heat treatments of CS

The heat treatments of CS were carried out in a vertical cylindrical furnace, using a stainless steel reactor provided with gas outlet and inlet and a temperature/time programmer. The device is schematised in Fig. 1. Samples of about 100 g of CS were heated from room temperature to 600 °C in the atmosphere of the products released as a result of the pyrolysis of CS, nitrogen (flow rate = 200 cm³ min⁻¹), or air (flow rate = 200 cm³ min⁻¹). The heating rate was

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