Preparation and Characterization of Activated Carbon from Coffee Waste: Removal of Organic

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Abstract

The coffee fruits processing is one of the most pollutant activities in agriculture due to a large amount of waste generated in the process. In this work, two types of coffee waste, coffee bean pulp and parchment, were employed as precursor for the production of carbons activated with $ZnCl_2$. In a typical preparation the raw material was impregnated with 50% (m/m) of $ZnCl_2$. The mixture was dried at 383 K for 24 h. The dried mixture was pyrolyzed at 773 K for 3 h. The pyrolyzed material was washed with HCl 20% and water. The materials were characterized by N_2 adsorption/desorption at 77 K, infrared spectroscopy (FTIR), scanning electronic microscopy (SEM).The activated carbons were tested as adsorbent for the removal of the methylene blue dye from aqueous medium. In comparison with the commercial carbons, the activated carbons from coffee waste showed higher specific surface areas with values of 974 m^2g^{-1} for pulp and 522 m^2g^{-1} for parchment. Both materials showed mainly micropores structure. Methylene blue removal capacity showed to be comparable to commercial product, with adsorption capacities of 500 mgg^{-1} for pulp and 188 mgg^{-1} for parchment.

Introduction

Agriculture generates residues, which can be used, furnishing by-products with more added values or disposed, providing waste and problems. The use of waste resources instead the use of other resources is a necessity that comes rising and techniques or process that make it possible is suitable and desirable. The coffee fruits processing is one of the most pollutant activities in agriculture due to a large amount of waste generated in the process. For each kilogram of processing coffee we have a kilogram of waste. For the produce of soluble coffee the amount of residue is up to 97%. In 2006, Brazil consolidated its position as the world's largest producer and exporter of coffee. The main market segment for coffee in Brazil is still the export of green grains, but in the last four years, we also were exporting soluble coffee (Abreu, 2007). All this production, however, results in a large amount of coffee waste (husk, parchment and pulp) that has to be management. The inadequate disposal of these wastes can contaminate water recourses and soils. The scheme of a coffee bean showing the several parts of the fruit can be seen in Figure 1.

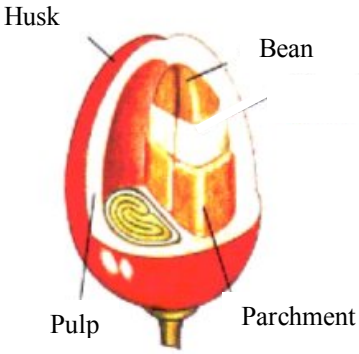

Figure 1. Scheme of a coffee bean (*Coffee arabica*)

Other problem is the large amount of dyes industries wastewater discharged in water streams. Industries such as paper, rubber, plastics, cosmetics, foods and others also use dyes in some step of the process and, consequently, produce colorized wastewater. In particular printing and dyeing unit wastewater contain several types of coloring agents with are difficult to be treated by biological methods (Namasivayam & Kavitha, 2002). One of the most important treatment for the removal of dissolved organics from water is the use of activated carbon as adsorbent. Thus, the objective of this study was use coffee residues (husk+pulp and parchment, Figure 1), a low cost and abundant source, to produce carbon, activated with $ZnCl_2$. Namasivayam and Sangeetha, using agricultural solid waste to produce activated carbon observed that the material activated with $ZnCl_2$ has a high surface area if compared to the area of carbon prepared in the absence of $ZnCl_2$

After the activation the carbons from coffee residues were tested in adsorption experiments, for removal methylene blue dye (basic dye with cationic characteristics) from water.

Materials and Methods

Materials

Coffee husk+pulp (HP) and coffee parchment (PC) were provided by the experimental farm of EPAMIG (Agricultural Research Enterprise of Minas Gerais, Machado, MG, Brazil). The organic model molecule used in the adsorption tests was methylene blue (Merck), a basic dye. The commercial activated carbon used to compare the methylene blue adsorption capacity by the coffee activated carbons (Aldrich).

Preparation of the activated carbons

The materials were sieved to 250-420 μm particle size, dried at 110°C for 24 h, impregnated with $ZnCl_2$ 1:1 weight ratio and pyrolyzed at 500°C for 3 h under N_2 (100 mL min^{-1}). After the activation, carbon was washed with a 0,1 M HCl solution and with water until neutral pH.

Characterization of the materials

BET area and pore volume of the samples were determined by nitrogen (77K) adsorption-desorption isotherms measured by Gas Sorption Analyzer (Quantachrome NOVA-1200). The surface areas were calculated using BET equation and the pore volumes were calculated using the BJH methods.

The Fourier transform infrared spectra (FTIR) were recorded on a Digilab Excalibur–FT3000 using 0,1% of carbon in a KBr pellet.

The BET areas were analyzed by scanning electronic microscopy (SEM) using a LEO EVO 40XVP microscope.

Adsorption of methylene blue

The adsorption isotherms were obtained by stiring 10 mg of carbon in a 10 mL of methylene blue solution in several concentrations (10, 25, 50 100, 250, 500 e 1000 mgL^{-1}) for 24 h at 25°C. After, the supernatant was centrifuged (Sigma 3K30) at 10000 rpm for 15 min and analyzed spectrophotometrically, to determine the amount of residual adsorbate. The analyses were carried out in a UV/Vis Biosystems SP-2000 at 660 nm (wavelength of maximum absorption of methylene blue). The Langmuir equation was used to determine the maximum adsorption capacity of the prepared carbons.

Results and discussion

Specific surface area and pore volume

Figure 2 shows the N_2 adsorption-desorption isotherms of parchment (PC) and husk+pulp (HP) activated carbons. The isotherm adsorption type furnishes qualitative information about the adsorption mechanism and porous structure of the activated carbon. The isotherms show in Figure 2 exhibited type I, typical of micropores solids (porous smaller than 20Å). The gradient of the initial part of the isotherm, from P/P_o values from zero to about 0.05 are indicative of the dimensions of the microporosity, the steeper the gradient the narrower are the micropores (Marsh & Rodríguez-Reinoso, 2006). In these isotherms the micropores filling occurs more intensively in a low partial pressure. At 0.2 P/P_o the adsorption process is almost completed.

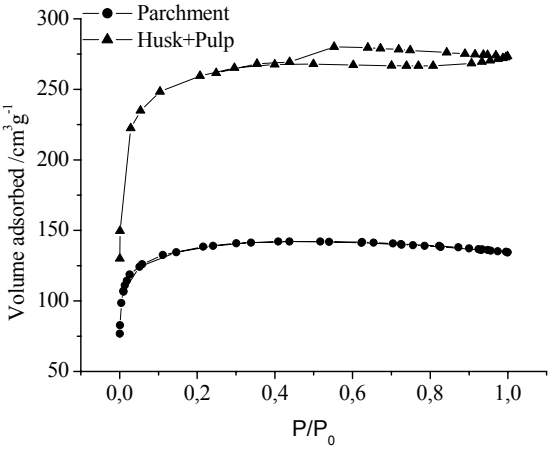

Figure 2. Nitrogen adsorption-desorption isotherm of PC and HP activated carbons.

Commercial activated carbons have BET surface area around 900 to 1200 m^2g^{-1}. BET surface area obtained for PC and HP activated carbons were 522 and 974 m^2g^{-1} respectively.

Porous size distribution of coffee PC and HP activated carbons are show in Figure 3. The maximum pore volume for PC and HP occur around 5 and 10 Å respectively, confirming the micropores structure of the prepared carbons.

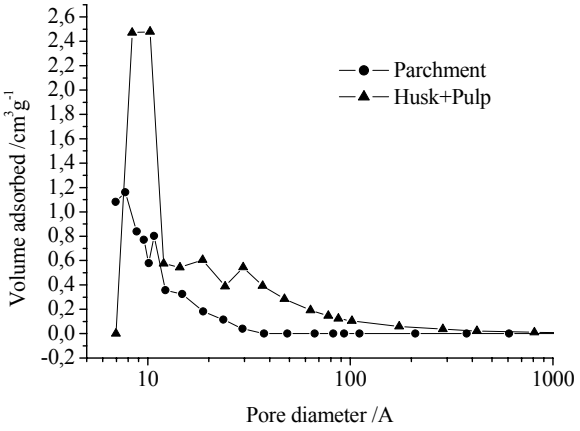

Figure 3. Porous size distribution of coffee parchment (PC) and husk+pulp (HP) activated carbon

The FTIR spectrum of the carbons precursors (HP and PC) show characteristics band of lignocellulosic materials (Figure 4). A strong broad O-H band in ~ 3400 cm^{-1}; a band in ~2900 cm^{-1}, referent to a C-H stretching vibrating in methylene group; a band in ~1650 cm^{-1}, referent to a C=O stretching vibrating in ketone, a band in ~1500 cm^{-1}, referent to a C=C stretching vibrating in aromatics and a band in ~1000 to 1200 cm^{-1} referent to a C-O of cellulose, hemicelluloses and lignin. This region we can also indicate the presence of C-N stretching vibrating. Boonanmnuayvitaya, Chaiya *at al*, and Boonanmnuayvitaya, Sae-ung *et al*, in studies using activated carbon from coffee residues obtained similar data.

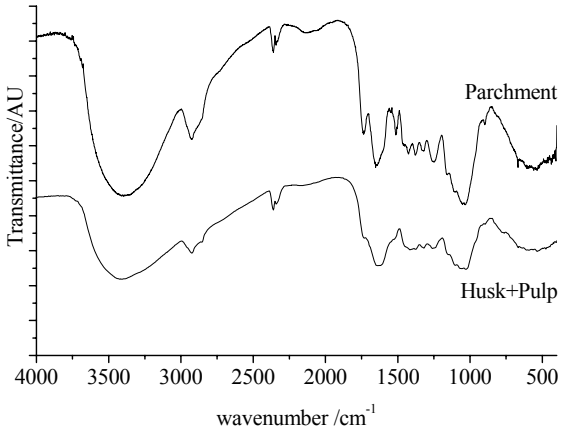

Figure 4. FTIR of coffee husk+pulp (HP) and parchment (PC), precursors of the carbons

After the pyrolysis of the materials the band in ~3400 cm^{-1} (refers to O-H hydrophilic group) is still observed (although less intense), however, is stronger for the HP carbon (Figure 5). On the other hand, the band in ~2900 cm^{-1} (C-H hydrophobic group) appears only in the HP carbon spectrum. The band in ~1650 cm^{-1} (C=O hydrophilic group) is more intense in HP and PC spectra. HP activated carbon seems to have more hydrophilic groups than PC and Commercial activated carbons.

Finally, comparing Figure 4 and 5 we can observe that the band in ~2900 cm^{-1} almost disappear, suggesting the carbonization of the material. It should be notice a band in ~1000 cm^{-1}, present in the HP carbon spectrum and not present in the other spectra. This band can suggests the presence of a C-N bond, since the amount of nitrogen in HP is three times higher than the amount in PC (Brum, 2006).

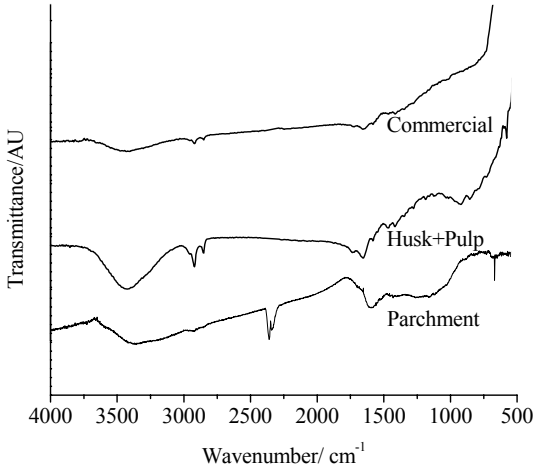

Figure 5. FTIR of coffee husk+pulp (HP) and parchment (PC) activates carbons

Figure 6 show the micrographs of the coffee residues and respectively activated carbons produced. PC surface shows to be quite uniform and plain. The activated carbon (Figure 6-b) seems to be a sponge like structure, showing fractures and wrinkles. The SEM micrograph (c) shows a fibrous structure and in (d) we can observe a honey comb like structure.

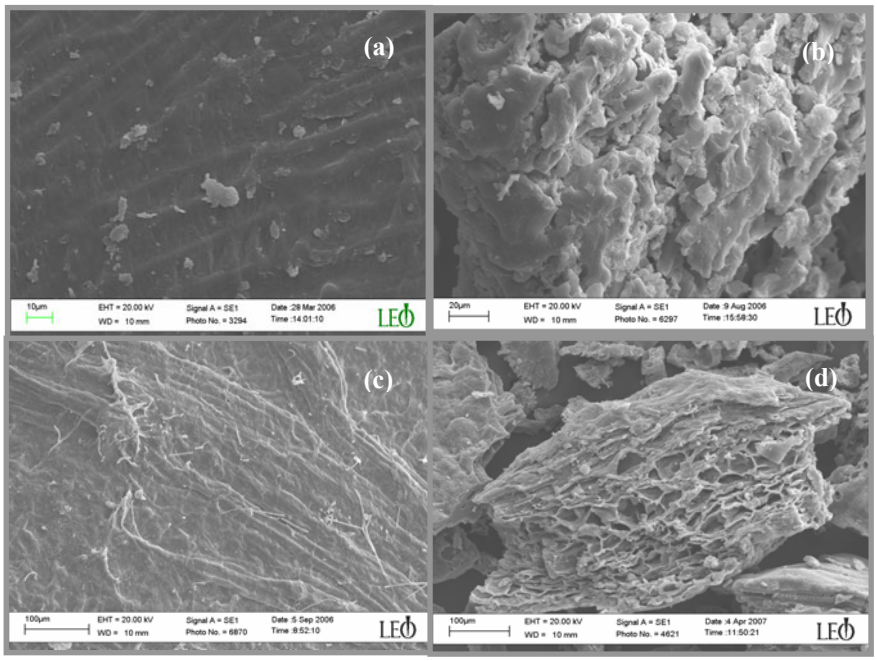

Figure 6. SEM micrographs of: (a) PC, (b) PC activated carbon, (c) HP, (d) HP activated carbon.

The adsorption test results are show in Figure 7. The methylene blue molecule presented more affinity by HP carbon than by the other carbons (PC and Commercial). This is confirmed by the order of methylene blue dye adsorption capacity: HP ($500 mg_{dye} g^{-1}_{HP}$) > Commercial ($232\ mg_{dye} g^{-1}_{commercial}$) > PC ($188 mg_{dye} g^{-1}_{PC}$). Figure 7 shows the isotherms for the two tested materials (PC and HP) and the Commercial activated carbon.

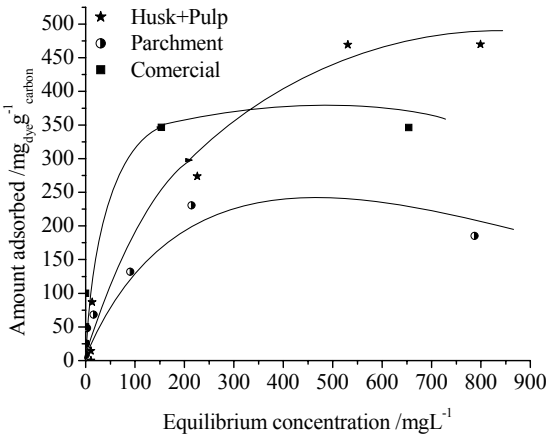

Figure 7. Absorption isotherms, at room temperature, of the methylene blue dye on the activated carbons.

Conclusions

The present study shows that the activated carbons obtained from coffee residues (husk+pulp and parchment) are good adsorbents for methylene blue dye if compared with the Commercial activated carbon. The best results were obtained from HP carbon which yields the largest BET area and the highest adsorption capacity.

Acknowledgment

Authors are grateful to the Chemistry Department, CAPQ and LME laboratories and financial support from CAPES, FAPEMIG and CNPq.

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