MAKING AND SOME PROPERTIES OF ACTIVATED CARBON PRODUCED FROM AGRICULTURAL INDUSTRIAL RESIDUES FROM ARGENTINA

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Received August 21, 2003. Accepted in Final Form: September 4, 2003

Abstract

The objectives of this work were to develop a modified method to produce activated carbon from walnut shell and to compare their main physical and morphological characteristics with the activated carbon obtained from peach stone. Walnut shells and peach stones were carbonized in an inert atmosphere and then the char was mixed with a solution of potassium hydroxide. The mixture was then activated thermally in a nitrogen atmosphere and finally washed and dried to obtain the activated carbon. The internal structure of the activated carbon was analyzed with scanning electronic microscopy (SEM) and the adsorption capacity of each carbon was determined according to the ASTM specifications (American Society for Testing and Materials). The activated carbon obtained from the walnut shell showed a heterogeneous carbonaceous structure compared to the activated carbon from the peach stone and an adsorption capacity 48% less.

Resumen

Los objetivos del trabajo fueron, por una parte, desarrollar un método para producir carbón activado a partir de la cáscara de nuez y, por otra, comparar sus principales características físicas y morfológicas con el carbón obtenido de carozos de durazno. Las cáscaras y carozos de los materiales mencionados anteriormente fueron carbonizados en atmósfera libre de oxígeno y posteriormente se mezclaron con una solución de hidróxido de potasio. La mezcla se activó a 900ºC en atmósfera de nitrógeno y, finalmente, se lavó y secó para obtener el producto terminado. Sobre este último, se realizaron observaciones de la estructura interna y se registraron mediante microfotografías SEM. Posteriormente se determinó la capacidad de adsorción de cada uno de los materiales de acuerdo a normas ASTM (American Society for Testing and Materials). El carbón activado obtenido de cáscara de nuez presentó una estructura carbonosa heterogénea comparada con la del carbón obtenido de carozos de durazno y una capacidad de adsorción 48% menor.

Introduction

Waste matters from the agricultural and food industries constitute an environmental problem that needs to be studied, e.g., the situation of walnut production. In Argentina, the major concentration of walnut production is located in the provinces of La Rioja and Catamarca being the latter the most important one. The national walnut production oscillates between 6000 and 7000 tons per year [1]. The walnut shell represents 67% of the total weight of the fruit. If the 70% of the production is employed to obtain unshelled walnut, the process generates more than 2800 tons of shell. On account of the success in the cultivation of new walnut trees, mainly of Californian varieties, the waste matter will be greater in a near future [2].

Carbonaceous adsorbents have been found to be particularly useful due to their good kinetic properties and high adsorption capacities (milligrams of adsorbate retained per gram of carbon). Thus, they can adsorb different sort of substances from gaseous or liquid phases. Therefore, activated carbons are widely used in many fields, e.g., water and air purification, separation of industrial gases, off-gas cleaning in pharmaceutical and food industry, discoloring pharmaceuticals, as well as in making oral carbon tablets, and antidotes raw materials [3 - 6].

General process to produce activated carbon is based on carbonizing and activating the starting carbonaceous material. The activation methods can be physical or chemical. Physical methods consist basically in a thermal treatment, which occurs in two stages: carbonization of the precursor and controlled gasification or activation of the crude char. In the former, elements such as hydrogen and oxygen are eliminated from the precursor to produce a carbon skeleton possessing a latent pore structure (crude char). During gasification the crude char is exposed to an oxidizing atmosphere that increases the pore volume and surface area of the product. A typical physical method yields 30-35 % of activated carbon (based on weight of starting material) [7 - 13].

In the chemical method, the starting material is impregnated with an agent and the blend is heated to a temperature of 450 – 700ºC. Chemical activation reduces the formation of tar and other by-products, thereby increasing carbon yield [7 - 13]. Lane and Yunes [14] reported a physical method to obtain a hydrophobic microporous activated carbon from coconut shell, with micropores smaller than 7 Å. The process was followed at 800ºC in presence of steam. At lower temperature (450ºC) and using a chemical agent (phosphoric acid) they obtained a hydrophobic carbon with pores greater than 20 Å.

Traditional activated carbons possess a wide range of pore size, typically from 2 to 2000 Å. Although, they have a large surface area, the adsorption selectivity is limited because it is based on the shape and size of molecules. An increase in selectivity, and hence a narrower pore size distribution is highly desirable for separation purposes. This can be achieved by tailoring the preparation conditions. The products obtained behave as molecular sieves and are referred to as carbon molecular sieves [15].

This work had as a primary objective to obtain activated carbon from walnut shell and peach stone and to analyze their internal structure through scanning electronic microscopy (SEM). Moreover, it was proposed to determine the pore size of each type of carbon and to measure their iodine adsorption capacity.

Experimental

Clean walnut shells and peach stones were used as starting materials and manually chosen and grinded with a roller mill. The product was passed through sieves to obtain three samples with different particle size: from 1 to 2 mm (sample 1), from 0.5 to 1 mm (sample 2) and minor than 0.5 mm (sample 3). The samples were carbonized separately in a muffle furnace in nitrogen atmosphere at 600ºC during 1 h. These conditions were selected from the literature [16 – 20] and previous experiments in our laboratory. Samples 2 and 3 were incinerated completely, thereby they were discarded. The char obtained from sample 1 was cooled at room temperature and then mixed with a solution of potassium hydroxide (50%, W/W), in a ratio of 1:1 (KOH solution /char, W/W). This ratio was selected from published data [15], which show that the adsorption capacity increases remarkably with increasing KOH/char ratio up to 1:1. The mixture was dehydrated at 300ºC for 3 h and subsequently activated at 900ºC in absence of air during 1 h. These conditions were used by Hu and Vansant [15] that reported that higher temperatures (900ºC) favor the production of an adsorbent with larger adsorption capacity due to an increase in micropore size. The products formed were thoroughly washed with deionized water and dried in stove at 100 ºC during 2 h. The activated carbons were stored in hermetic containers for later studies.

SEM experiment was carried out in two steps; first the activated carbon samples were put on a slide in a Fine Coat Ion Sputter JFC-1100 apparatus, which works in vacuo, 1.2 kv of voltage and 10 mA of current. The samples received three discharges of a golden-palladium bath. Each discharge took 3 min and formed a 100 Å thickness coat. After, photographs with different enlargements were taken using a microscope SEM 501 B Philips. The micropore and macropore size were determined using 640x and 5000x respectively.

The adsorption capacity was measured according to the ASTM D 4607-94(1999) specifications. Three representative samples of both, walnut and peach activated carbons obtained as described previously, were weighted and transferred separately to a 250 ml erlenmeyer flasks equipped with ground glass stoppers. First, 10 ml of the hydrochloric acid solution (5% by weight) were added into each flask. The flasks were shaken gently until the carbon was completely wetted. Then, the stoppers were removed and the flasks were place on a hot plate and their contents were brought to boil (30 seconds). After cooling at room temperature, 100 ml of the standardized iodine solution (0.1N) were added into each flask. The flasks were closed and shaken vigorously for 30 seconds. The content of each flask was filtered using Whatman #2 paper. 50 ml of each filtrate were titrated with a standardized sodium thiosulfate solution (0.1 N) until a pale yellow color developed. Finally, 2 ml of starch solution (0.1 %P/V) were added and the titration was carried on until a colorless solution was produced. The adsorption capacity was calculated as follows:

$$\frac{X}{M} = \frac{A - (DF)\,BS}{M} \tag{1}$$

Where X/M is the weight, in milligrams, of the iodine adsorbed per gram of sample; S is the volume, in milliliters, of the standardized sodium thiosulfate solution used; and M is

the weight in grams of the sample. A= (N2) x (12693), in which N2 is the normality of the standardized iodine solution; B= (N1) x (126.93), in which N1 is the normality of the standardized sodium thiosulfate solution. The dilution factor (DF) was obtained using the equation DF= (I + H)/ F, in which I is the volume, in milliliters, of the iodine solution used in standardization procedure; H is the volume, in milliliters, of hydrochloric acid solution used; and F is the volume, in milliliters, of the filtrate used.

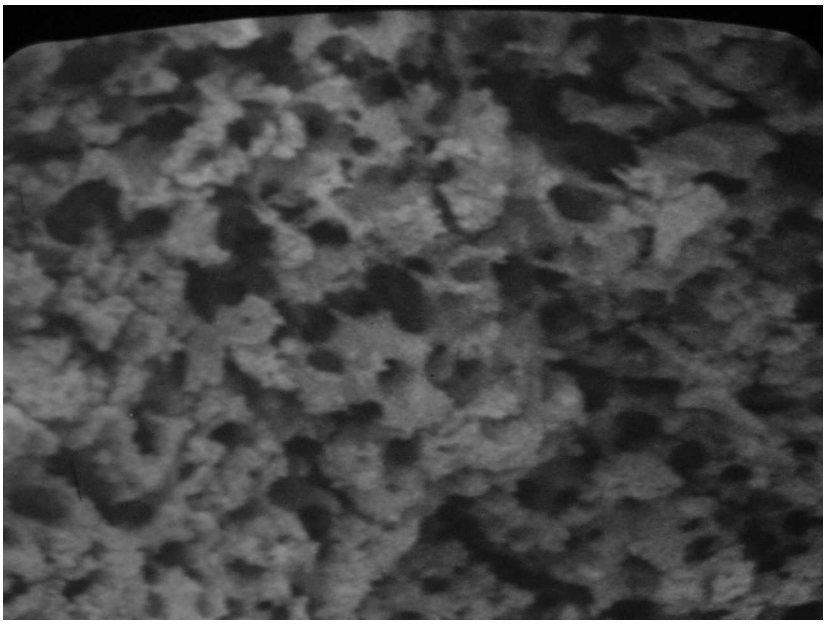

Figure 1: *Activated charcoal from walnut shell*

Results and Discussion

The carbonization yields were 20.8% for walnut shell and 22.2% for peach stones. The activation yields were 18.1% and 16.3%, respectively.

The obtained SEM images of the activated carbon from walnut shells show an average micropore size between 8.05 10-4 μm and of 2.13 10-4 μm (see Figure 1). Average values for the activated carbon from peach stones were 7.29 10-3 and 3.73 10-4 μm for the meso and micro pores sizes (see Figure 2), respectively.

On the other hand, the adsorption capacity per gram for the walnut shell carbon was 406 mg of iodine, while the one corresponding to the peach stone carbon was 777 mg of iodine/g of carbon. Therefore, each carbon showed a characteristic pore size depending on the starting material used. It has been reported [3] that microporous carbons like the one obtained from walnut shells are more effective to retain little molecules. On the contrary, mesoporous carbons like the ones obtained from peach stones are better to adsorb large molecules, e.g., dye molecules. Macropores only show a transport function to meso- and micropores, which are responsible for the major part of the activated carbon surface.

Conclusion

This work provides a simple method to obtain carbonaceous adsorbents of controlled pore size, from two industrial wastes: walnut shell and peach stone. The activated carbon obtained from walnut shell shows a heterogeneous structure with smaller pores than those of the peach stone carbon.

The adsorption capacity of the peach stone carbon was 52% higher than that of the walnut shell. On the other hand, it was comparable to the adsorption capacity of a commercial activated carbon (700 – 1100 mg of iodine/ g of carbon).

The adsorption capacity may be increase by changing the activation conditions, such as temperature, activation time and concentration of activating agent. Hu and Vansant [15] demonstrated that intensified activation conditions favor the production of adsorbents with a high adsorption capacity and wider pore size distribution. Changing the activation time and the concentration of KOH solution it is possible to alter those parameters. Accordingly, the peach stone and walnut shell could be promising materials to produce carbonaceous adsorbents at low cost, with their consequently economic increase value.

Furthermore, the utilization of walnut shells to make activated carbon may have a positive influence on the environment, in view that in the future the production of walnut will increase and the waste matter, that nowadays it is mainly used as a fuel, will be greater to.

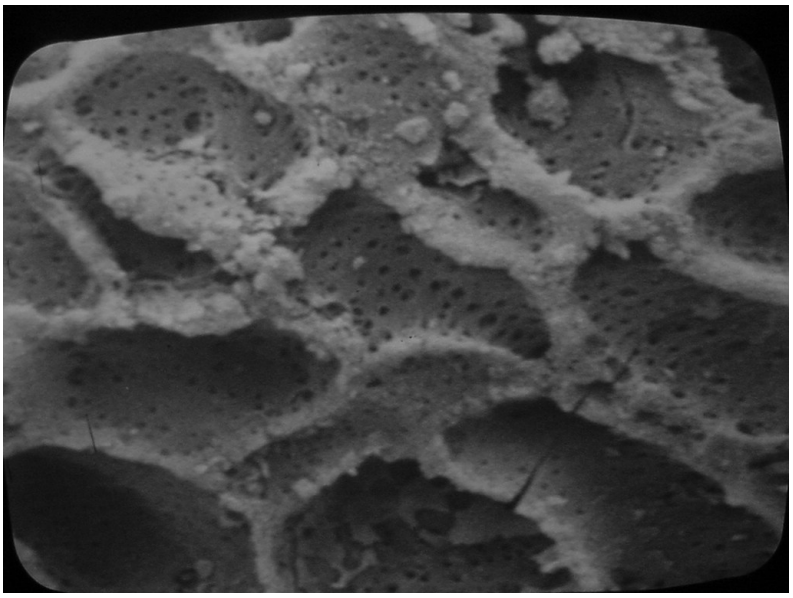

Figure 2: *Activated charcoal from peach stone*

Acknowledgements

To Mr. Ricardo Valdez, Aeronautic Departament of the National University of Córdoba, in charge of the upkeep and out optimal of the equipment.

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