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PRODUCTION AND CHARACTERIZATION OF ACTIVATED CARBON MEMBRANES[1]

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Abstract
The objective of this work is the production and characterization of ultrafiltration membranes composed of activated carbon (AC) in epoxy resin matrix. In order to produce these composite membranes, with a desired final porosity of 60%, national grade micropores powder AC, with different particle size distribution was used. The AC and the composite activated carbon membranes (CACMs) were characterized for their thermal stability, chemical composition, specific surface area and porosity. The results indicates that AC has a high specific surface area; the apparent porosity is in the range of 50-58%, thermal stability up to 370°C, where the decomposition of the organic constituents started and that the composition and structure of the CACMs to be almost of the epoxy resin and AC with the absence of the solvent.
Key words: Activated carbon; Epoxy resin; Composite membranes.

PRODUÇÃO E CARACTERIZAÇÃO DE MEMBRANAS DE CARVÃO ATIVADO

Resumo
O objetivo deste trabalho é a produção e a caracterização de membranas de ultrafiltração compostas de carbvão ativado (AC) em matriz de resina epóxi. Para a produção das membranas com porosidade final desejada de 60% foi utilizado AC nacional, microporoso na forma de pó com diferentes distribuições de tamanho de partículas. O AC e as membranas compostas de carvão ativado (CACMs) foram caracterizados para suas estabilidade térmica, composição química, área superficial específica e a porosidade aparente. Os resultados obtidos mostraram que o AC tem elevada área superficial específica, a porosidade aparente das CACMs variou entre 50-58%, uma estabilidade térmica de até 370°C, onde a decomposição dos constituintes orgânicos foi iniciada e que a composição e estrutura das CACMs é praticamente da resina epóxi and AC com ausência do solvente.
Palavras-chave: Carvão ativado; Resina epóxi; Membranas compostas.

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1 INTRODUCTION

Activated carbon is recognized as effective and reliable means in removing impurities. It has a tremendous adsorptive capacity, an affinity for a wide variety of dissolved organics and chlorine,[1] that is why It has been employed in a wide range of applications on an industrial scale, including technologies for the purification of gases; the removal of organic pollutants from water (i.e., purification of drinking water and wastewater). The primary raw material used to produce activated carbon is any organic material with high carbon content (coal, wood, peat, coconut shells). The carbon-based material is converted to activated carbon by thermal decomposition in a furnace using a controlled atmosphere and heat or by chemical methods. The resultant product has an incredibly large surface area per unit volume, and a network of submicroscopic pores where adsorption takes place. The walls of the pores provide the surface layer molecules essential for adsorption.[2] In simple terms, physical adsorption occurs because all molecules exert attractive forces, especially molecules at the surface of a solid (pore walls of carbon), and these surface molecules seek other molecules to adhere to. The large internal surface area of carbon has many attractive forces that work to attract other molecules.

Membrane filtration is expected to be one of the alternatives for complicated, laborious and costly processes used for purification, because in principle it can make the process very compact and the treatment cost lower. However, membranes to be employed in water treatments must satisfy the following requirements: (i) the practical water flux through the membrane is essential, (ii) not only suspended solids but also dissolved organics should be simultaneously removed, (iii) the fouling of the membrane should be minimized, and (iv) the sufficient mechanical strength is needed. Unfortunately, it is difficult so far to find a commercial membrane which meets all the above-mentioned demands. Activated carbon membrane is considered to be a promising candidate for this purpose.[3]

In this work, the objective is the production and characterization of activated carbon and epoxy resin composite membranes for ultrafiltration applications, specifically speaking this study is part of a project intended to construct innovated prototype of tubular, multichannel membranes similar to the capillary polymeric membranes, for potential use in hemodialysis and desalination of water in the north-east of Brazil. Both applications look forward to overcome the high cost of the imported polymeric membranes for hemodialysis and solving the lack of drinking water in that region.

Epoxy resin is widely used in industrial applications in relation to adhesives, coatings, electronics and aerospace structures. Due to its attractive mechanical and chemical properties, such as excellent bonding ability, high tensile and compressive strengths, good chemical resistance and high heat distortion temperature, epoxy is the dominant matrix material for lightweight polymer–matrix structural composites, such as carbon fiber composites. The superior mechanical and chemical properties of epoxy are due to the three-dimensional network structure that results from the curing process, in which a low molecular weight resin is transformed into a high molecular weight polymer.[4-6]

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2 MATERIALS & METHODS

To obtain ultrafiltration membranes, powdered micropores activated carbon was used with the following particle size distributions: as received (CR), less than sieve #170 and #325. The activated carbon is national grade obtained from coconut shell, essentially microspores, produced by Carbomafra.

The composite activated carbon membranes (CACMs) were produced with certain volume fractions of activated carbon (impregnated with a solvent) and epoxy resin: the volumetric fraction of the pores that is needed for the CACMs with an adequate permeability is projected to be 60%.The mixture of the constituents having the required volumetric fractions was made in tubular shapes; after curing the material was fired for the complete evaporation of the solvent and then it was ready for analysis.

To characterize the activated carbon and the CACMs the following analysis were executed: specific surface area of the samples, based on the adsorption and desorption isotherms was determined by nitrogen adsorption at 77K with an accelerated surface area and porosimetry system (NOVA-1200 gas sorption analyzer of Quantachrome Corporation): Each sample was degassed at 150^{o}C for 2 h, prior to the adsorption test. The collected data was made by NovaWin-9.0 program employing the DR (Dubunin-Radushkevich) equation: which gives evaluation of the total surface area and total pore volume and permits the calculation of the average pore radius for relatively hard materials or materials with high surface area like activated carbon.

The apparent porosity, specific mass, and specific mass of the solid part were measured by Arquimedes method for at least three samples of the membranes then the average was calculated.

To evaluate the thermal stability of the CACMs, about 20 mg from each of the samples was subjected to thermogravimetric analysis (TGA) runs carried out in flowing nitrogen gas with heating rate of 20^{o}C/min using Netzsch STA 409 equipment.

To verify the structure of the CACMs and to insure the full evaporation of the solvent, Fourier Transform Infrared (FTIR) spectra of fresh powder samples of CACMs were obtained by making a pellet of 200mg of KBr with 1mg of membrane sample and measuring in the range of 400–4000 cm^{-1} using Nicolet-4700 FTIR spectrometer of Thermo Scientific.

3 RESULTS AND DISCUSSION

3.1 Specific Surface Area Pore Volume and Pore Width Analysis

The adsorptive capacity of adsorbent is related to its internal surface area and pore volume. Generally, the larger the specific surface area of the adsorbent, the better its adsorptive performance will be.[7] Adsorption, desorption isotherms were evaluated by DR routine and the results were listed in Table-1 which shows the high value of the specific surface area of the as received activated carbon (CR) as well as the fine activated carbon of sieves #170 and #325. However, these values were higher than 534 and 657 m^2/g reported for carbon black samples prepared from coconut husk and jute fibers.[8] It can be noted that; the finest are the activated carbon particles (sieve #325), the more they account for a largest specific surface area and micro pore volume, and this result is in agreement with the findings of

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Zhang et al.[9] Beside specific surface area, pore diameter (or pore width) is also an important characteristic of the activated carbon; the average pore size is found to be in order of 5nm varied slightly within the limit of sensitivity of the equipment, this value classified this activated carbon as mesoporos. The volume of micro- and mesopores can be an important parameter depending on the type of pollutant to be removed as well as the media from which they have to be removed. Thus, preparation conditions of the activated carbon to obtain an optimal micro or mesoporos is very important.[10]

Table 1: Specific surface area and average pore size of activated carbon as obtained from isotherms by DR equation

Sample	Micropore surface area (m^2/g)	Micropore volume (cc/g)	Average pore width (nm)
CR-micro	716.744	0.253	5.03
CA #170	769.407	0.272	5.33
CA #325	818. 100	0.289	5.09

Table 2: The apparent specific mass, apparent specific mass of the solid part and apparent porosity of the CACMs calculated by Arquimedes principle

Sample	Apparent Specific mass (g/cm^3)	Apparent Specific Mass of the Solid Part (g/cm^3)	Apparent Porosity (%)
CC#CR	0.580	1.386	58.22
CC#170	0.588	1.350	56.64
CC#325	0.609	1.324	53.00

The results of apparent porosity, specific mass and the specific mass of the solid part of the activated carbon are shown in Table 2. Taking into account that the apparent porosity of the CACMs was designed to be of 60% porosity, however, in practice; it was found to be on an average 56 %: this apparent porosity is reasonable for liquid permeation but it can be improved. It was also noted that, the apparent porosity decreases with the sieve size: the finest is the activated carbon; the lower is the apparent porosity. The density of the CACMs didn't vary much with the sieve size.

It may be concluded that pore sizes and their distributions, including surface area and porosity of the activated carbon, can be designed by varying the sieve size.

3.2 Thermogravimetric Analysis (TGA)

The TGA curves with their derivatives (DTG) of the activated carbon and the CACMs were shown the Figures 1 and 2 and summarized in Table-3. From Figure-1 it can be seen that there are a small amount of weight losses below 100°C (T_1) for all the samples due to desorption of the physisorption water. For the carbon materials, to some extent, the amounts of physisorption water reflect their hydrophilicity and pore structures. The activated carbon exhibits the largest water adsorption capacity in ambient condition, implying its superior hydrophilicity and pore volume.[11,12]

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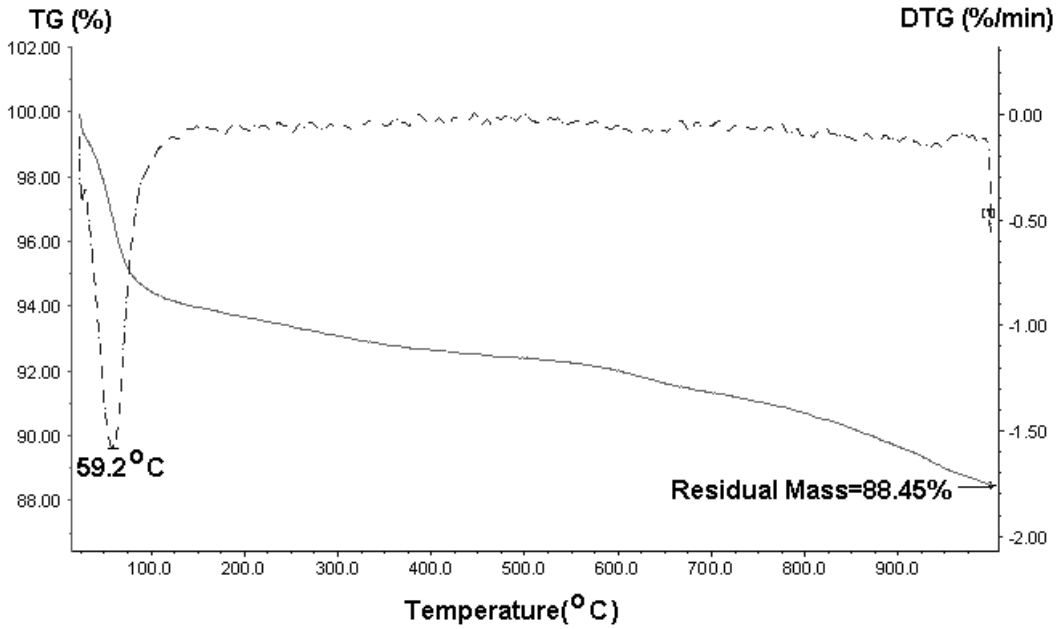

Figure 1: The TGA curve and its derivative showing the thermal decomposition temperature and the residual mass of as received activated carbon (CR-micro).

In Figure 2 and Table 3, two stages of weight loss were shown by the DTG curves: the first one below 100°C (T_1) is attributable to the removal of mainly hygroscopic water. On the other hand, the second one is the pronounced weight loss that took place in the ranges of 360–380°C can be ascribed to the pyrolysis of epoxy resin.

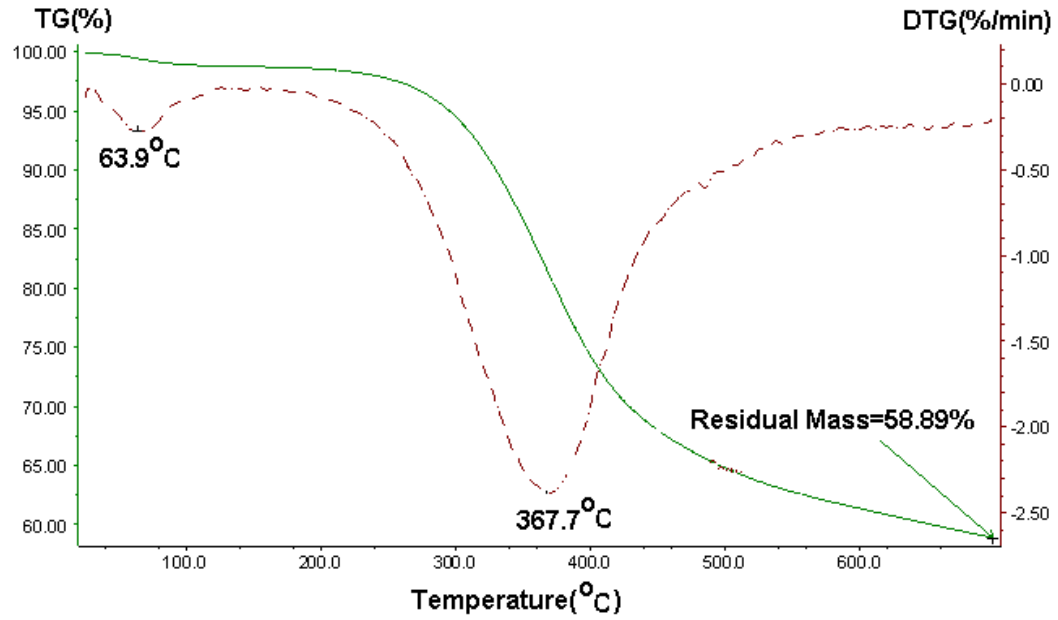

Figure 2: The TGA curve and its derivative of CACM (CC-CR) showing the thermal decomposition temperatures and the residual mass of its constituents.

The humidity loss temperatures (T_1) are a little bit higher in the CACMs than in the activated carbon (CR). The decomposition temperature (T_2) of the later starts at 368°C in inert gas atmosphere, this will be different in oxidative one.

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Table 3: Decomposition temperature and residual mass of the activated carbon and the CACMs

Sample	T_1/°C	T_2/°C	Residual Massa (%)
CR-Micro	59,2	-	88,45
CC#CR	63,9	367,7	58,89
CC#170	76,6	375,4	33,99
CC#325	76,2	372,5	52,82

Studies on CACMs and epoxy resin showed that the introduction of activated carbon decreases the curing temperature of the epoxy resin: this effect is consistent with the high specific surface area of activated carbon,[13-15] that is to say: increasing the specific surface area of activated carbon accelerates the curing of epoxy resin. In this study, TGA didn't show the curing temperature of epoxy resin because the curing occurred during the preparation step of the CACMs. In Table 3, the residual mass of 88.45% is found after heating activated carbon up to 1200°C, this confirms the high stability of the activated carbon in contrast to lower one of the CACMs, this obvious due to pyrolysis the epoxy resin upon heating till 900°C.

3.3 Fourier Transform Infra Red (FTIR)

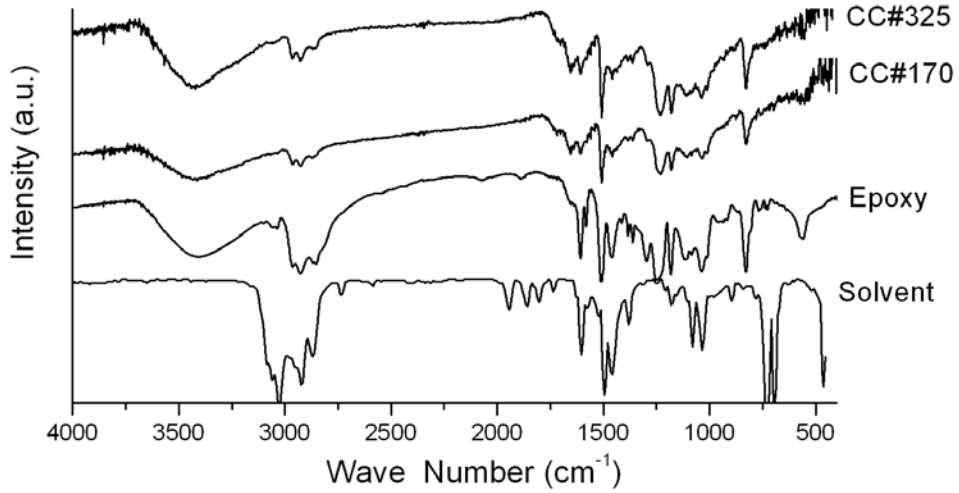

Figure 3: FTIR spectra of the CACMs compared with the epoxy resin and the solvent spectra.

Figure 3 compares the FTIR spectra of the CACMs, epoxy resin and the solvent used to impregnate the activated carbon, it can be inferred that the structure of the CACMs is practically of the epoxy resin with intensities consistent with the proportions adopted during the preparation, and it is very clear that there is no trace left of the solvent in the CACMs.

4 CONCLUSIONS

The characterization showed the following satisfactory results:

1- Concerning the specific surface area and apparent porosity are reasonable considering that the volumetric fraction of the pores which is needed for adequate permeability is between 40 and 75%.
2- Thermal stability, another important factor in the applications of ultra filtration membranes was achieved in the CACMs developed in this work.

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3- The sieve size is shown to have an effect on the apparent porosity but it has no significant effect on either TGA or FTIR results.
4- The complete removal of the solvent (after helping in mixing the activated carbon and the resin) from the CACMs has no effect on their structural integrity.

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REFERENCES

1 Huang, C.P., Wu M.H. The removal of chromium (VI) from dilute aqueous solution by activated carbon. Water Res. v. 11, p. 673-679, 1977.
2 Halena, J., Andrej. A., Jerzy, C., Active Carbon. London: Ellis Horwood Limited, 1991.
3 Sakoda, A., Nomura, T. and Suzuki, M. Activated carbon membrane for water treatments: application to decolorization of coke furnace wastewater, Adsorption v. 3, 93-98, 1996.
4 Park S.-J. Electrochemically modified PAN carbon fibers and interfacial adhesion in epoxy–resin composites. J. Mater Sci Lett. v. 8, n. 1, p. 47–49, 1999.
5 Fjeldly, A., Olsen T., Rysjedal J.H., Berg J.E. Influence of the fiber surface treatment and hot–wet environment on the mechanical behavior of carbon/epoxy composites. Composites Part A. v. 32, n. 3–4, p. 373–378, 2001.
6 Hughes J. Carbon fibre/epoxy interface, a review. Compos Sci Technol v. 41, n.1, p.13–45, 1991.
7 Smisek, M., Cerny, S. Active Carbon Manufacture, Properties and Applications, New York: Elsevier, 1997.
8 Phan N.H., Rio, S., Faur, C., Coq, L.L., Le Cloirec, P., Nguyen, T.H. Production of fibrous activated carbons from natural cellulose (jute, coconut) fibers for water treatment applications. Carbon v. 44, p. 2569–77, 2006.
9 Zhang, Y., Cui, H., Ozao, R., Cao, Y., Chen, B. I.-T., Wang, C.-W., Pan, W.-P. Activated Carbon from Chicken Waste and Coal, Energy & Fuels, v. 21, n. 6, p. 3735-3739, 2007.
10 Izquierdo, M.T., Martinez de Yuso, A., Rubio, B., and Pino, M.R. Conversion of almond shell to activated carbons: Methodical study of the chemical activation based on an experimental design and relationship with their characteristics". Biomass and bioenergy, v. 35, p. 1235-1244, 2011.
11 Li, P., Zhao, T.-J., Zhou, J.-H., Sui, Z.-J., Dai, Y.-C., Yuan, W.-K. Characterization of carbon nanofiber composites synthesized by shaping process Carbon, v. 43, p. 2701–2710, 2005.
12 Wei Li, a.b., Yanga, L., Penga, J., Zhanga, L., Guoa, S. and Xia, H. Effects of carbonization temperatures on characteristics of porosity in coconut shell chars and activated carbons derived from carbonized coconut shell chars, industrial crops and products, v. 28, p. 190–198, 2008.
13 Bae, J., Jang, J., Yoon, S.-H. Cure behavior of the liquid–crystalline epoxy/carbon nanotube system and the effect of surface treatment of carbon fillers on cure reaction. Macromol Chem Phys. v. 203, n. 15, p. 2196–2204. 2002.

ISSN 1516-392X

14 Opalicki, M. Cure kinetics of neat and carbon fiber reinforced TGDDM/DDS epoxy systems. J Appl Polym Sci. v. 61, n. 6, p. 1025–1037, 1996.
15 Puglia, D. Effect of single-walled carbon nanotube incorporation on the cure reaction of epoxy resin and its detection by Raman spectroscopy. Diamond Relat Mater, v. 12, n. 3–7, p. 827–832, 2003.