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Preparation and characteristics of activated carbon from olive stones and walnut shells

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Abstract

The preparation of activated carbon from agricultural waste could increase economic return and reduce pollution. Activated carbon has been processed from different types of agricultural material, such as olive stone, acorn, pecan, walnut shells, and stone fruits. The objectives of this study were to prepare and to characterize activated carbon from two abundant waste material produced in Argentina. Activated carbon was made from olive pits (OP) and walnut shells (WS) by treatment with 50 and 75% (w/w) of KOH. The two types of activated carbon obtained were evaluated by iodine adsorption. The characterization of surface carbons was performed by scanning electron microscopy (SEM). Activated carbon yields from OP was higher than WS. The highest carbon yields were obtained with 75% KOH concentration in both OP and WS. The characteristics of the starting materials, the activating agent concentration, and the carbon particle size influenced the iodine adsorption capacity. Adsorptive properties were highest in the OP powdered carbon obtained at 75% KOH concentration. The WS-activated carbon had macrocroporous structures with a pore size distribution more homogeneous than OP.

Keywords: Activated carbon; Olive; Walnut shells

1. Introduction

The commercial production of olive (*Olea europea* L.) and walnut (*Junglans regia* L.) in Argentina are two important agricultural activities, especially, in semiarid regions that are considered marginal areas for conventional crops. Unfortunately, the agricultural and industrial activities derived from such crops generate waste that constitutes a serious environmental problem. Some agricultural byproducts, such as those derived from the walnut and olive industries have been used as precursors for the preparation of activated carbon (Plaza de los Reyes et al., 1997; Lafi, 2001; Aygün et al., 2003; Ng et al., 2003). In addition to removal of polluting waste materials, the preparation of activated carbon from such agricultural by-products

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would also include economic gains for products manufactured from the abundant waste sources.

Although activated carbon was the first recognized absorbent and is still widely used in industry, the development of appropriate methods to make them and the understanding of their porous structure still continue.

The general process to produce activated carbon is based on carbonizing and activating the original carbonaceous material. Activation may be achieved either physically or chemically (Rodríguez-Reinoso and Molina-Sabio, 1992). A typical physical method consists in a thermal treatment that is carried out in two stages: (1) carbonization of the precursor and (2) controlled gasification (steam flow, temperature, heating rate, etc.) of the crude char (González et al., 1994). In the chemical method, the starting material is impregnated with a chemical agent, acid or base, and the blend is heated to a temperature of 450–700 °C. Chemical activation reduces the formation of tar and other byproducts, thereby increasing carbon yield (González-Serrano et al., 1997; Evans et al., 1999). The type and the amount of the chemical agents used are important to enhance the quality and quantity of the activated carbon obtained.

The objective of this work was to investigate the effect of two different concentrations of potassium hydroxide on carbon yield and porosity of activated carbons obtained from walnut shell and olive stone. In addition, the influence of particle size on decolorant capacity was also determined.

2. Experimental

Walnut shells were obtained from El Rodeo, Catamarca province, Argentina. Olive stones were obtained from the Cruz del Eje location, Córdoba province, Argentina. The starting materials were manually chosen, cleaned with deionized water, dried at 100 °C, and ground with a roller mill to obtain samples of 1–3 mm particle size. The samples were carbonized separately in a muffle furnace heated from room temperature to 600 °C (1 h) under a constant flowing nitrogen atmosphere. The chars obtained were cooled at room temperature and the weight losses due to carbonization were determined. Chemical activation was carried out using potassium hydroxide at two different concentrations (50 and 75%, w/w), at a ratio of 1:1 (KOH solution/char, w/w). This ratio was selected from previous investigations (Hu and Vansant, 1995; Martínez et al., 2003), which showed that the adsorption capacity increases remarkably with increasing KOH/char ratio up to 1:1. After the char was mixed with the KOH solution, the mixture was dehydrated at 300 °C for 3 h and immediately activated at 900 °C in nitrogen atmosphere for 1 h. The activated carbons obtained in a granular form (1–2 mm particle size) were thoroughly washed with deionized water, dried at 100 °C for 2 h, cooled at room temperature, and stored in hermetic–sealed containers for analyses.

Scanning electron micrographs of the activated carbons were recorded by the Philips 501 B scaning electron microscope (Eindhoven, The Netherlands).

The adsorption capacity was measured according to the ASTM D 4607-94 (1999) specifications. To measure the adsorption capacity of the activated carbons in a powdered form, the granular samples were pulverized manually in a mortar. Powdered activated carbons were <0.05 mm.

Adsorption capacities of the different samples were compared with a commercial charcoal (Mallinckrodt) obtained by a steam activation process.

3. Results and discussion

The results of the weight losses due to carbonization and activation processes are summarized in Table 1. Most of the weight losses were due to carbonization. However, losses during carbonization were somewhat lower than those reported in the literature (González et al., 1994; El-Sheikh et al., 2003).

The characteristics of the starting material affected the carbon yield determined as a percentage of the original mass. The amount of KOH (50 and 75%) used affected the carbon yield. In both WSC and OPC, the highest yields were obtained at 75% KOH concentration. A 25% increase in KOH concentration resulted in increased carbon yields of 102% for WSC and 55.2% for OPC.

Iodine adsorption capacity was affected by the characteristics of the raw materials, by the changes in the concentration of the activating agent, and by the particle size of the activated carbons. In general, the olive stone activated carbon was more effective in their iodine

Table 1
Sample identification, percentage weight losses, and activated carbon yields of walnut shell (WCS) and olive pit (OPC)

Sample	Carbonizaton (% weight loss)[a]	[KOH][b]	Activation (% weight loss)[a]	Carbon yield (%)[a]
WSC	77.60 ± 1.64	50	90.37 ± 1.19	9.63 ± 0.08
		75	80.55 ± 1.01	19.45 ± 0.19
OPC	74.85 ± 2.05	50	86.98 ± 1.06	13.02 ± 0.15
		75	79.79 ± 0.97	20.21 ± 0.20

Mean values ± standard deviations, $n = 3$.
[a] Refers to weight of starting material.
[b] KOH concentration (%, w/w); KOH solution/char ratio, 1:1 (w/w).

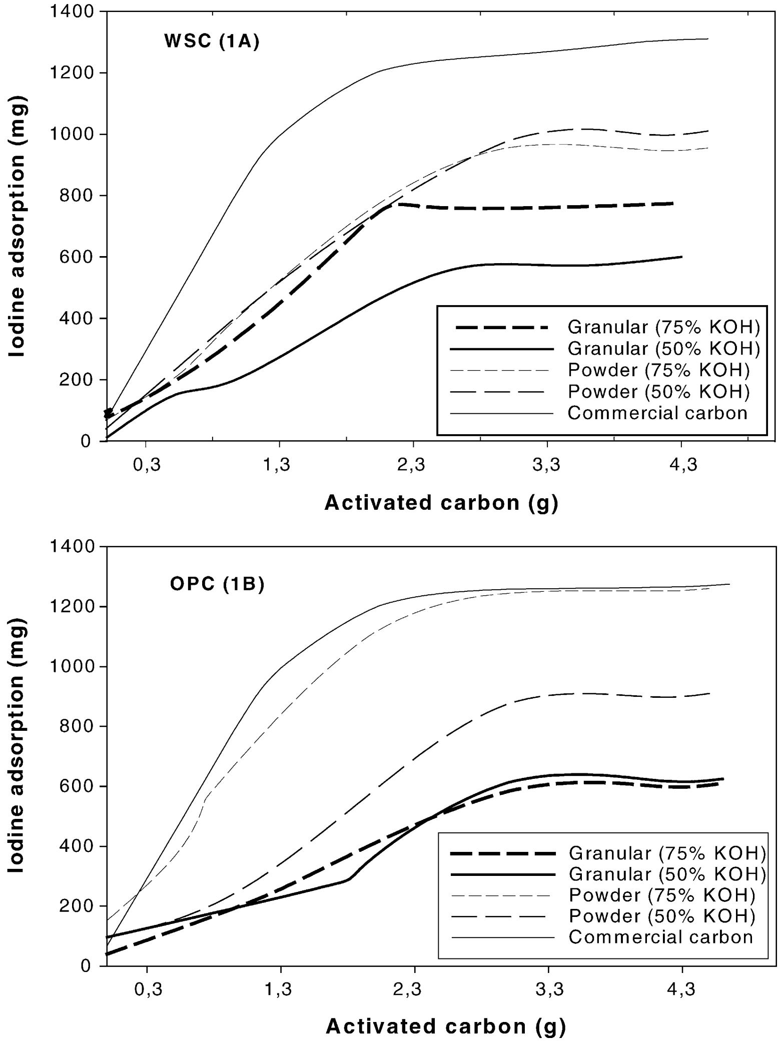

Fig. 1. Iodine adsorption capacities of: (A) walnut shell carbons (WSC) and (B) olive pit carbons (OPC).

adsorption capacity than walnut shell, although these results were dependent on the carbon particle size. Particle size reduction (powdered carbon versus granular carbon) increased iodine adsorption capacity. This fact was noteworthy for OPC, where powdered carbon obtained at a 75% KOH concentration had an adsorption isotherm similar to commercial carbon (Fig. 1A and B).

According to Galiatsatou et al. (2001), the pores of activated carbons are classified into three groups depending on pore width (pw): micropores (pw < 20 Å); transitional mesopores (20 Å < pw < 500 Å); macropores (pw > 500 Å). During adsorption, macro- and mesopores allow rapid transport of the adsorbate into the interior of the carbon for subsequent diffusion into the micropore volume. Consequently, a well-developed porous network in all pore size ranges results in improved adsorption properties of the carbon.

Scanning electron microscopy (SEM) showed that carbon texture and development of porosity was

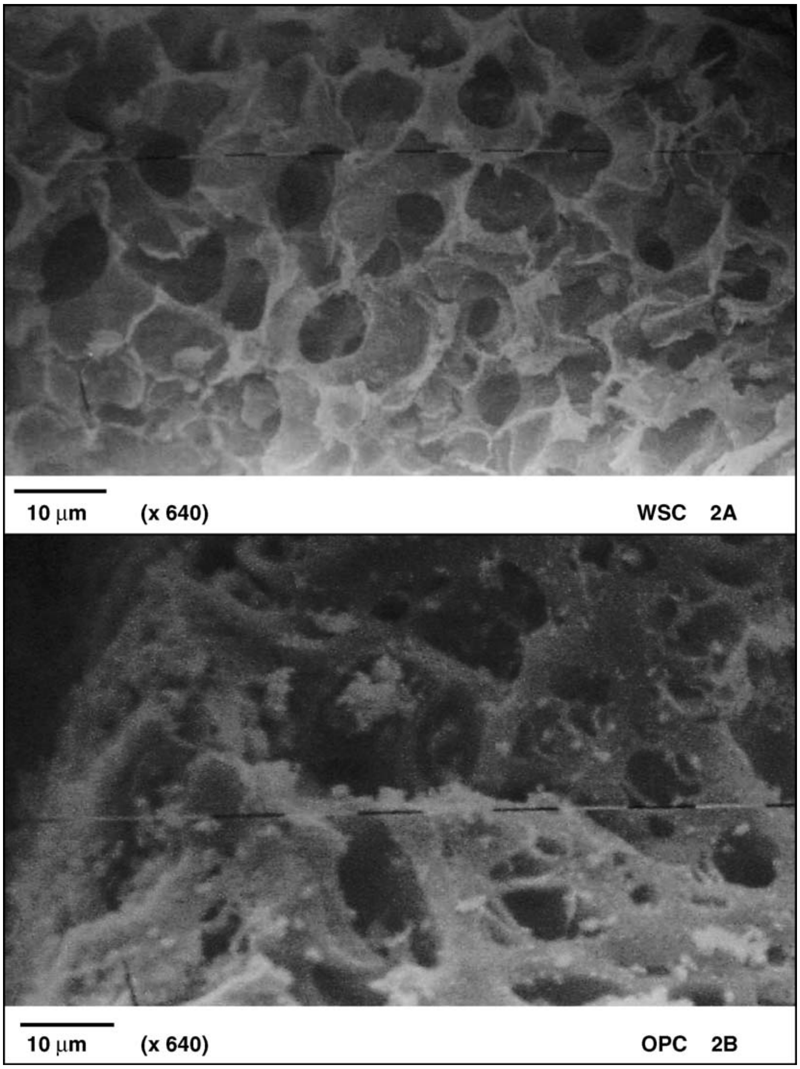

Fig. 2. Scanning electronic microscopy of: (A) walnut shell (WSC) and (B) olive pit (OPC) granular carbons prepared by activation with 50% (w/w) of KOH.

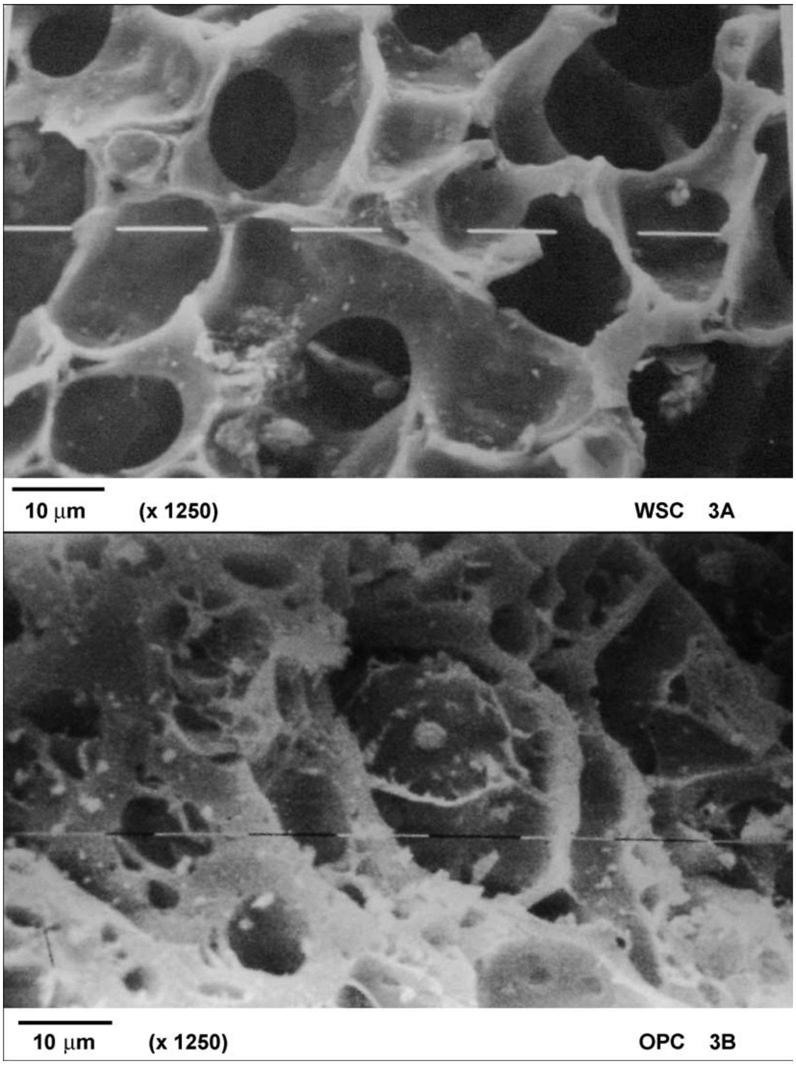

Fig. 3. Scanning electronic microscopy of: (A) walnut shell (WSC) and (B) olive pit (OPC) granular carbons prepared by activation with 75% (w/w) of KOH.

strongly affected by characteristics of the starting materials. Carbons obtained from walnut shells had an homogeneous structure with a predominance of macropores with an average 12 µm diameter. OPC-activated carbon gave rougher textures with heterogeneous surfaces and a greater variety of randomly distributed pore size. A comparison between OPC and WSC obtained at different KOH concentrations did not show major differences in their external surface characteristics (Figs. 2A, B and 3A, B.

4. Conclusions

The activated carbons prepared from walnut shells and olive stones differed in their microscopic characteristics and adsorptive properties. Most of this variation seems to be due to the properties of the starting material, but KOH concentration used for activation and particle size of the carbons obtained can also modify the adsorption capacity of the products.

The concentration of the activating agent used exerted a large effect on iodine adsorption capacity especially, in powdered olive stone activated carbon. Samples of powdered OPC activated at 75% KOH concentration had the best iodine adsorptive properties. The behaviour of these materials seems to be determined by their external surface texture. However, increasing KOH amount used for activation may contribute to the development of internal microporous cavities resulting in an increased surface area that is considered to be most important factor for adsorption (Hu and Vansant, 1995; El-Sheikh et al., 2003). The enhancement in adsorption capacity by reduction in particle size may also be due to an increase in surface area. All these treatments should be considered to improve the adsorptive properties of any activated carbon for iodine molecules or similar adsorbates.

Acknowledgements

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