



Preparation of granular activated carbons from grape seeds by cycles of liquid phase oxidation and thermal desorption



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ABSTRACT

Activation of grape seed char upon successive cycles of liquid phase oxidation followed by high temperature desorption permits a tailored development of porosity. In this work three different oxidants (HNO_3 , H_2O_2 , and $(\text{NH}_4)_2\text{S}_2\text{O}_8$), have been tested and the desorption temperature has been varied within 850–950 °C upon 10 activation cycles. A high increase of BET surface area was observed in the first five cycles with HNO_3 as oxidizing agent giving rise to values higher than 1200 $\text{m}^2 \text{g}^{-1}$ at around 50% burn-off. Activation with H_2O_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ led to a significantly lower development of surface area, with 600 and 800 $\text{m}^2 \text{g}^{-1}$ respectively at that burn-off. The analysis of the pore size distribution showed that porosity was generated through the creation of new micropores and widening of existing ones upon activation with HNO_3 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$, whereas H_2O_2 mostly led to the widening of the narrow micropores already existing in the starting char. The activated carbons obtained are essentially microporous, with some small contribution of mesoporosity in the HNO_3 series ($V_{\text{micro}} = 0.69 \text{ cm}^3 \text{ g}^{-1}$; $V_{\text{meso}} = 0.07 \text{ cm}^3 \text{ g}^{-1}$). SEM images showed that the activated carbons maintained the granular morphology of the seeds after 10 cycles showing a hollow core structure with a wall thickness of about 200 μm .

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1. Introduction

Activation by cyclic oxygen chemisorption–desorption allows the preparation of porous carbons with tailored development of porosity for targeted applications [1,3]. The method consists of an oxidation stage under conditions that promote oxygen uptake by chemisorption, usually at relatively low temperature, followed by desorption in an inert atmosphere at high temperature [4]. This chemisorption step permits a better control of porosity development while the desorption step involves partial gasification of carbon, thus leading to burn-off. The sequence can be repeated until convenient porosity development is achieved. This method provides an efficient way to create porosity from a precursor and to controllably modify the porous structure of a carbonaceous material while maintaining the physical integrity of the particle [5].

We have used cyclic activation of grape seed char with oxygen as oxidizing agent in previous works [5] with interesting and promising results. The best results were obtained at chemisorption temperatures between 200 and 300 °C. Depending on the chemisorption and desorption temperature the burn-off per cycle ranged between 0.4 and 9.0%. Activated carbons with BET surface areas up to 1300 $\text{m}^2 \text{g}^{-1}$ were obtained while maintaining the granular morphology of the precursor even after ten activation cycles. The activated carbons prepared by this procedure were essentially microporous materials. In a former work

[6] we reported that the preparation of activated carbons from waste tire char upon successive cycles of oxidation–desorption using nitric acid, hydrogen peroxide and ammonium persulphate as oxidizing agents in liquid phase led to different patterns in burn-off and porosity development ($\text{HNO}_3 > \text{H}_2\text{O}_2 > (\text{NH}_4)_2\text{S}_2\text{O}_8$). The activated carbons obtained in general showed a well developed mesoporosity. Other authors [7] used the cyclic activation with liquid phase oxidation with H_2O_2 at high pressure and further heat-treatment at 900 °C in inert atmosphere to obtain microporous activated carbons from sucrose and cellulose with surface areas of 950–1600 $\text{m}^2 \text{g}^{-1}$ (DR method from N_2 isotherms) and burn-offs ranging between 18 and 39%, concluding that the method provides materials with suitable textural properties for application in electrochemical capacitors.

The results above indicate the potential of liquid phase oxidation to tune the porosity development in cyclic activation, although the starting material may also be an important factor. In general, liquid phase oxidation is used to modify the surface chemical composition (creating oxygenated functional groups) [6–10] and the porosity of carbon materials, being the oxidants most commonly used nitric acid, hydrogen peroxide or ammonium persulphate [6–17]. Liquid phase oxidation has been mainly used for the modification of commercial activated carbons [6–10] and own-made activated carbon from biomass precursors [11–17]. The extent of the textural changes depends on both the structure of the starting activated carbon and the oxidation treatment. In general, the extent of oxidation follows the order is $\text{HNO}_3 > \text{H}_2\text{O}_2 > (\text{NH}_4)_2\text{S}_2\text{O}_8$ [6,9,11,17]. The higher oxidizing action of HNO_3 is attributed to higher fluidity and greater diffusion in the pores of the activated

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carbon [14]. In contrast, H_2O_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ suffer from decomposition in aqueous solution and a larger molecular size, which confers a different oxidizing action [14]. In all cases, after oxidation, a decrease in surface area and pore volume of activated carbons is reported, generally explained by the restriction of the pore volume available for N_2 adsorption due to the formation of oxygen-containing groups at the entrance and/or on the walls of micropores and by the destruction of the pore walls and its collapse when oxygenated terminal groups are created. That is especially the case for HNO_3 oxidation treatment which provokes a severe damage of pore walls [9,11–13,16].

Liquid phase oxidation of activated carbons also leads to the formation of various functional groups common for the three oxidants such as carboxylic, lactonic, phenolic and carbonyl groups. But the intensity of IR absorption peaks is modified depending of the oxidizing agent, being that effect more important for nitric acid oxidation [9–14,16,17].

Depending on the ability of the oxidizing agent to diffuse into the carbon pores, the surface groups introduced seem to be preferentially located on the external or non-microporous surface upon oxidation with H_2O_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ while nitric acid oxidation creates more oxygen complexes on the internal surface of the carbon particles [9,12,16,17]. This could be linked to a higher erosion of the particle surface that facilitates the access of nitric acid [11,12,17].

The aim of this work is to explore the preparation of activated carbon from grape seed char by cyclic liquid phase oxidation and desorption. The influence of the type of oxidizing agent, the desorption temperature and the number of cycles applied is studied in order to achieve a convenient development of porosity at low burn-off, so that the morphology of the char is preserved as well as its physical integrity.

2. Materials and methods

The raw material used in this study consisted of seeds collected from grapes of the red variety “Tinta de Toro” harvested for red wine manufacture in Toro (Zamora, Spain). The seeds were washed, dried and then extracted with hexane to remove essential oil before pyrolysis [18]. The oil content of grape seeds depends on the grape variety, though usually ranges around 10–16 wt.% on a dry basis [19]. In our case it amounted 9%. The char used as starting material was obtained by flash pyrolysis of the extracted seeds at 800 °C, as reported in a previous work [18]. The char yield was 34% of the extracted seeds' weight on a dry basis.

2.1. Sample characterization

Surface area and total pore volume of the carbon samples were measured in an automated volumetric gas adsorption Micromeritics apparatus (Tristar 3020) by adsorption of N_2 at 77 K, and CO_2 at 273 K. Approximately 0.15 g of sample was used in each test which was placed in a glass container and degassed at 150 °C for 7 h at atmospheric pressure prior to the adsorption measurements, using a Micromeritics sample degas system (VacPrep 061). Samples were kept in dry atmosphere immediately after pyrolysis and activation. The apparent surface area was calculated from the N_2 isotherm using the Brunauer–Emmett–Teller (BET) equation (S_{BET}) [20], the t-method was used for the micropore volume and BJH method was used to obtain the narrow and total mesopore volume and the mean mesopore size, whereas Dubinin–Astakhov (DA) model (with an equation exponent value of 2) was applied to the CO_2 isotherms obtained in the 10^{-5} –0.03 P/P₀ range, to determine the DA surface area (S_{DA}) and micropore volume [21]. The area S_{DA} was used here as an apparent surface area for comparative purposes since it is based on volume filling. Mercury intrusion porosimetry was used to determine the macropore volume (V_{macro}). The non-local density functional theory (NLDFT) method was used to calculate the pore size distribution [22].

Fourier transform infrared spectroscopy (FTIR) was used to characterize the main functional groups of the activated carbon surface using

a spectrometer FTIR Bruker IFS66v connected to a MCT detector whose spectral measurement range goes from 7000 to 550 cm^{-1} .

The morphology of grape seed char and activated carbons was analyzed by Scanning Electron Microscopy (SEM), using a Hitachi S-3000N apparatus. The specimens for SEM observation were metalized with gold to prevent electrical charging during examination using a Sputter Coater SC502. Imaging was done in the high vacuum mode under an accelerating voltage of 20 kV, using secondary electrons.

2.2. Cyclic activation

The procedure followed for the oxidation step was different depending on the oxidizing agent. Oxidation with 30% HNO_3 was carried out by boiling under reflux for 20 min. Oxidation with 30% H_2O_2 and 1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was performed at 20 °C for 24 h under stirring. After oxidation the samples were washed with distilled water until neutrality and dried in a muffle at 105 °C. These conditions are reported in the literature as commonly used to effectively oxidize the surface of carbons for different applications [7,12].

The desorption step was carried out in a vertical quartz tube (70 cm length and 3.5 cm internal diameter) placed in a clam-shell electrical furnace at 850 °C and 950 °C for 2 h using a flow rate of 100 mL min^{-1} of nitrogen and a heating rate of 10 °C min^{-1} . These desorption conditions were established according to previous works [2,4,5]. After each activation cycle the reactor was cooled under nitrogen flow, the activated carbon was collected, and the yield and textural properties were determined before starting a new cycle.

The activated carbons were designated by the activating agent, desorption temperature and the number of cycles applied, e.g. for sample H_2O_2 -850 C1, oxidation was carried out with H_2O_2 at 850 °C desorption temperature and 1 activation cycle was completed.

3. Results and discussion

Under all the combinations of oxidizing agent and desorption temperature tested, the burn-off increased almost linearly with the number of activation cycles applied (Fig. 1). Likewise, burn-off showed, as a general trend, an increase with desorption temperature. The highest burn-off values were observed for the activated carbon series prepared with HNO_3 , and the lowest for the H_2O_2 one.

The nitrogen adsorption–desorption isotherms of the starting char and the activated carbons resulting after five activation cycles are shown in Fig. 2. The activated carbons yielded isotherms representative of essentially microporous solids with low contribution of mesoporosity, which increases for the samples with higher burn-off as suggested by a

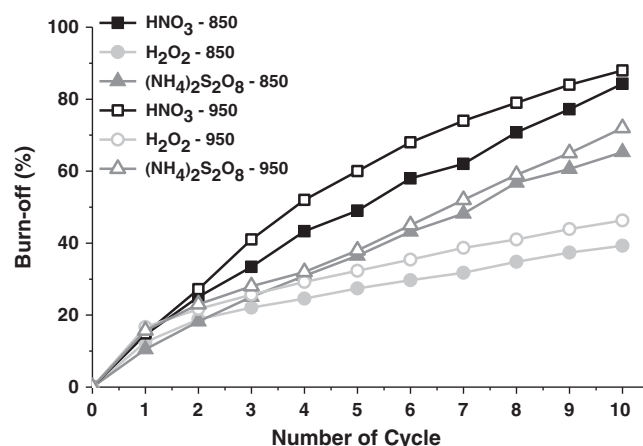


Fig. 1. Burn-off vs number of activation cycles with different oxidizing agents and desorption temperatures.

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