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ACTIVATION TIME EFFECT ON ACTIVATED CARBON FROM COCONUT SHELL TO ENHANCE CO_2 ADSORPTION

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Abstract. *This work discusses the adsorption evaluation of carbon dioxide, CO_2, on physically activated carbons, from coconut shell (Cocos Nucifera, L.). The maximum temperature used in the rotary electric kiln during the whole thermal processes was 950 ºC, the heating rate being 10 °C.min^{-1}. Two residence times were used for the activation: 25 min and 50 min. The physicochemical characteristics of the adsorbents produced were obtained from scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and surface area determination (BET, micropore surface area and pore size). The adsorption tests were carried out at a constant temperature of 27 ° C for 120 min, using a CO_2 flow rate of 50 mL.min^{-1}. With regard to the activation time, it was noticed that the adsorptive capacity of the carbons on CO_2 removal, is directly proportional to its magnitude. For example, the interval of 50 min provided a CO_2 removal 8.0% larger than that achieved with 25 min. Two other factors directly correlated with the increasing of CO_2 adsorption capacity were noticed: the existence of functional groups and the extension of the micropores area.*

Keywords: *adsorption, activated carbon, coconut shell, carbon dioxide*

1. INTRODUCTION

The general concern for reducing gas contamination in the environment, and the consequent increasing of the greenhouse effect, has been motivating the quest for new techniques to improve gas separation and purification processes. One such gas is carbon dioxide (CO_2), and a convenient solution could be the use of materials having high adsorption capacity and great diameter size selectivity and fast reaction kinetics (Nugent et al., 2013). In fact, activated carbon has been widely used as a catalyst, support for catalysts and adsorbent in gas and liquid separation processes due to its high porosity, specific surface area and high degree of surface reactivity (Dias et al., 2007). In our research, physically activated carbons were produced via pyrolysis (absence of oxygen), and consequent exposure to steam or to CO_2 flow. Such a process of production presents low costs, especially when using biomass rejects as precursor. In the preparation of activated carbons, the heating rate, time of residence, temperature of pyrolysis, or of activation, have great influence on their quality. This work examines the influence of the time of activation on the characteristic of activated carbons produced in an electrical rotary kiln using coconut shell as raw material. These effects were also considered in experimental tests to evaluate the contribution of this parameter on the CO_2 removal. The characterization of the activated carbons was done using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and BET surface analysis.

2. EXPERIMENTAL PROCEDURE

2.1 The raw material preparation

To facilitate the removal of the remaining endosperm, the coconut shells were exposed to the sun in the open air, see Figure 1 (I). Then, the following procedures were applied: 1. take out of the flesh residues; 2. removal of the fibers on the outer shell, with the aid of a grinder, see Fig. 1 (II); 3. Crushing of the shell using a hammer mill, see Fig. 1 (III). 4. the raw material was screened through a vibratory sieve shaker, shown in Figure 1 (IV), of 4 mesh.

Figure 1. Phases of preparation of the raw material (coconut shell) to serve as precursor for activated carbons. (I – coconut shell open air drying, II – The grinder III – Hammer mill, IV – Electromagnetic sieve shaker).

2.2 Pyrolisis and Activation Process (Activation Carbon Production)

Both pyrolysis and the activation process were performed in an electrical rotary kiln, having temperature and heating ramp rate control. The kiln was coupled with a water steam boiler, see Figure 2. All activation process was done under a ramp of 10 $°C.min^{-1}$, and the temperature went from room temperature (30 °C) up to 950 °C. After reaching 950 °C the samples remained under a steam flow of 1.0 $kg.h^{-1}$, for two different situations: 25 min of activation time (activated carbon CS25) and 50 min of activation time (activated carbon CS50).

Figure 2. Electrical rotary kiln coupled to a water steam boiler

2.3 Scanning electron microscopy

The adsorbent morphology was characterized by MEV-LEO model VP1430; Carl Zeiss, Oberkochen, Germany, using voltage of 20 kv. see Fig. 3. The samples were mounted on an aluminum platform using a strip of carbon with a thin layer of gold deposited by Emitech Spray of K550X.

Figure 3. MEV (LEO modelo VP1430; Carl Zeiss, Oberkochen, Germany)

2.4 The adsorbent characterization

A Fourier transform infrared (FTIR) spectroscopy was used to identify the functional groups on the surface of the produced activated carbon. FTIR analysis was performed on an IRPrestigie-21 Shimadzu spectrophotometer where the small and dried particle size samples, were mixed with KBr, powder and measured (ASTM, 2011a).

An indirect method using a determined mass of activated carbon within a flask with a known volume was employed to determine the apparent specific mass. The sample of the activated carbon was dried at 105 °C for about 1 hour and allowed to cool to room temperature in a desiccator, thus, avoiding gain of humidity. Thereafter, a 5 cm^3 test tube was weighed and 1 cm^3 of activated carbon was added. The whole set was then weighed. The corresponding specific mass was determined by Eq. (1):

$$D_{Aparente} = \frac{M_{CA} - M_p}{V} \tag{1}$$

Where,
$\mathbf{D}_{Aparente}$ is the apparent specific mass
$\boldsymbol{M_{CA}}$ is the activade carbono mass
$\boldsymbol{M_p}$**:** mass of the test tube
$\boldsymbol{V}$**:** activated carbono filled volume

To determine the activated carbons textural characterization data, a Micromeritics ASAP 2020 microporosimeter, see Figure 4, was employed. Adsorption isotherms of nitrogen at 77 K were performed to evaluate the surface area, volume and size of pores of activated carbons, from samples of 0.25 g, degassed at 300 °C (Medeiros et al., 2008).

Figure 4. Diagram of shear modulus versus frequency at 303 K

2.5 CO_2 adsorption

The adsorptive capacities to capture CO_2 (99.98% purity) of the produced granular activated carbons, were determined using a thermogravimetric analyzer (TA Instruments TGA), see Figure 5. About 30 mg of adsorbent was placed on the TGA sample pan. Nitrogen gas entering the furnace from the balance chamber flows direct across the sample, which was heated at 120 °C, for one hour, to purge out the volatile components (moisture, solvents and residual monomers). At the end of the experiment the sample was cooled to 25 °C, when it was exposed to a 50 $mL.min^{-1}$ flow of CO_2 during 200 min (ASTM, 2011b).

Figure 5. Thermogravimetric analyzer (TA Instruments TGA)

3. RESULTS AND DISCUSSION

Carbon dioxide adsorption isotherms for both CS25 and CS50 carbons are shown in Fig. 6. These isotherms are type II according to the IUPAC classification and H4 hysteresis. The H4 hysteresis is often related to Types I and II isotherms, generally associated with higher gas capture rate, at low partial pressure, as a result of the existence of micropores. The H4 hysteresis are often found in mesoporous zeolites and micro-mesoporous carbons (Thommes *et al*., 2015).

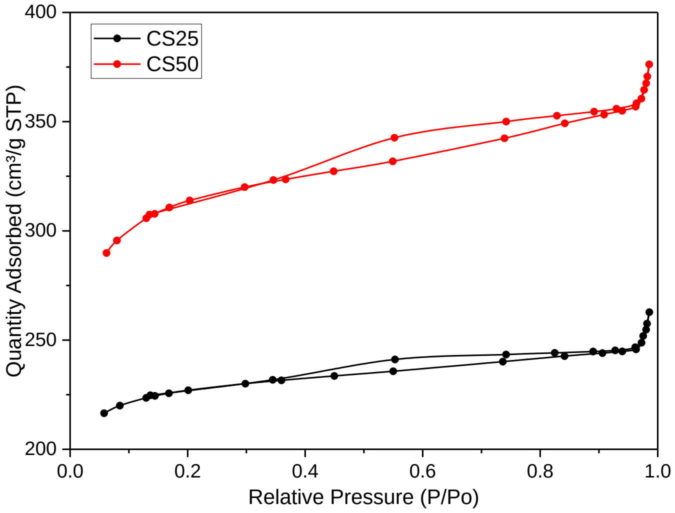

Figure 6. Nitrogen adsorption–desorption isotherms for CS25 e CS50

Table 1. Surface characteristics of activated carbon produced.

Composite Properties	BET (m^2.g^{-1})	Micropores (m^2.g^{-1})	Average pores size (nm)	apparent density (g .cm^3)
CS25	765.66	632.80	2.06	0,6277
CS50	1065.33	814.07	2.13	0,5289

The basic difference between the activated carbons CS25 and CS50 was a 25 minutes rise in activation time to prepare the CS50. Such an increase seems to have contributed to improve the activated carbon surface characteristics, see Table 1. The consequent effects: a larger BET surface area (1065.33 m^2.g^{-1}) and a greater microporous area (814.07 m^2 .g^{-1}). On the other hand, the values of the average pore size do not seem to have been influenced by the time of activation.

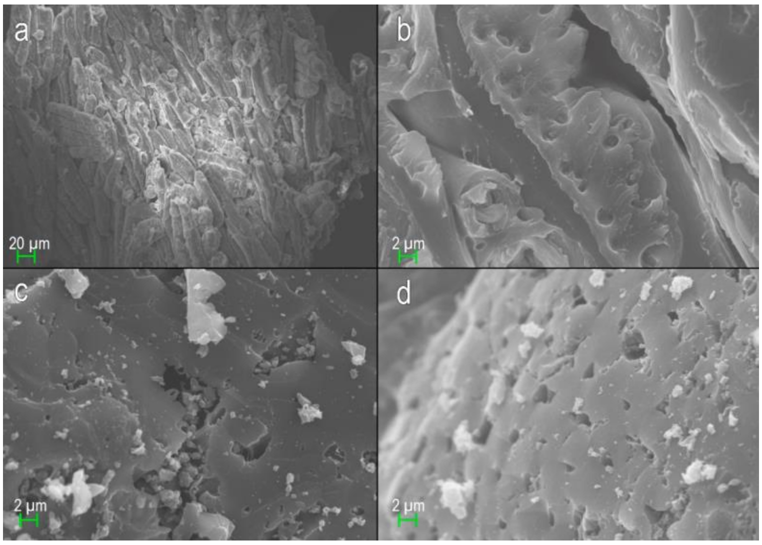

Figure 7. Scanning electron micrographs of (a-b) coconut shell, (c) CS25 and (d) CS50

Figures 7a and 7b show the MEV results of the raw material surface with a large amount of lignocellulose. Such a condition guarantees its rigid structure with few number of pores. In Figures 7c and 7d, it is possible to see the action of the activation treatment, as well as the influence of the increased time of activation, which enlarged the number of pores of the activated carbon CS50, in relation to CS25, giving the former a better CO_2 adsorption capacity, see Figure 8a.

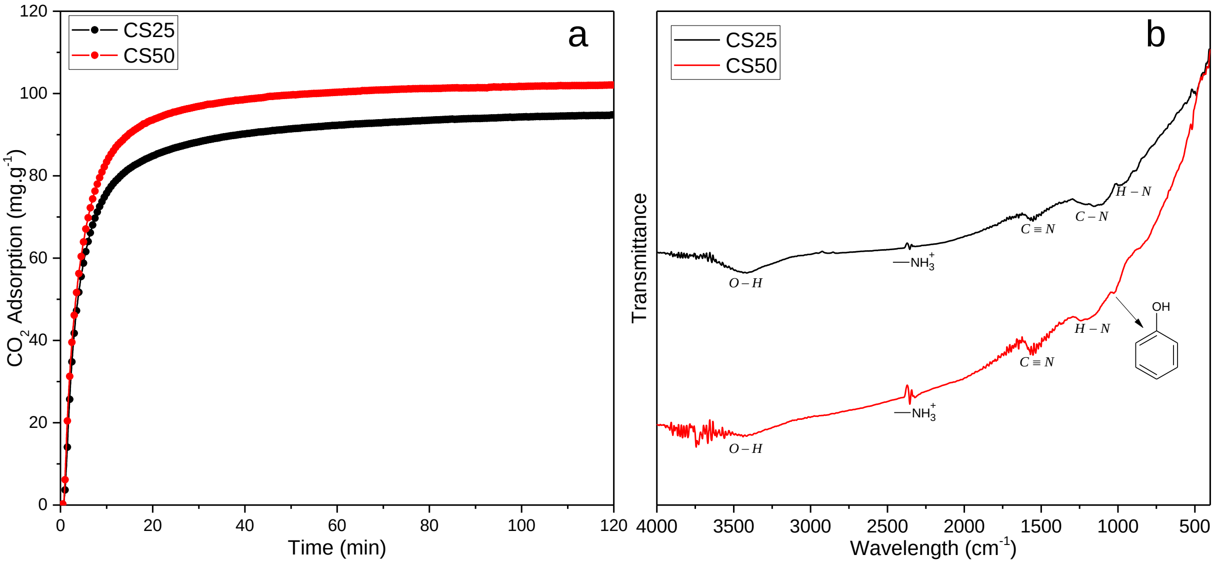

Figure 8. (a) Adsorption isotherm of CO_2 at CS25 and CS50 to 27 °C (b) Solid FTIR spectra of activated carbon CS25 and CS50.

The CO_2 adsorption capacities of the CS25 and CS50 activated carbons were, respectively, 94.89 mg.g^{-1} and 102.42 mg.g^{-1}. The expressive difference in these values may be explained by the dissimilar appearance registered by the FTIR analysis, see Fig. 8b, showing adversity in the chemical composition of the surfaces of both activated carbons, as, a result of the different times of activation considered. As well known, porous materials presenting organic amines on their surface, which was the case, have a tendency to interact chemically with CO_2 molecules, increasing the substance potentiality to capture CO_2 (Shafeeyan et al., 2010).

4. CONCLUSIONS

As shown in the results, the increase in activation time favors the enlargement of microporous area, improving the activated carbon capacity to remove CO_2. The ability of these activated carbons to adsorb CO_2 was also influenced by the fact that the raw material used was biomass. As we know, biomass can contribute to enhance the presence of high amount of amine groups on the activated carbon surface, and their capacity to capture CO_2 (Meng et al., 2009).

5. ACKNOWLEDGMENTS

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6. REFERENCES

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7. RESPONSIBILITY NOTICE