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ACTIVATED CARBONS BY CHEMICAL ACTIVATION OF COTTON

J.C. Moreno-Piraján [1*], G.A. Rodríguez [2], L. Giraldo [2], Y. Ladino [3],

[1] Department of Chemistry, Faculty of Sciences, Research Group of Porous Solids and Calorimetry. Universidad de Los Andes.
[2] Department of Chemistry, Faculty of Sciences, Uiversidad Nacional de Colombia. Bogotá, Colombia.
3 Department of Chemistry, Faculty of Sciences and Technology. Universidad Pedagógica Nacional. Bogotá, Colombia.

[*] Author correspondence: jumoreno@uniandes.edu.co

ABSTRACT

In the present study, fibers of activated carbon are prepared from two 100% cotton knit materials with different densities through the impregnation with diluted $ZnCl_2$ and H_3PO_4 solutions and their posterior carbonization using carbon dioxide atmosphere.
The characterization of the prepared carbonaceous materials is carried out by adsorption isotherms of N_2 at 77 K, immersion calorimetry, X-Ray diffraction, FTIR and optical microscopy.
The results allow stating that the impregnation and carbonization parameters developed on the cotton precursor materials permit to obtain activated carbons with superficial area values that range between 700 and 1200 $m^2\ g^{-1}$, micropore volumes between 0,41 and 0,52 $cm^3\ g^{-1}$ and contraction and efficiency percentages between 45 and 18%, respectively.
Similarly, the obtained values for immersion enthalpy of the activated carbons in carbon tetrachloride are between 90 and 140 J g^{-1}.

Key words: Activated Carbons, Cotton, Chemical Activated, Immersion Enthalpy.

INTRODUCTION

The fibers of activated carbon are carbonaceous adsorbents that can be efficiently used in separation, storage, purification and recovery processes of many pollutants such as phenolic compounds and derivates, heavy metals and volatile organic compounds. The fibers of activated carbon constitute a flexible way of activated carbon that due to its high porous nature, present advantages over the granular and powered activated carbon because its fine fibrous constitution yields fast adsorption kinetics in aqueous and gaseous phase.

The preparation of activated carbon fibers is developed from knit materials, mainly from viscous rayon precursors, and by the known methods of activation: chemical and physical. In the present work, fibers of activated carbon are prepared by chemical activation of knit materials, physical adsorption of gases, immersion calorimetry, X-ray diffraction and infrared and optical microscopy.

METHODOLOGY

Precursor Materials: Two 100% cotton comercial knits are used: *Índigo Calypso* and *Drill super 8*, plane texture, showing densities of onz yd $^{-2}$ and 12 onz yd $^{-2}$, respectively.

Carbonization: 10 x 10 cm segments of the precursor materials are submerged for 2 minutes in 1% solutions of $ZnCl_2$ and H_3PO_4 and dried in a horizontal oven with *Eurotherm Thermolab* temperature controller. Fibers are carbonized at 1123 K for one hour under a CO_2 flux of 100 cm^3 min^{-1} and linear heating velocity of 5 K min^{-1}.

Textural Characterization: The porosity of the prepared carbons are evaluated by physical adsorption of nitrogen at 77 K in a conventional volumetric equipment, Autosorb 3B, Quantachrome. El micropore volume is calculated using the Dubinin-Radushkevich equation and the apparent superficial area is calculated by the application of the BET model.

Immersion Enthalpy: The immersion enthalpies of the prepared materials are determined in a Calvet-type microcalorimeter of heat conduction, using a calorimetric cell of stainless steel. 50-100 mg of the activated carbon fibers are weighted. When the equipment reaches the thermal equilibrium, the immersion takes place and the generated heat is recorded as a function of time. Finally, a calibration is carried out, electrically.

Infrared Spectroscopy: The spectra are taken using a Thermo Nicolet FTIR Nexus in a wave number range between 400 and 4000 cm^{-1}. The spectrum is recorded with 128 scans at a 4cm-1 resolution. The spectra are interpreted by peak deconvolucion.

X-Ray Diffraction: The diffractograms of the prepared carbon fibers are taken in a Rigaku RU-300 equipment with a CuK_α (λ=1,5418 Å lamp operated at 40 kV and 80 mA with a scan between 10 y 40 2Θ.

Optical Microscopy: Images of the precursor material and the activated carbon fibers are obtained by optical microscopy in a Nikon SMZ 800 equipment using two objectives: 1,5-zoom 2,0 and 1,5-zoom 6,3, in order to visualize changes on the solids surface.

RESULTS

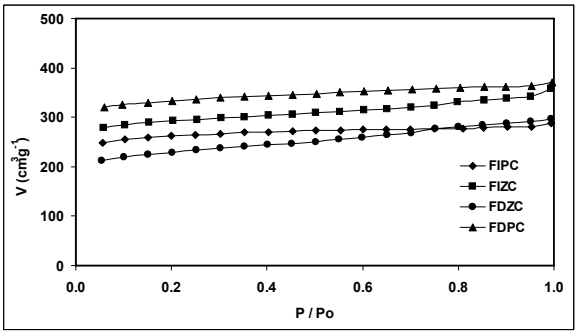


Figure 1. N_2 Adsorption Isotherms at 77 K

In figure 1, the N_2 adsorption isotherms at 77 K are shown. The shape of the isotherms allow seeing the differences among the prepared materials, all the isotherms are I-type corresponding to microporous solids. However, it is interesting that the FDZC fiber tends to high relative

pressures, indicating mesopores presence, which is confirmed by the fact that this fiber presents the lowest value of micropore volume, as may be seen in table 1.

Table 1. Parameters obtained from the N_2 Adsorption Isotherms at 77 K

Fiber	BET Specific Area ($m^2\ g^{-1}$)	Total Pore Volume ($cm^3\ g^{-1}$)	Micropore Volume ($cm^3\ g^{-1}$)	Characteristic Energy ($kJ\ mol^{-1}$)
FIZC	790	0.55	0.47	13.0
FIPC	709	0.45	0.42	13.1
FDZC	639	0.46	0.37	10.7
FDPC	897	0.57	0.53	14.0

The obtained values for the four prepared materials showed substantial values for BET specific area and micropore volume, taking into account the relatively short impregnation time. In the same way, differences between the two precursor materials and impregnater agents used. For the materials prepared from the indigo, it can be observed that the highest value of superficial area corresponds to the material impregnated using zinc chloride while for the materials prepared from drill; the greatest superficial area is obtained for the material impregnated with phosphoric acid. On the other hand, the reported values for the characteristic energy show differences in the four materials being the highest one, the corresponding to the activated carbon fiber with the highest micropore volume; and the lowest one, the corresponding to the activated carbon fiber with the lowest micropore volume, although these fibers were prepared from the same precursor.

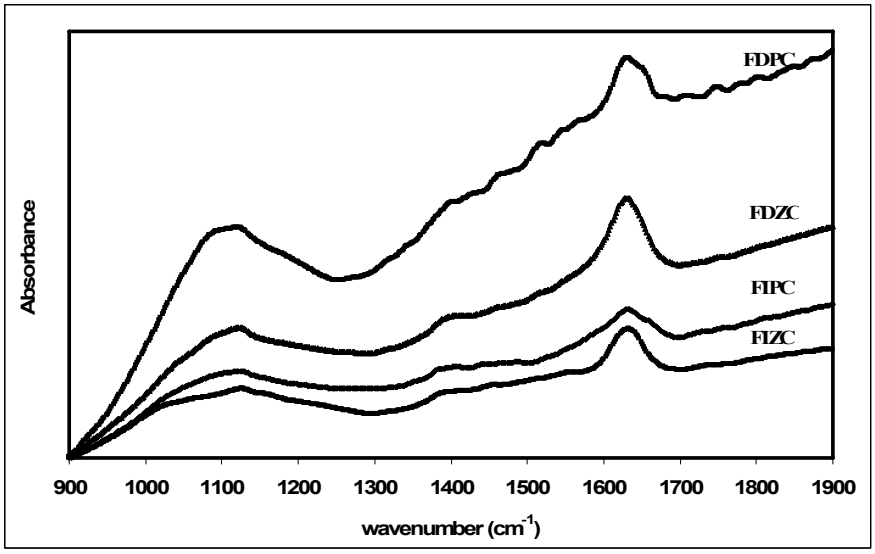


Figure 2. FTIR Spectra of the Activated Carbon Fibers

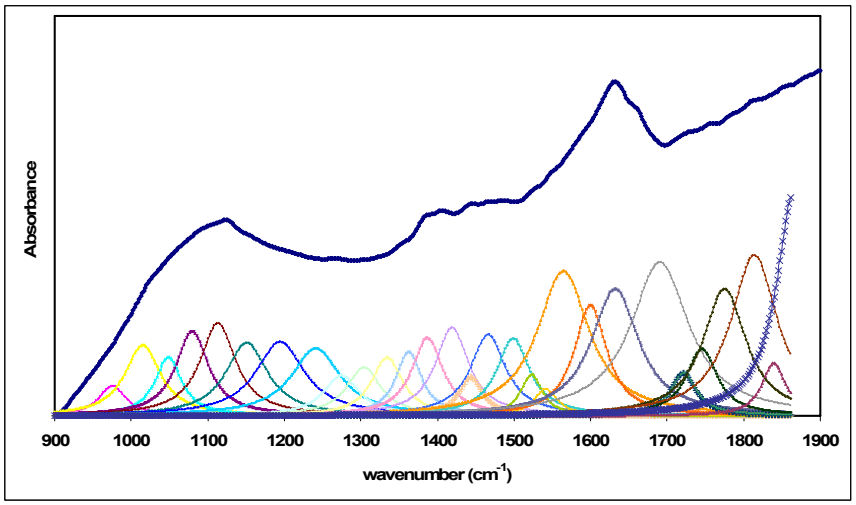


Figure 3. FT-IR Spectra Deconvolución

In figure 2, the FT-IR spectra of the prepared fibers of activated carbon are shown. The analysis of the spectra is achieved by deconvolution, as may be seen in figure 3. In the spectra shown in figure 2, differences for the four materials prepared may be seen. All samples present absorption bands at 1630 cm^{-1} attributed to C=O stretching corresponding to carboxylic and carbonyl groups. Additionally, at this absorption band, an overlapping is observed for the materials impregnated with phosphoric acid (FIPC and FDPC), which might be related to the presence of quinones or conjugated ketones. By the other side, for the FDPC fiber, absorption bands located at 1460cm^{-1} corresponds to O-H deformations in carboxyl groups and the bands found at 1740 cm-1 are associated with C=O stretching vibrations corresponding to lactonic groups that are not present in the other samples.

Table 2. Immersion Enthalpies in different calorimetric liquids

Material	-ΔHim H_2O (Jg^{-1})	-ΔHim HCl (Jg^{-1})	-ΔHim NaOH (Jg^{-1})	-ΔHim CCl_4 (Jg^{-1})
FIZC	4.25	10.4	43.9	114
FIPC	4.32	13.4	4.03	124
FDZC	4.18	22.3	19.8	91.0
FDPC	4.43	12.3	45.3	134

The immersion enthalpies in different liquids are shown in Table 2. These results allow noticing that there is a relation between the enthalpies in water and carbon tetrachloride, and it may be seen that the highest values correspond to the materials impregnated using phosphoric acid (FIPC and FDPC), that are the materials having the highest values for characteristic energy. On the other hand, the immersion enthalpies in NaOH and HCl solutions that have relation with the interaction with the acid and basic groups located on the surface, allow seeing the differences among the materials for being in a wide range. The FDZC sample shows the lowest value of enthalpy in HCl and the FIPC sample that shows the lowest value in NaOH. In figure 4, an immersion thermogram of materials in NaOH is illustrated, making the immersion and instrument calibration peaks, evident.

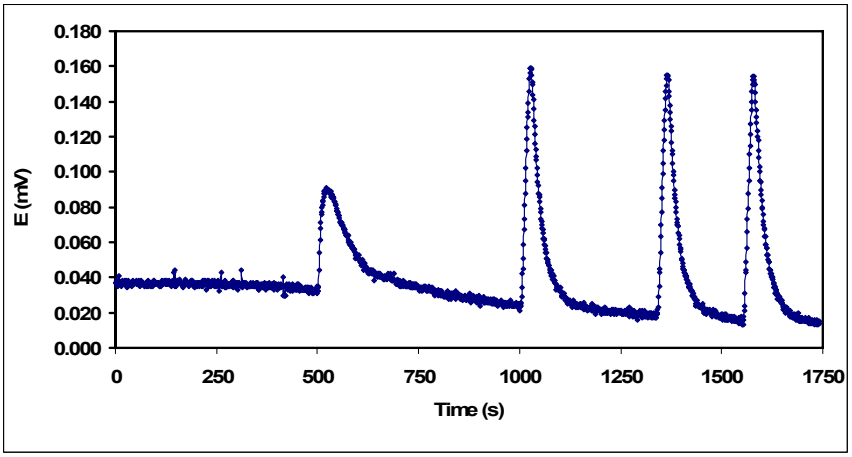


Figure 4. Immersion thermogram of one of the activated carbon fibers in NaOH solution

The X-ray diffractograms of the four samples are shown in Figure 5. The peak found between 2θ= 20-25° corresponds to the 002 reflection of the carbons due to the piled-up structure of the aromatic layers, and the widening of the 002 peak may be interpreted in terms of the small dimensions of the crystals perpendicular to the aromatic layers. In figure 5, the differences among the diffraction peaks of the plane 002 for the four materials, as a product of the precursor and impregnater agent used for the activation are shown. The materials impregnated with phosphoric acid show diffraction peaks to one angle while the materials prepared with zinc chloride, present diffraction angles in different positions in the mentioned range.

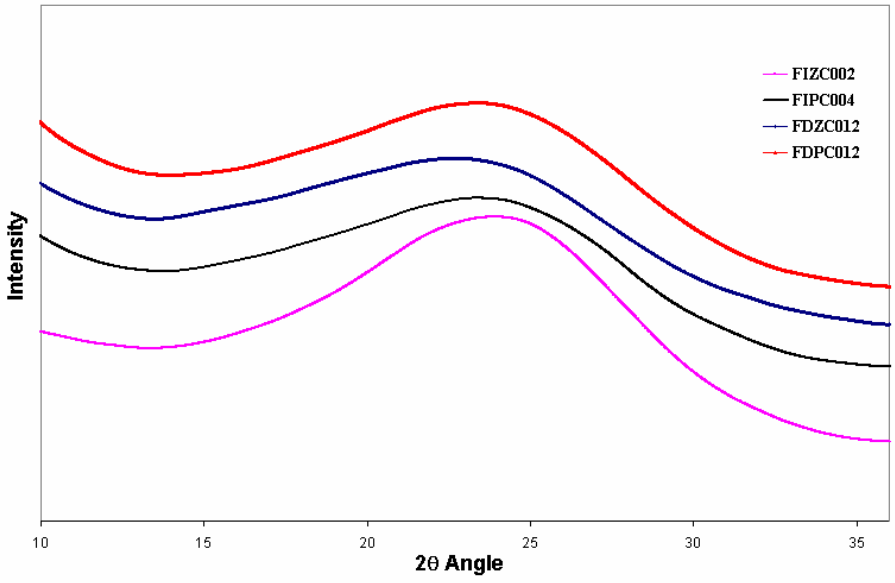
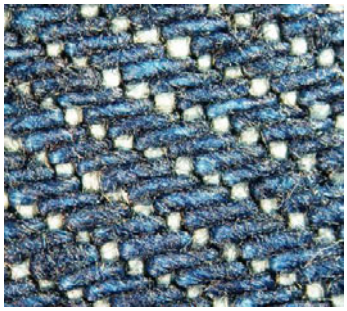


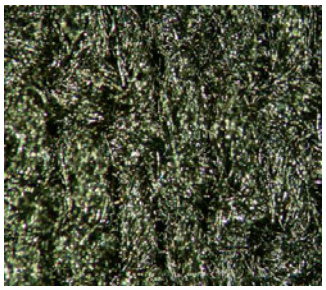
Figure 5. X-Ray Diffractograms

Optical Microscopy

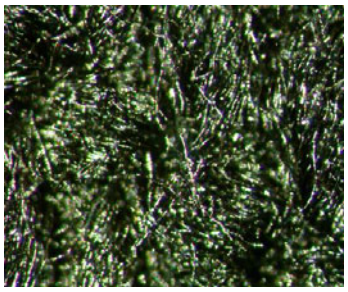


PRECURSOR 1.5X1.0

FDPC 1.5 x 1.0



FDPC 1.5 x 3.0



FDPC 1.5 X6.3

The photographs allow observing the texture of the fibers prepared for the sample that showed the highest value of superficial area –FDPC-. On them, the action of the employed gas for the carbonization process may be seen, as well as the change in texture in regard to the original material.

CONCLUSIONS

Fibers of activated carbon prepared by chemical activation of commercial knit materials made of cotton are obtained. The textural characteristics of these materials, that are reflected on the values for superficial areas and micropore volumes found between 630 and 890 m^2g^{-1} and 0.450 and 0.57 cm^3g^{-1}, respectively; indicates that the obtained fibers posses adequate properties to be used as adsorbents. Since the impregnation time and drying of the cotton material is reduced, same as the activation temperature, some experimental conditions are established in order to obtain activated carbon fibers as flexible carbonaceous material that keep their shape posterior to the thermal process of activation using CO_2.

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REFERENCES

- Sing K.P., Mohan D., Tandom G.S., Gupta G.S.D., Ind. Eng. Chem. Res. 2002; 41: 248.
- Huidobro, A., Pastor, A.C., Rodríguez-Reinoso, F., Carbon 2001; 39:389. Garrido, J., Linares-Solano, A., Martín-Martínez, M., Molina Sabio, M., Rodríguez-Reinoso, F., Torregrosa, R., LAngmuir 1987; 3:76.
- Pradhan, B. K., Sandle, N. K., Carbon 1999; 37:1323.
- Shin, S., Jang, S., Yoon, H., Mochida, I., Carbon 1997;35:1739.
- Moreno-Castilla, C., López-Ramón, M.V., Carrasco-Marín, F., Carbon 2000; 38:1995.
- Silvestre-Albero, J., Gomez de Salazar, C., Sepúlveda-Escribano, A., Rodríguez-Reinoso, F., Collolids and Surfaces A 2001; 187-188:151.
- Yoshizawa, N., Maruyama, K., Yamada, Y., Zielinska-Blajet., M., Fuel 2000; 79:1461.
- Iwashita, N., Rae Park, C., Fujimoto, H., Shiraishi, M., Inagaki, M., Carbon 2004; 42:701.
- Takagi, H., Maruyama, K., Yoshizawa, N., Yamada, Y., Sato, Y., Fuel 2004; 83:2427.