



Research article

Superactivated carbons by CO₂ activation of loquat stonesM. Plaza-Recobert^a, G. Trautwein^a, M. Pérez-Cadenas^b, J. Alcañiz-Monge^{a,*}^a Grupo de Materiales Carbonosos y Medio Ambiente, Dpto. Química Inorgánica Facultad de Ciencias, Universidad de Alicante, Ap. 99, E-03080 Alicante, Spain^b Dpto. Química Inorgánica y Química Técnica, Facultad de Ciencias, UNED, Senda del Rey 9, E-28040 Madrid, Spain

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ABSTRACT

This work presents CO₂ activation approach towards controlled preparation of superactivated carbons (SAC) from a new lignocellulosic residue: loquat stones. This study demonstrates the potential use of loquat stones as a precursor in the preparation of SAC, reaching maximum BET surface area 3500 m²/g and total micropore volume 1.84 cm³/g. Studies on CO₂ activation at different temperatures reveal two interesting results: 1) Loquat stones can be activated at high temperatures, up to 1100 °C, achieving similar volumes of porosity with short maintenance times (30 min). 2) The greater facility for eliminating mineral matter content of the loquat stones, as well as the scarce presence of K in its composition.

The high volumes both of total and narrow microporosity that are obtained in the activation of carbonized loquat stones can be explained both by the traces of mineral matter that they contain and the carbonaceous microstructure of its carbonized state.

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1. Introduction

One of the most important characteristics of activated carbons (CA) is their specific micropore volume and their specific surface area. In general it is easy to synthesize CA with specific volumes around 0.6 cm³·g⁻¹ and BET specific surface areas around 1500 m²·g⁻¹ using any carbon precursor and preparation method [1]. However, in the last decade, in many of their applications, like gas storage, electrochemical supercapacitors and the removal of pollutants, there is an increasing demand for the synthesis of CA with high specific micropore volume and specific BET surface areas larger than 2500 m²·g⁻¹. These have been called superactivated carbons (SAC) [2]. Most of the SAC have been obtained through chemical activation with KOH from petroleum coke [2–5]. Thus in 1978 Wennerberg and O'Grady (from the Amoco company) synthesized, on a small scale, SAC called PX21 of 3700 m²·g⁻¹ BET and a total specific volume of microporosity of 1.75 cm³·g⁻¹. Later on, using the procedure developed in Amoco, SAC have been marketed by the Anderson Development Company (AX-21 of BET 2800–3500 m²·g⁻¹ and Vmicro 1.4–2.0 cm³·g⁻¹) and Kansai Coke and Chemicals (Maxsorb-31, BET 3200 m²·g⁻¹ and Vmicro 1.8 cm³·g⁻¹). More recently, with the same aim, SAC with BET specific surface areas of around 3200 m²·g⁻¹ have been developed from carbonized material obtained from metal carbides [6], or carbonized material obtained using zeolites as templates [7,8].

Although lignocellulosic precursor are widely used to produce AC, their application to obtain SCA has been scarcely analyzed in the

literature, thus, almost all the published studies related with the synthesis of AC overlook this possibility. This is due to it is difficult to obtain SCA starting from these precursors. In recent studies our group has prepared activated carbon from lignocellulosic precursors by CO₂ activation, where it has been shown that loquat stones could be used to obtain AC with BET surface areas of 3100 m²·g⁻¹ [9]. The present work deals with studying the activation of this precursor which hardly figures in the literature, focusing on the possibility of obtaining SAC with a simple process: precursor, a lignocellulosic material, and activation process, activation with CO₂.

2. Materials and methods

2.1. Materials

In this study Japanese loquat stones were extracted from the Algeria variety of the fruit which came from a plantation in Partida de Algar (Callosa d'Ensarrià, Spain). They were washed by agitation (at a speed of 200 rpm for 120 min) to completely remove all the fruit pulp. They were subsequently ground in a propeller grinder to a very fine powder (100 mesh). 10 g of powdered loquat stone was then washed for 24 h with agitation (120 rpm) in an 150 cm³ aqueous solution of H₂SO₄ (10% vol.), thus eliminating the mineral matter from the loquat stone. The washed solution was filtered, the solid paste was washed repeatedly with distilled water until the washing water had a neutral pH. The paste was subsequently dried in a drying oven at 100 °C. Similar treatments have been done with other lignocellulosic precursors: walnut shells, almond shells, coconut shells and cocoa bean husk.

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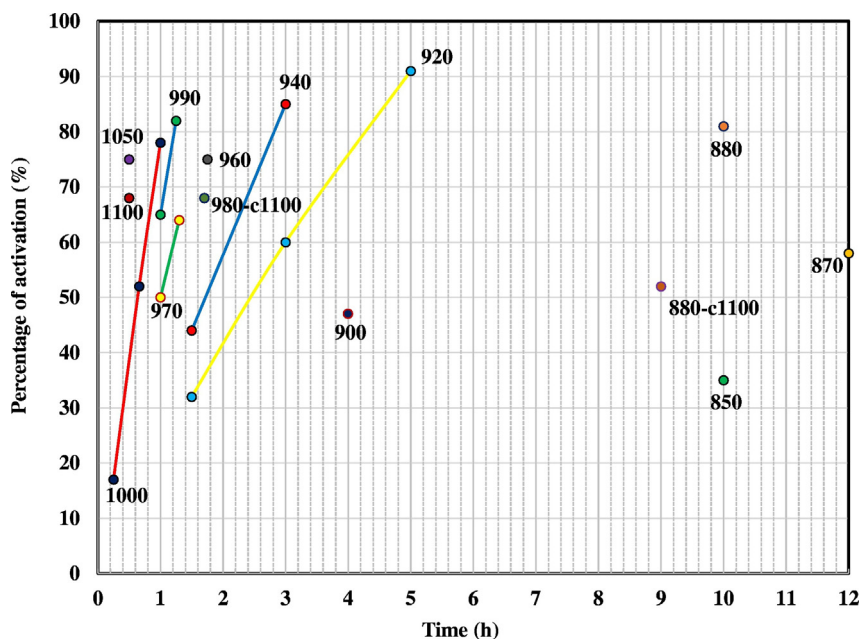


Fig. 1. Evolution of the percentage of activation with time for CO₂ activation at different temperatures (indicated as number) of carbonized loquat stones at 1000, 1050 and 1100 °C (indicated as -c1100 for activations at 880 and 980 °C). Samples activated at the same temperature are connected by a line.

The washed and dried powdered loquat stones (0.5 g) were carbonized in a tube furnace (Ø 6 cm, L 150 cm) in an inert atmosphere (He 100 cm³/min) up to 1000 °C, at a heating rate of 10 °C/min, and kept at the maximum carbonization temperature for 30 min. Some carbonized samples at 1000 °C were also subjected to a second carbonization procedure at 1050 and 1100 °C under He flow (100 cm³/min) for 30 min.

The carbonized matter (N) was activated in a tube furnace at a range of temperatures between 850 and 1100 °C. All the samples were given the following thermal treatment: 0.5 g of carbonized matter were heated in He 100 cm³/min until reaching the temperature of activation, and then changed to a current of CO₂ 100 cm³/min for different maintenance times (from 15 min to 10 h), at the end of which period they were cooled in an oven in a current of He. The activation percentage (BO) was determined by mass balance.

Activated carbon was also prepared in large quantities in a single carbonization-activation batch. About 7.5 g of washed loquat stones were carbonized in this process, after being maintained 30 min at a temperature of 1000 °C (He 150 cm³/min), the temperature was then adjusted to that of activation (990 °C and 920 °C), and there was a change to a flow of CO₂ (150 cm³/min) maintained for different time periods (3–9 h).

The nomenclature for the activated carbonized loquat stones (N) at 1000 °C included two/three numbers at the beginning which indicate the temperature of activation and two at the end which indicate the BO (i.e. 99 N65, a sample activated at 990 °C with 65% BO); the samples carbonized at 1100 and 1050 °C are marked with a **t** at the end. The samples made in large quantities have a letter **g** at the end.

2.2. Characterization

The ash content (related with the mineral matter) in the washed lignocellulosic precursors was determined using thermogravimetric experiments (TA Instruments, SDT 2960). 10 mg of carbonized matter were given a thermal treatment in an atmosphere of He (60 cm³/min) at 20 °C/min up to 950 °C, and once this temperature was reached, the gas flow was changed to synthetic air maintaining the temperature for some 60 min.

The carbonized and activated material were analyzed using Transmission by Electron Microscopy (TEM: JEOL; JEM-2010) and x-ray

powder diffraction (Seifert diffractometer JSO Debye-Flex 2002, with Cu K_α radiation).

The analysis of the porous texture was carried out by N₂ adsorption at −196 °C and CO₂ adsorption at 0 °C. Adsorption isotherms were determined using an Autosorb 6 equipment. The samples were degassed at 250 °C under vacuum (1 Pa) (4 h). The distribution of specific pore volumes was calculated as follows [10]: i) the volume of narrow micropores (pore size < 0.7 nm) was calculated by applying the Dubinin-Radushkevich (DR) equation to the CO₂ adsorption data at relative pressures < 0.015; ii) the total micropore volume (pore size < 2 nm), which includes the volume of the narrow micropores and of supermicropores, was calculated by applying the DR equation to the N₂ adsorption data at relative pressures < 0.14. The total pore volume V_{total} was calculated using the amount of N₂ adsorbed at P/P₀ 0.98. The specific surface

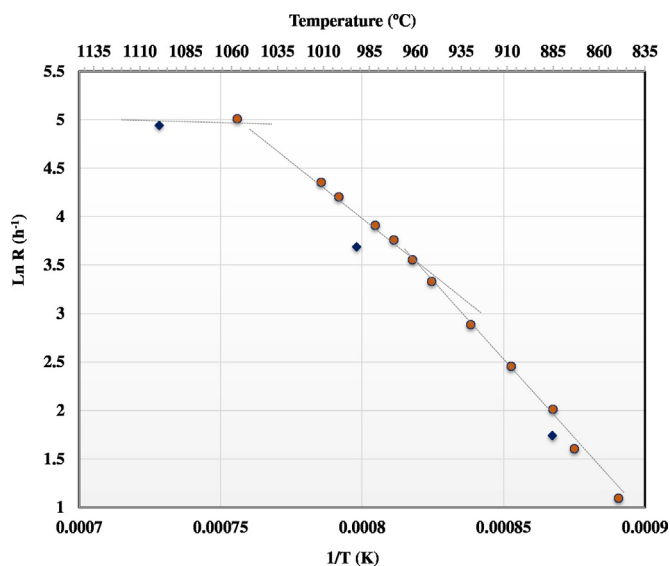


Fig. 2. Arrhenius representation of the data from CO₂ activation of loquat stones performed at different temperatures. Circles carbonized samples at 1000 °C and rhombi carbonized samples at 1100 °C.

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