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Micro Mesoporous Activated Carbon from Coffee Husk as Biomass Waste for Environmental Applications

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Abstract Activated carbons (ACs) with a highly developed porosity have been prepared from a lignocellulosic precursor (coffee husk) for environmental pollutant adsorption. Characterization results show that these materials exhibit a high amount oxygen groups and high specific surface area with micro mesopores. From SEM results we can see the collapse of large pores at longer activation times. The ACs obtained from coffee husk waste is a promising adsorbent material, with high adsorption capacity for the methylene blue dye (MB). Thus, the use of the coffee husk for AC preparation, with porosity development, showed as a good alternative for the waste transformation. Results also showed that the adsorption of MB by the AC-1/1 was much better than commercial AC from Merck.

Keywords Activated carbon · Coffee waste · Micro mesoporous · Methylene blue adsorption

Introduction

The growing concern with the conservation of natural resources has been one of the main issues since the beginning

of this century. Together with the global population growth, the amount of wastes generated has also increased and consequently the environmental pollution. Brazil, for being basically a country with an agrarian economy, has an immense variety of agro industry wastes whose processing would be extremely advantageous and of good economic and social interest. Currently, a great amount of lignocellulosic waste is discarded or simply burned, constituting a serious environmental problem (soil contamination and water and air pollution). As such, the study and development of a technology for the use of those wastes, besides reducing the size of the environmental problems, transforming it into value added materials, is very important.

A promising alternative for the transformation of lignocellulosic wastes is activated carbon (AC) production. The AC possesses countless applications, such as: gas storage, use in the pharmaceutical industry, water and air treatment, environmental decontamination processes, catalysis and the food industry. When activated, the starting materials undergoes partial oxidation in the walls of the pre-existing channels, thus developing a high surface area (usually over 400 m² g), forming AC, a porous carbonaceous material with a non-graphitic crystalline structure [1].

The specific surface area, porosity and surface properties are important characteristics for determination of AC application. They depend on different parameters of AC preparation such as the activating agent, activation temperature, gas flow, activation time and the precursor characteristics [2].

For the production of AC with high surface area and developed porosity, several precursors are used, from virgin materials to a wide variety of wastes. Some authors report the AC from peach pit, herb residues [3], coconut husk [4], cotton waste [5], coffee wastes [6], cherry pit [7], palm seed [8], wood wastes [9], straw or rice husk [10], leather waste [11], and others.

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Our group has worked with several wastes for the activated carbons (ACs) preparation, among them coffee wastes, such as coffee beans [12] and parchment [13]. The aim of this work was to prepare ACs from coffee husks, activated with ZnCl_2 with high surface area and porosity development. Also, we proposed the application of the obtained ACs in the adsorption process using methylene blue dye molecules as a model.

Experimental

Preparation of Activated Carbons

The coffee husk was used as precursor for AC preparation in this work due the amount produced in Brazil, (about 2.5 million tons year) [14]. This waste was obtained from the EPAMIG experimental farm, located in the municipal district of Machado-MG. The waste was washed and dried for 24 h at 383 K and ground to a size between 500 and 1,000 μm . Soon after, it was impregnated with ZnCl_2 at different mass proportions (see in Table 1), at 383 K for 24 h and activated in a tubular oven (Blue Lindberg) under N_2 flow (100 mL min^{-1}) at 773 K, in different time (Table 1) with a heating rate of 10 K min^{-1} . After the activation, the ZnCl_2 was completely removed with HCl solution (5 mol L^{-1}) at 353 K. The excess acid was removed with distilled water and the AC obtained was dried overnight at 383 K. The pH of ACs was measured and showed value between 4.5 and 5.0.

It is important to report that the temperature was optimized in previous studies by thermogravimetric analysis in other experiments in our group [6].

Characterization of Activated Carbons

The adsorption/desorption of nitrogen at 77 K was performed with ACs samples treated at 523 K for 4 h in a

Quantachrome Autosorb apparatus. The apparent specific surface area was obtained by Brunauer–Emmett–Teller (BET) equation, micropore volumes (V_{N_2}) by the Dubinin–Radushkevich (DR) equation and the mesopore volume was calculated by the difference between total pore volume ($V_{0.95}$) and V_{N_2} . The pore size distribution was obtained by DFT application to the nitrogen adsorption.

The morphology of the ACs was analyzed by scanning electron microscopy (SEM) in a LEO EVO 40XVP equipment; the elemental analysis of carbon, hydrogen, nitrogen and oxygen (CHNO) were carried out in a FLASH EA apparatus, 1,112 series; the ash content was determined in a Lindberg Blue tubular oven under air atmosphere at 1,173 K for 4 h. The analysis of the surface groups present on ACs was carried out by temperature programmed desorption (TPD), where the CO and CO_2 gases were monitored using Balzers OmnistarTM equipment with mass detector. A 100 mg sample was used in a quartz reactor, under a He flow of 50 mL min^{-1} with a heating ramp of $10 \text{ }^\circ\text{C min}^{-1}$ up to 1,000 $^\circ\text{C}$. For quantification, the calibration was conducted with calcium oxalate monohydrate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$).

Evaluation of AC Efficiency in the Adsorption Process

The evaluation of the adsorption capacity of the prepared carbons was carried out with the model compound methylene blue dye (MB). The adsorption was conducted in batch, where 10 mg of AC were put in contact with 10 mL of solution of the methylene blue dye (MB), $\text{pH } 5.0 \pm 0.5$, at the concentrations of 25, 50, 100, 250, 500 and 1,000 mg L^{-1} , for a period of 24 h at room temperature ($298 \text{ K} \pm 2$). That period was determined based on other adsorption kinetics work conducted by our group [15]. The remaining concentration was evaluated in a UV–VIS spectrophotometer (Biosystems SP-2000) at a wavelength of 665 nm. The same procedure was carried out with commercial AC from Merck in order to compare the maximum adsorption capacity.

Results and Discussion

Characterization of Carbons

A good precursor should present, mainly, high carbon and low ash content, in order to obtain a material with high surface area and porosity development. The coffee husk analysis (Table 1) shows that waste possesses all those characteristics, a low ash content level ($<2 \%$) and a high amount of carbon (40 %). After the activation, the ash content found for all ACs was low (between 2 and 3 %). That was due to the chemical composition of the precursor and it is also indicative of the removal efficiency of the ZnCl_2 (quantified by atomic absorption $<0.1 \%$). In the

Table 1 Experimental conditions for the AC preparation and elemental analysis (CHNO) of the ACs and husk

AC ^a	Waste/ ZnCl_2	Time (h)	C ^b (%)	H (%)	O ^c (%)	Ash (%)
Husk	–	–	40	6	50	1.5 (± 0.3)
AC-4/1	4/1	1	58	3	34	2.0 (± 0.3)
AC-1/1	1/1	1	62	3	30	2.3 (± 0.1)
AC-1/2	1/2	1	68	3	23	3.0 (± 0.2)
AC-2 h	1/1	2	68	3	23	3.0 (± 0.3)
AC-3 h	1/1	3	67	3	23	3.0 (± 0.4)
AC-4 h	1/1	4	68	3	22	3.0 (± 0.2)

^a Average of three repetitions; standard deviation, ^b ± 2 , and ^c ± 1

literature ash content values from 0.3 % to 15 % are reported for AC, depending on the activation method, activating agent removal and chemical composition of precursor [1]. The ACs obtained showed a good yield, between 25 and 32 %.

The highest activation time eliminated part of the oxygenated groups from the precursor, confirmed by the elementary analysis. The highest oxygen content (30 %) and lowest carbon content (62 %) were found in AC-1 h. These values are in agreement with reports in the literature [16], analyzing different ACs found an amount of carbon between 54 and 72 % and 20 % oxygen.

The alteration in the coffee husk morphology by the activation process was evaluated by scanning electronic microscopy (SEM). Figure 1 presents the micrographs of coffee husk and ACs at different activation times at the 1/1 mass proportion (waste/ZnCl₂). It is verified that a

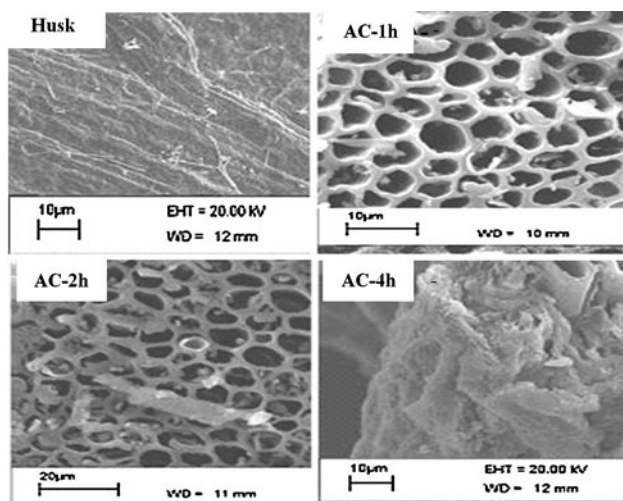


Fig. 1 Micrographs of coffee husk and different ACs

considerable change occurred in the husk morphology after the activation process. The change is more accentuated for the carbons prepared under shorter activation times, 1 and 2 h, forming a beehive type structure, with wide pores (macropores > 500 Å) attributed only to the decomposition of volatile compounds [17]. A decrease of the macropores with longer activation time (3 and 4 h) occurs, which can be due to their collapse in function of the prolonged time under high temperatures.

Nitrogen adsorption–desorption isotherms at 77.4 K (Fig. 2) clearly exhibits a combination of Type I and Type IV isotherms, characteristic of microporous materials with presence of mesopores for the AC-1/1 and AC-1/2 samples [18]. The form of the shape formed, under low relative pressure, indicates pore size distribution heterogeneity, with narrow micropores and the desorption hysteresis is evidence of mesopores [3]. As can be observed in pore size distribution (Fig. 3), samples AC-1/1 and AC-1/2 exhibit an important contribution between 10 and 15 Å, which must correspond to the micropores, together with a second contribution between 20 and 30 Å, corresponding to the mesopores, in close agreement with isotherms. For other ACs, the isotherms can be classified as Type I, characteristic of microporous materials; this is confirmed by the pore size distribution (Fig. 3). That is in agreement with data from the literature, where most of the carbons activated with ZnCl₂ possess microporous characteristics [10].

As can see in Fig. 2, AC 1/1 and AC 1/2 presented the highest N₂ adsorption while the low proportion of activating agent, AC 4/1, seems not to be enough for the complete activation. The ACs with longer activation time (4 h) showed lower N₂ adsorption capacity than others with less duration. That can be due to ZnCl₂ evaporation at high temperature (500 °C) and long activation times, followed by pore collapse, evidenced in the ACs micrographs.

The apparent surface area found for the ACs (Table 2) was high when compared with data in the literature. Boon-amnuayvitaya et al. [19], activating coffee waste with CO₂ and ZnCl₂ at a duration from 2 to 4 h, found area values

Fig. 2 Isotherms of N₂ adsorption/desorption at −196 °C: (a) effect of activation time, and (b) effect of the activating proportion

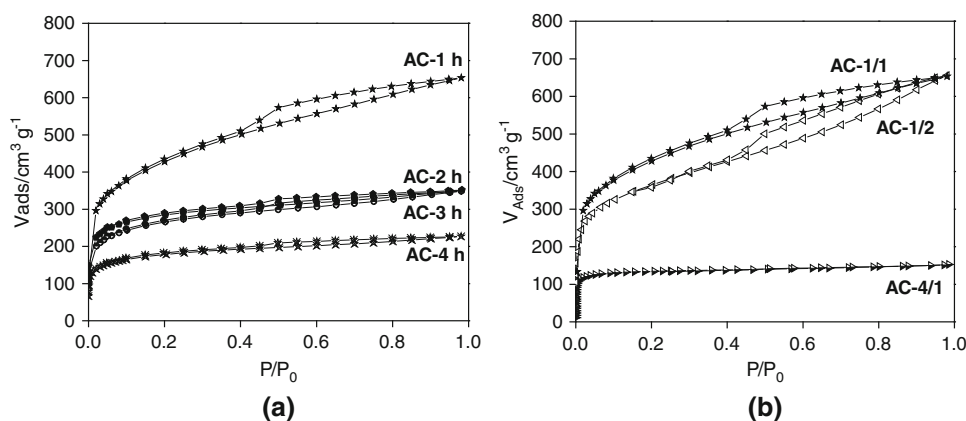


Fig. 3 Pore size distributions profile after application of the DFT method to the nitrogen adsorption: (a) effect of activation time, and (b) effect of the activating proportion

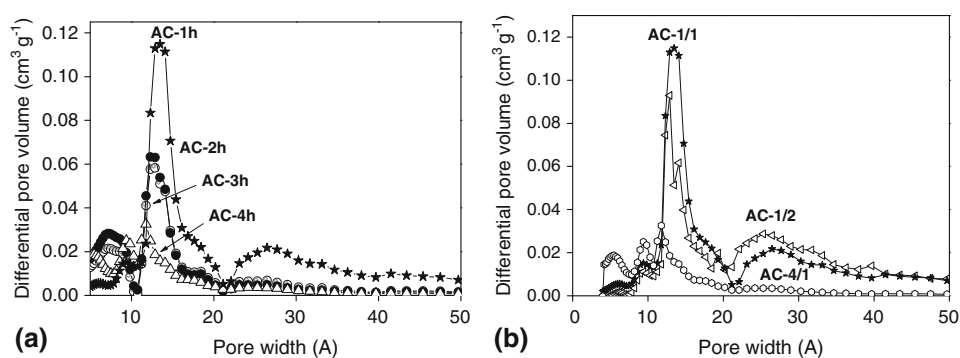


Table 2 Textural analysis: BET (S_{BET}) surface area and pore size distribution and oxygen surface group quantification for the different AC

AC	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	$V_{0.95}$ ($\text{cm}^3 \text{g}^{-1}$)	V_{N_2} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)	CO_2 (mmol g^{-1})	CO (mmol g^{-1})
AC-4/1 ^a	490	0.23	0.22	0.01	2.00	7.18
AC-1/1 ^a	1,530	0.99	0.65	0.34	2.43	6.25
AC-1/2 ^a	1,300	0.98	0.56	0.44	2.20	5.38
AC-2 h ^b	1,030	0.54	0.41	0.13	2.30	4.62
AC-3 h ^b	960	0.53	0.37	0.16	2.12	4.58
AC-4 h ^b	640	0.35	0.25	0.10	3.12	4.72

^a Activation time: 1 h

^b Waste/activating

between 140 and $913 \text{ m}^2 \text{g}^{-1}$. In other works developed in our group with other coffee wastes, such as defective grains and parchment, activated in same proportion (1/1), the surface area found was 516 and $521 \text{ m}^2 \text{g}^{-1}$ respectively [13, 14].

The nature of the oxygen groups on the AC can be analyzed by temperature-programmed desorption experiments (TPD), in which these groups are analyzed in the forms of CO and CO_2 . According to CO_2 and CO desorption profiles, all ACs were very similar (data not shown here). Figure 4 shows the CO_2 and CO desorption profiles for the AC-4 h and AC-1 h in the 298–1,223 K temperature range.

As can be observed in TPD profiles, the ACs exhibit one peak between 373 and 873 K for CO_2 decomposition, which can be attributed the carboxylic, anhydride or lactone groups. The peak for CO_2 decomposition at high temperature, around 873–973 K, can indicate the oxygen in the form of ethers and carboxylic anhydride groups [20]. Also one peak is observed centered at 873 K for CO decomposition, which can be attributed to decomposition of the quinone, pyrone, phenol, carboxylic anhydride or carboxylic groups [20].

Although the TPD profile for CO_2 and CO are very similar for all ACs, the amount of these groups, obtained by the integration of the areas of the TPD, is different. According to results in Table 2, the amount of oxygen groups evolved as CO, decreased after a longer activation time (6.25 – 4.52 mmol g^{-1}). However, the longer activation time, did not show an effect on the total amount of

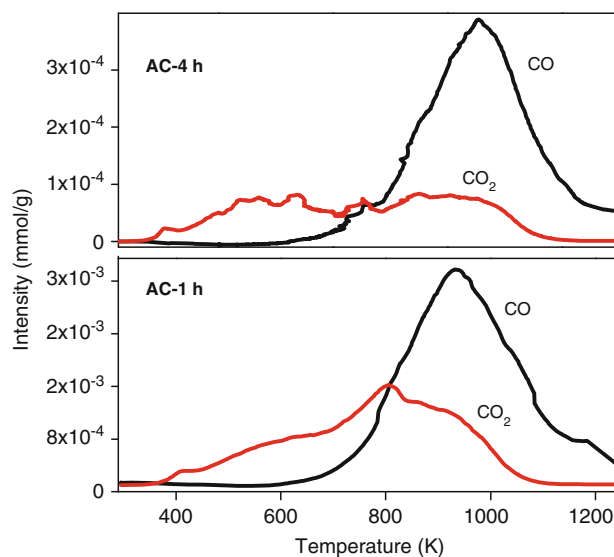


Fig. 4 Temperature programmed desorption (TPD) for the activated carbons at 1 and 4 h at a 1/1 ratio (waste/activating)

oxygen groups evolved as CO_2 (2.42 – 2.12 mmol g^{-1}). This can be attributed to the oxidation undergone by the long exposure time to the atmospheric air (4 months), that is, the gradual aging of AC. According to Menendez et al. [21], the materials treated with N_2 possess a more reactive surface and when exposed to the air, tend to oxidize quickly.

Fig. 5 Methylene blue adsorption isotherms (average of three repetitions): (a) AC activated with different waste/activating proportions and methylene blue molecule; (b) ACs in different activation time. Reaction conditions: initial pH = 5.0 ± 0.5 , room temperature (25°C)

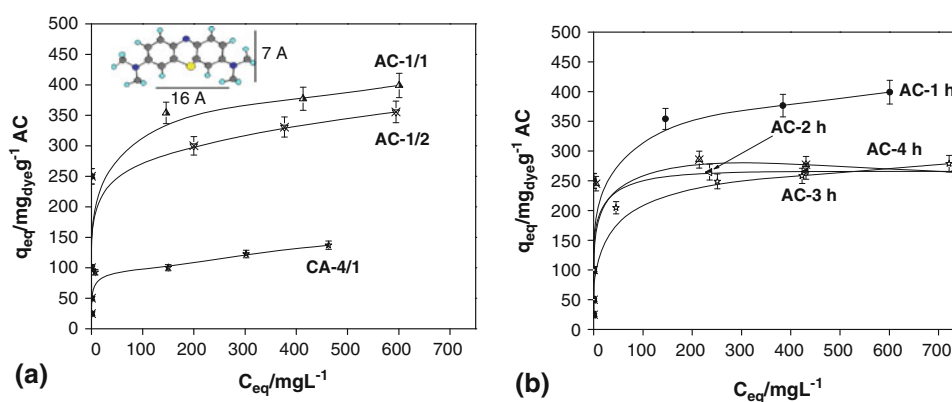


Table 3 Langmuir parameters for adsorption of MB isotherms for the all ACs

AC	AC-1/1	AC-1/2	AC-4/1	AC-2 h	AC-3 h	AC-4 h
q_m (mg g^{-1})	398	344	133	263	270	277
K_L (L mg^{-1})	0.27	0.18	0.09	6.33	0.31	0.11
r^2	0.99	0.99	0.99	0.99	0.99	0.99

For ACs activated at different proportions, an increase of oxygen groups, evolved as CO, with decrease of mass proportion of activating agent was observed ($5.38\text{--}7.18 \text{ mmol g}^{-1}$). The high concentration of oxygenated groups present in the AC-4/1 (7.18 mmol g^{-1}), can be evidence that the activation was not effective, corroborating with the N_2 adsorption and SEM data obtained. The amount of oxygenated groups found was relatively high when compared with some literature data. Dandekar et al. [22], analyzing a commercial Norit A8933 carbon, found values of 1.52 and 1.76 mmol g^{-1} respectively for CO_2 and CO. Rey et al. [23], characterizing different carbons, found amounts of CO_2 of 2.8 and 3.3 mmol g^{-1} for the Centaur HSL and Norit Row 0.8 Supra carbons, respectively. However, the amount of oxygen groups, desorbed as CO, is very similar to that found by Zhuang et al. [24] ($0.67\text{--}7.06 \text{ mmol g}^{-1}$) for the carbon resins.

Evaluation of the Adsorptive Properties of the Carbons

The adsorption over AC is not only influenced by the pore size and surface area, but also the high amount of oxygen groups, mainly in the adsorption of polar molecules. The adsorption tests in liquid phase were conducted with a cationic molecule, methylene blue (MB), which presents a surface area of $1.93 \text{ m}^2 \text{ g}^{-1}$ and molecular size of $0.7 \times 1.6 \text{ nm}$ (based on Van der Waals radius) [25].

The MB adsorption isotherms (Fig. 5) are characteristic of the Langmuir model, which the adsorption occurs in monolayers, reaching equilibrium at low concentrations. This was confirmed by the Langmuir linearization and the parameters obtained as: q_m , a monolayer adsorption capacity (mg g^{-1}) and K_L , the constant related to the free energy (Lg^{-1}), are showed in Table 3.

The AC with the highest adsorption capacity was AC-1/1, with a maximum adsorption of 398 mg g^{-1} , a value higher than that of a commercial Merck AC (237 mg g^{-1}). The high adsorption capacity of this AC can be attributed to its higher microporosity because the pH of carbons does not present significant difference. The small size of MB favors its adsorption in microporous carbons. The AC-4/1 removed only 133 mg g^{-1} , showing that the surface area and porosity are the decisive factor for the MB adsorption capacity. The other ACs activated in different time, 2, 3 and 4 h, did not present considerable difference among the maximum adsorption, removing approximately 270 mg g^{-1} . The MB adsorption capacity is similar to many carbons from waste found in the literature such as: Cotton stalk (180 mg g^{-1}) [26], jute fibre (225 mg g^{-1}) [27], olive seed (263 mg g^{-1}) [28] and other agriculture wastes (398 mg g^{-1}) [29]. Therefore, using a short activation time (1 h), we can obtain a micro mesoporous AC from an abundant waste, which would be inadequately discarded.

Conclusion

The use of the coffee husk, as precursor in the preparation of AC by chemical activation (ZnCl_2) using 1/1 mass proportion (waste/activating) and 1 h of activation time, was shown as a viable option for the use of this waste, transforming it into a material with aggregate value. The prepared carbon possesses properties appropriate for use as an adsorbent and/or application as a reactive adsorbent (catalyst in oxidation reactions). Under the conditions evaluated, an AC with high surface area, micro mesoporosity presence and high amount

of oxygenated groups and with a MB adsorption capacity higher than a commercial AC was obtained. The adsorption of methylene blue in this material was not influenced by the amount of oxygen groups, only by the surface area.

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