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DOI: 10.1590/0001-3765201420140143

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Brazilian natural fiber (jute) as raw material for activated carbon production

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Manuscript received on March 25, 2014, accepted for publication on August 4, 2014

ABSTRACT

Jute fiber is the second most common natural cellulose fiber worldwide, especially in recent years, due to its excellent physical, chemical and structural properties. The objective of this paper was to investigate: the thermal degradation of *in natura* jute fiber, and the production and characterization of the generated activated carbon. The production consisted of carbonization of the jute fiber and activation with steam. During the activation step the amorphous carbon produced in the initial carbonization step reacted with oxidizing gas, forming new pores and opening closed pores, which enhanced the adsorptive capacity of the activated carbon. N₂ gas adsorption at 77K was used in order to evaluate the effect of the carbonization and activation steps. The results of the adsorption indicate the possibility of producing a porous material with a combination of microporous and mesoporous structure, depending on the parameters used in the processes, with resulting specific surface area around 470 m².g⁻¹. The thermal analysis indicates that above 600°C there is no significant mass loss.

Key words: activation, adsorption, carbonization, jute fiber, thermogravimetry.

INTRODUCTION

Jute fiber is by far the most common natural fiber in the world. Its use has increased significantly due to its unique combination of physical, chemical and structural properties, and also due to the growing concern with the environment (Alves et al. 2010, Zhou et al. 2013). The characteristics of a typical jute fiber are shown in Table I.

There is a growing interest regarding the use of lignocellulosic materials such as jute, sisal, coconut, banana and *curauá* fibers as precursors for

the production of activated carbon (Asadullah et al. 2013, Roy et al. 2012, Williams and Reed 2006, Phan et al. 2006, Senthilkumaar et al. 2005) as well as to strengthen polymeric matrixes of composites (Ramesh et al 2013, Ku et al. 2011).

Ioannidou and Zabaniotou 2007 mention that activated carbon from natural fibers exhibit specific surface areas ranging from 80 m².g⁻¹ to 900 m².g⁻¹, with porous structure containing mostly micropores when produced at heating rates of 2°C. min⁻¹, at temperatures between 200°C and 300°C during carbonization and at activation heating rates of 4°C.min⁻¹, with final temperature of 800°C.

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TABLE I
Characterization of *in natura* jute fiber (Bledzki and Gassan 1999, Phan et al. 2006, Ramesh et al. 2013).

Parameter	Bledzki and Gassan 1999	Phan et al. 2006	Ramesh et al. 2013
Cellulose	64.4% ^a	58.0% – 63.0%	50.0% – 57.0%
Hemicellulose	12.0%	20.0% – 22.0%	-
Lignin	11.8%	12.0% – 15.0%	8.0% – 10.0%
Water soluble	1.1%	-	-
Water	10.0%	-	-
Wax	0.5%	-	-
Density	1.3 g.cm ⁻³	-	1.4 g.cm ⁻³
Elongation	1.5% – 1.8%	-	1.8%
Tensile strength	393 MPa – 773 MPa	-	400 MPa – 800 MPa
Young's modulus	26.5 GPa	-	30.0 GPa

^a mass based values

Some studies have indicated that activated carbon from natural fibers reach adsorption rates 2 to 50 times faster the ones from coal, due to the small diameter of the fibers, around 10 µm, presenting a larger external surface area in contact with the fluid (Baudu et al. 1991). Furthermore some studies have shown its potential to withdraw water pollutants such as phenol, pesticides and dyes (Asadullah et al. 2013, 2010, Banerjee and Dastidar 2005, Hameed et al. 2007, Ahmaruzzaman and Gayatri 2010, Kumar et al. 2008).

Aiming at the use of available natural resources and the search for economical alternatives for activated carbon production, the objective of this work was to characterize the jute fiber (*in natura*) and to produce and characterize the resulting activated carbon.

MATERIALS AND METHODS

CHARACTERIZATION OF *IN NATURA* JUTE FIBER AND ACTIVATED CARBON PRODUCED

Thermal analyses were carried out with an analyzer from NETZSCH, model TG 209, with controller also from NETZSCH, model TASC 414/3. They used 5 mg samples, with final temperature of 950°C and heating rates of 1°C.min⁻¹, 3°C.min⁻¹, 5°C.min⁻¹ and 10°C.min⁻¹.

Immediate analyses were carried out in order to determine the moisture content as well as the ash, volatile and fixed carbon contents. The analyses followed norm D1762-84 reviewed in 1985 (ASTM), which addresses such analyses for char and wood substances.

The activated carbon was characterized by gas adsorption (N₂ at 77K). All samples were degassed under vacuum at 150°C, and a gas adsorption analyzer (Quantachrome Corp. model Autosorb-1MP) was used to measure the pore distribution, pore volume and specific surface area. Data from the adsorption isotherms for nitrogen at 77K were used to determine the specific surface area according to the method proposed by Brunauer, Emmet and Teller (Rouquerol 1994, IUPAC 1985). The micropore (pore diameter narrower than 2.0nm) area was obtained by applying the t-plot method. The total pore volume was determined by converting the volume adsorbed at the saturation point $P/P_0 \approx 0.99$ into liquid volume, whilst the micropore volume was calculated at the point of interception of the linear region of the t-plot after saturation of the micropores.

CARBONIZATION AND ACTIVATION OF JUTE FIBER

The raw material was submitted to carbonization followed immediately by activation in the same

run. Samples 190mm long were placed within a quartz reactor capable of accommodating 50g.

The experimental set-up is shown in Figure 1. Heat was supplied by an electrically heated 630mm vertical furnace (1) to a 700mm long 60mm diameter quartz reactor (2). Temperature and heating

rates were controlled (3). A flask (9) was heated by resistances (8) connected to a power source (11). Temperatures were measured by thermocouples inside (4) and outside (5) the reactor as well as inside the flask (10). The whole set-up was placed under an exhausting system (6) to vent off gases.

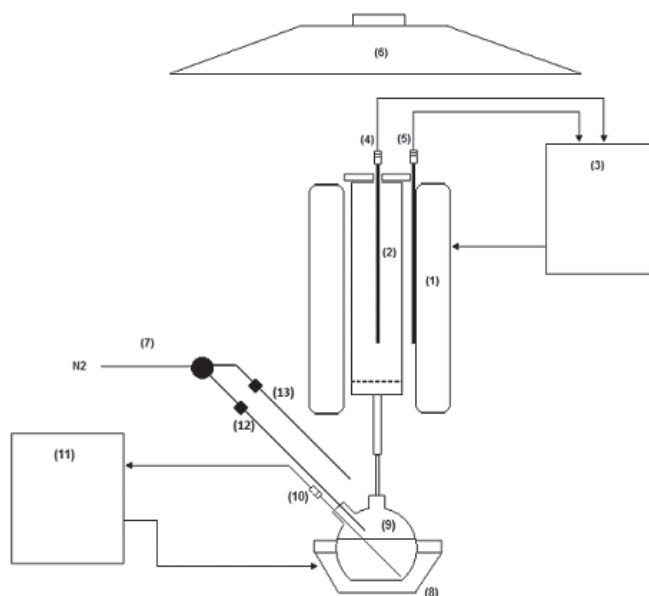


Figure 1 - Apparatus for carbonization and activation of jute fibers.

The N_2 flow rates to carry steam were previously tested and defined for all experiments: $200\text{mL}\cdot\text{min}^{-1}$ of N_2 carried $0.17\text{mL}\cdot\text{min}^{-1}$ of water (activation steam), $300\text{mL}\cdot\text{min}^{-1}$ of N_2 carried $0.33\text{mL}\cdot\text{min}^{-1}$ of water and $400\text{mL}\cdot\text{min}^{-1}$ of N_2 carried $0.50\text{mL}\cdot\text{min}^{-1}$ of water.

Figure 2 shows the temperature profile selected for the production of steam activated jute fiber.

Some preliminary runs were carried out to determine the experimental parameter values. Temperatures below 600°C (T_2) produced activated carbons with too low specific surface area. Above 800°C the material was totally or partially degraded. Within these limits the following conditions were specified.

Conditions for the carbonization step:

heating rate up to temperature T_1 : $3^\circ\text{C}\cdot\text{min}^{-1}$;
carbonization temperature (T_1): 350°C ;
carbonization residence time: ($t_1 - t_2$): 30min;
inert gas (N_2) flow rate: $200\text{mL}\cdot\text{min}^{-1}$.

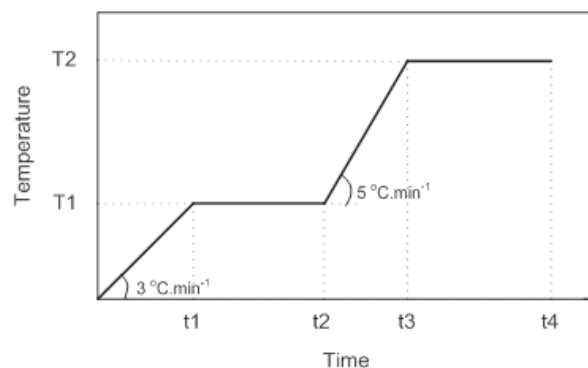


Figure 2 - Temperature profile for the production of activated carbon from jute fiber.

Conditions defined for the activation step:

heating rate: $5^\circ\text{C}\cdot\text{min}^{-1}$;
activation temperature (T_2): $600^\circ\text{C} - 800^\circ\text{C}$;
activation residence time ($t_2 - t_3$): 30min – 90min;
inert gas (N_2) flow rate: $200\text{mL}\cdot\text{min}^{-1} - 400\text{mL}\cdot\text{min}^{-1}$.

The heating rate used in the carbonization process and the activation process were based on information from previous values (Asadullah et al. 2010, Wu et al. 2013, Ioannidou and Zabaniotou 2007) and adapted to the result of immediate analyses.

Table II shows the variables investigated and their range of values used during the production of activated jute fibers.

TABLE II
Activated carbon production
process parameters.

Variables	-1	0	+1
(X ₁) Temperature (°C)	600	700	800
(X ₂) Activation time (min)	30	60	90
(X ₃) N ₂ flow rate for carrying steam (mL.min ⁻¹)	200	300	400

RESULTS AND DISCUSSION

THERMOGRAVIMETRIC ANALYSIS OF *IN NATURA* JUTE FIBER

The thermogravimetry (TG) was carried out with inert gas (20mL.min⁻¹ of N₂), carbonic gas (20mL.min⁻¹) and synthetic air (mixture of N₂ 20mL.min⁻¹ and O₂ 8mL.min⁻¹). Four heating rates were employed: 1°C.min⁻¹, 3°C.min⁻¹, 5°C.min⁻¹ and 10°C.min⁻¹. All analyses employed samples of 5mg and final temperature of 950°C.

The TG curves of *in natura* jute fibers with inert atmosphere, synthetic air and CO₂ are presented in Figures 3A, 3C and 3E, respectively. Their respective first derivative thermogravimetry (DTG) curves are presented in Figures 3B, 3D and 3F.

Figures 3A, 3C and 3D show that the heating rate did not affect the mass losses, indicating they depend only on temperature. Jute fiber degradation starts at about 260°C and proceeds fast with temperature rise. This behavior was also noticed by Cao et al. 2013, Monteiro et al. 2012 and by Banerjee and Dastidar 2005.

Comparing the DTG curve using inert gas (Figure 3B) with two other gases (Figures 3D and 3F), one observes that the first peak (9.5% mass loss)

around 80°C is common to both situations, which is due to the loss of adsorbed water in fiber (intra and intermolecular dehydration reactions); the second peak is also common, accounting for the major organic material loss (cellulose and hemicellulose), between 330°C and 380°C. However the third peak which appears when using O₂, indicating the loss of material due to an oxidizing reaction involving the lignin. For all situations, i.e., for all types of gases, all material loss occurs below 600°C.

CHARACTERIZATION OF ACTIVATED CARBON FROM JUTE FIBER

Jute fiber (*in natura*) presented moisture content of 9%, volatile content of 84%, ash content of 9% and fixed carbon content of 7%. In order to grant total volatile elimination, the heating rate must be low during the carbonization period, which also boosts pore formation.

Table III shows the variables investigated and the answer for yield (η) and specific surface area (SSA) for the jute fiber carbonization and activation with steam.

TABLE III
Experimental planning matrix with
answers for yield (η) and specific
surface area (SSA).

Sample	X ₁	X ₂	X ₃	η (%)	SSA (m ² .g ⁻¹)
JFA1	-1	-1	-1	20.67	361.50
JFA2	1	-1	-1	18.61	475.70
JFA3	-1	1	-1	19.95	396.00
JFA4	1	1	-1	17.33	477.00
JFA5	-1	-1	1	20.09	412.20
JFA6	1	-1	1	16.26	547.90
JFA7	-1	1	1	17.88	453.50
JFA8	1	1	1	11.46	748.90
JFA9	0	0	0	17.82	446.10
JFA10	0	0	0	19.56	404.10
JFA11	0	0	0	18.13	444.30

The data in Table III indicate a mass based average yield of 18% and average specific surface area of 470 m².g⁻¹. The highest the variable levels, the lowest the yield, and the highest the SSA.

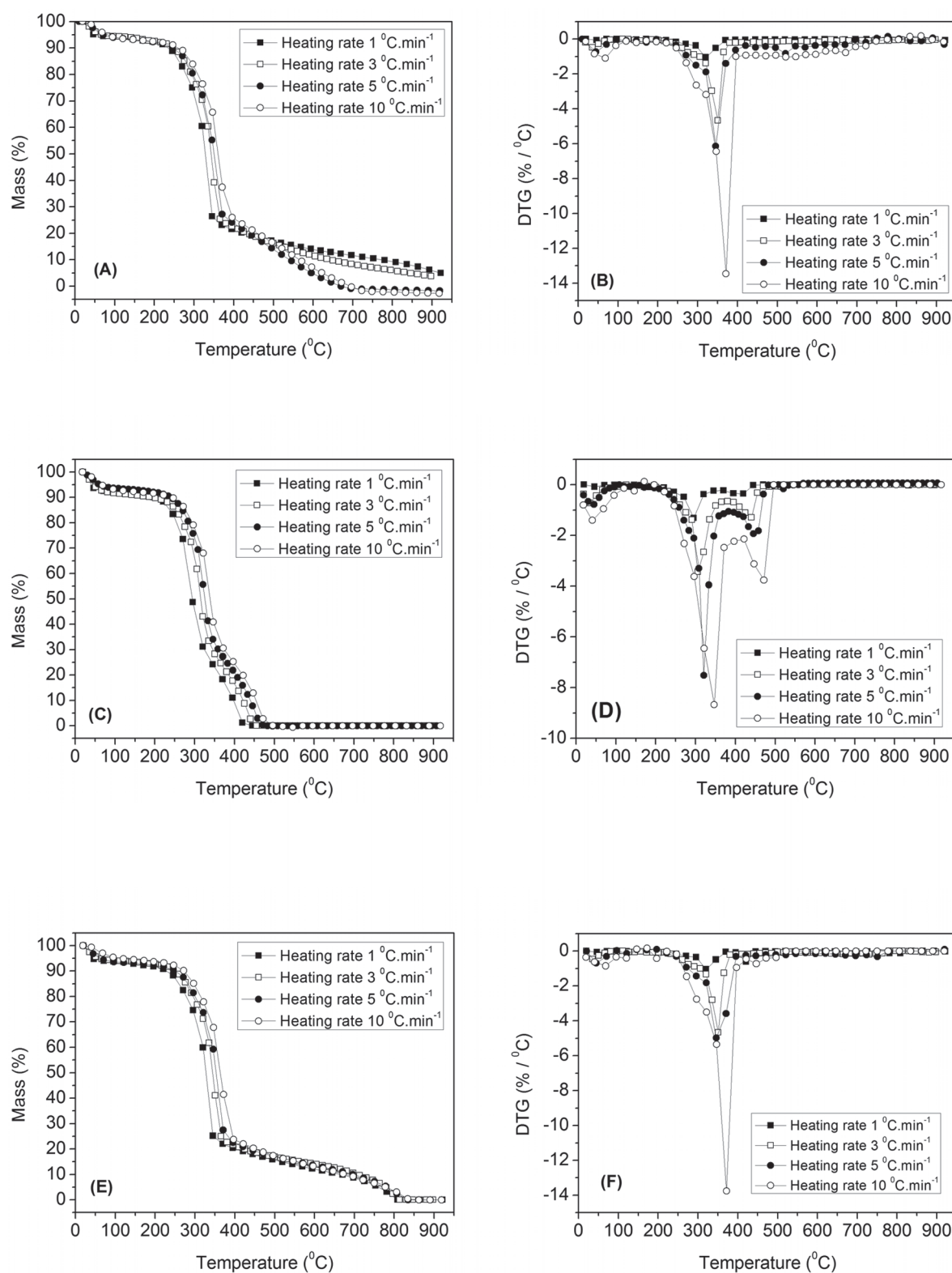


Fig. 3 - Jute fiber (*in natura*) thermogravimetry (TG) curves and derivate thermogravimetry (DTG) curves: (A) TG with inert gas; (B) DTG with inert gas; (C) TG with synthetic air; (D) DTG with synthetic air; (E) TG with CO_2 ; (F) DTG with CO_2 .

At the lowest temperatures and activations times, the highest yields were obtained, although with the lowest SSA values.

The low yield can be explained by the elimination of the large amount of volatile matter present in the raw material (carbonization) as well as by the reaction between fixed carbon and steam (activation). The yields obtained varied inversely with temperature. These results are in agreement with the ones from Asadullah et al. 2010.

The specific surface values vary proportionally with temperature, with maximum value ($730 \text{ m}^2 \cdot \text{g}^{-1}$) at 700°C , when starting the destruction pore wall.

Figure 4 shows the N_2 (77K) adsorption/desorption isotherms of activated carbon from jute fiber.

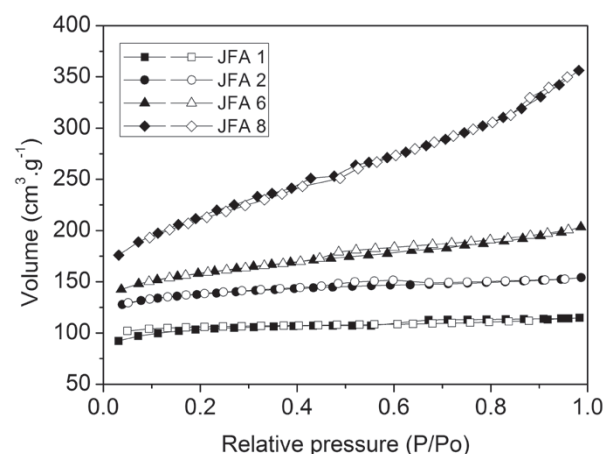


Fig. 4 - Adsorption (open symbols) and desorption (closed symbols) isotherms of N_2 at 77K.

The isotherms of Figure 4 show similar trend except JFA8 that presents an increase in the adsorption capacity at higher relative pressures. There was no hysteresis, which indicates no capillary condensation, typical of macro and mesopores. Sample JFA1 exhibited the lowest adsorption capacity, as also obtained by Asadullah et al. 2014.

Table IV shows that activated carbon from jute fiber is widely microporous. Around 95% of SSA belongs to micropores and 90% of the pore volume belongs to micropores. Only sample JF8 showed an average pore diameters larger than

2nm (2.95nm). All other samples had average pore diameter narrower than 2nm (according to IUPAC micropores). It is possible to conclude that the activated carbon obtained from the jute fiber is essentially microporous.

The increase of SSA is mostly related to wall destruction, turning micropores into mesopores, and not to the creation of new pores. This phenomenon has been reported in previous investigations (Phan et al. 2006, Asadullah et al. 2014).

Figure 5A shows pore size distributions of two samples (JFA1 and JFA2) and Figure 5B shows pore size distributions of JFA6 and JFA8, all obtained according to the Non-Local Density Functional Theory (NLDFT). Sample JFA1 exhibits just one peak, which is inside the micropore region (less than 2nm), confirming the data from the N_2 isotherms, coherent with the 98% of micropores in the sample. Sample JFA2 also contains a large presence of micropores (diameter narrower than 5nm). Samples JFA6 and JFA8 have similar behavior, with large incidence of micropores and two other smaller peaks in the mesopore region, in agreement with the data from Table IV, with area composed of 93% of micropores and only 7% pores with diameter wider than 5nm. The percentage of volume in the micropore region of these samples is 85%.

CONCLUSIONS

The thermogravimetric analysis heating rate did not affect the mass losses, indicating they depend only on temperature. The major portion of the volatile matter was removed within the range $260^\circ\text{C} - 430^\circ\text{C}$. Above 600°C there is no significant mass loss. For the inert and carbonic gas atmospheres the thermogramimetric analysis indicates the presence of two peaks of mass loss while for the synthetic air atmosphere it indicates the presence of three peaks of mass loss.

A mass based average yield of 18% and an average specific surface area of $470 \text{ m}^2 \cdot \text{g}^{-1}$ was observed. The activated carbon from jute fiber structure characterization indicates a microporous

Table IV
Activated carbon structure related data.

Analysis	JFA1	JFA2	JFA6	JFA8
<i>Surface area data</i>				
Multi BET ($\text{m}^2 \cdot \text{g}^{-1}$)	361.50	475.70	547.90	748.90
t-method external surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	1.74	3.90	15.60	53.00
t-method micropore area ($\text{m}^2 \cdot \text{g}^{-1}$)	359.80	471.80	532.30	695.80
NLDFT method cumulative surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	357.80	422.40	467.90	596.50
Micropore surface area (%)	99.50	99.20	93.7	92.90
<i>Pore volume data</i>				
Total pore volume for pores with diameter less than 1083.4 Å at $P/P_0 = 0.98173$ ($\text{cm}^3 \cdot \text{g}^{-1}$)	0.18	0.24	0.31	0.55
t-method micropore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	0.17	0.23	0.28	0.44
NLDFT method cumulative pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	0.16	0.21	0.28	0.50
Micropore volume (%)	97.80	95.90	88.30	79.00
<i>Pore size data</i>				
Average pore diameter (nm)	1.97	2.00	2.30	2.95
NLDFT method pore diameter (Mode) (nm)	1.54	1.54	1.54	1.47

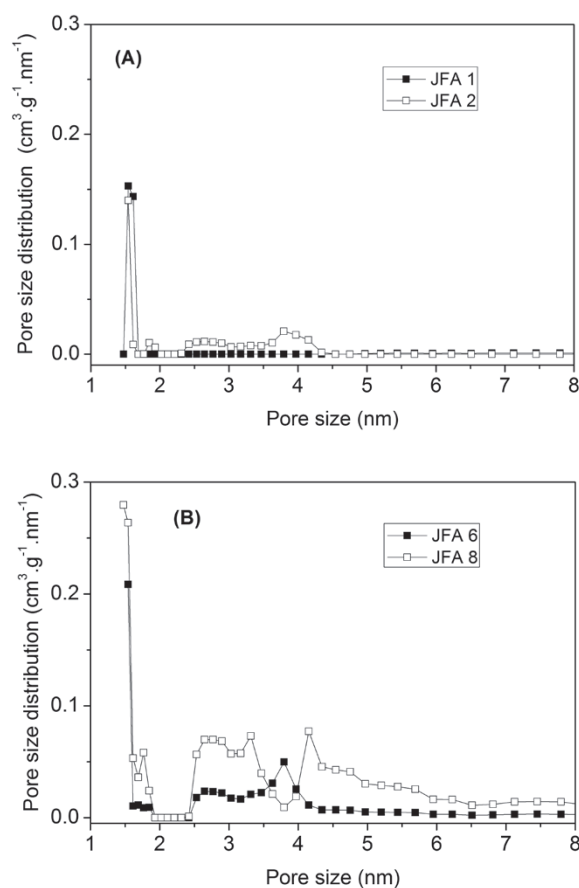


Fig. 5 - Pore size distribution: (A) sample JFA1 and JFA 2; (B) sample JFA6 and JFA8.

material with minor presence of mesopores, although this may be changed by activation conditions. Mild temperatures and mild steam flow rates produce low specific surface areas. The porous structure is made up of micropores, totalling 92% of total volume. It was also observed that extreme activation times and gas flow rates result in higher surface areas, but still with high concentration of micropores. Therefore the jute fibers proved to be a good and versatile precursor of activated carbon.

RESUMO

A fibra de juta é a segunda fibra natural de celulose mais comum no mundo, especialmente nos últimos anos, em virtude de suas excelentes propriedades físicas, químicas e estruturais. O objetivo deste trabalho foi investigar: a degradação térmica da fibra de juta *in natura*, e a produção e caracterização do carvão ativado obtido. A produção consistiu na carbonização e ativação com vapor d'água da fibra de juta. Durante a etapa de ativação, o carbono amorfo produzido na fase inicial de carbonização reagiu com gás oxidante, formando novos poros e abrindo os poros fechados, o que aumenta a capacidade de adsorção do carvão ativado. Adsorção de N_2 a 77K foi usada para

avaliar o efeito das etapas de carbonização e ativação. Os resultados da adsorção indicam a possibilidade de produzir um material poroso com uma combinação de estrutura microporosa e mesoporosa, dependendo dos parâmetros utilizados nos processos, com área superficial específica em torno $470 \text{ m}^2 \cdot \text{g}^{-1}$. A análise térmica indica que acima de 600°C não há perda significativa de massa.

Palavras-chave: ativação, adsorção, carbonização, fibra de juta, termogravimetria.

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