Activated Carbon from Leather Shaving Waste, Part II. Effect of Char Demineralization and Activation Time on Surface Area and Pore Size Distribution

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Abstract

Leather shaving wastes generated by the leather industry can be used for microporous activated carbon production. In this work, chrome leather shaving wastes were pyrolyzed in a semi-continuous pilot screw reactor at 450°C. The char obtained was activated using carbon dioxide in a tubular reactor at 900°C. The effect of using nitrogen or carbon dioxide in the heating step of the activation process on the pore size distribution and cumulative pore volume was evaluated. Carbon dioxide reduced the pore volume in the mesopore region. Changing time in the carbon activation (4 and 6 h) was not significant on the surface area, increasing it from 757.9 m^2g^{-1} to 927.4 m^2g^{-1}. However, the demineralization had a significant effect on the surface area, increasing it from 427.7 m^2g^{-1} to 927.4 m^2g^{-1} for 6 h of activation. The pore size distribution of non-demineralized activated carbon was very similar to the one of demineralized activated carbon, showing a cumulative pore volume mainly in the region of micropores.

Introduction

The leather industry generates great amounts of solid wastes. The conventional disposal methods are not practicable for chrome tanned leather waste since Cr^{3+} may leach from the waste and be converted into Cr^{6+}.[1] Leather biodegrades slowly and treatments using different chemicals during the tanning process make it resistant to chemical, thermal and microbiological degradation.[1] As an alternative, the production of activated carbon from leather waste has been presented by some authors.[2,3]

Pyrolysis is the main process for biomass thermal conversion. The process occurs in the absence of oxygen. The products formed during the pyrolysis are a condensable fraction (bio-oil), a non-condensable fraction (fuel gases), and a solid material rich in carbon (char). Char produced in the pyrolysis process can be treated for activated carbon production. The production of activated carbon can be performed in two steps: i) biomass is carbonized in an inert atmosphere generating a carbonaceous material (char); ii) char is activated in high temperatures (800°C – 1000°C). The activation process aims to promote an increase in the surface area and at the pores development. According to Yahya *et al.*,[4] the activation process opens previously inaccessible pores, develops new pores by selective activation and widens the existing ones. Generally, micropores increase the surface area, while the macropores work as a channel to access micropore surfaces.

The production of activated carbon from different biomass is reported in the literature.[5-8] However, just in few studies activated carbon is produced from leather waste. In one of these works, Gil *et al.*[9] presented leather waste pyrolysis process and the characterization of the gaseous, condensable and char fractions produced. The authors reported that pyrolysis processes need to present an optimal condensable and gaseous fraction for energy purposes and need to obtain enough carbon and solid yield to prepare activated carbon from the char. Kantarli and Yanik[3] studied carbon activation of char obtained from leather waste and showed a comparison of the physical and chemical activation process. Surface areas of 796 m^2g^{-1} and 820 m^2g^{-1} were found for physical and chemical activations, respectively, and promising results in dye, chromium, and

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phenol removal from aqueous systems were reported. Oliveira *et al.*[10] observed that activated carbon obtained from leather waste presented substantial differences in specific areas (889 m^2g^{-1} and 556 m^2g^{-1}) when produced with different activation times (0.5 h and 2 h). Furthermore, carbon produced in 0.5 h presented the type I isotherm and the carbon prepared with 2 h of physical activation presented type II isotherm, indicating the presence of, respectively, micro and mesopores. In the case of activated carbons from biomass, the main goal is to reach high surface areas. It is possible to achieve it by char demineralization. The demineralization step can be carried out with acidic or basic reagents and it is usually used to remove undesired minerals.[11]

In this work, the production of activated carbon from leather shaving waste was evaluated. Char obtained from pyrolysis was activated at 900°C for 4 and 6 h under carbon dioxide (CO_2) atmosphere. Char demineralization before the activation process was studied in order to evaluate its influence on the surface area.

Materials and Methods

Leather Waste

The leather shavings waste used in this work was supplied by Peles Pampa (Brazil) and its characterization[12-16] is presented in Table I. The samples were dried at 105°C to constant weight before the thermal treatments.

Characterization Methods

Mineral analysis was carried out according to the method 3111 of the Standard Methods for the Examination of Water and Wastewater.[13] Leather waste, char and activated carbon surface morphology was observed using a field emission gun scanning electron microscope (FEG-SEM) (TASCAN, Mira 3) equipped with an energy-dispersive X-ray analyzing system. Surface area, pore volume and pore diameter were characterized by N_2 adsorption/desorption isotherms at 77.3 K in a surface area and porosimetry analyzer (QUANTACHROME INSTRUMENTS, Nova 1200). Samples were outgassed under vacuum at 350°C for 20 h prior to testing. The surface area was determined by Brunauer-Emmett-Teller (BET) and pore size distribution by the density functional theory (DFT). The total pore volume ($V_{0.98}$) was determined from the amount of nitrogen adsorbed at P/P_0 = 0.98. The micropore area (S_{micro}) and the micropore volume (V_{micro}) were estimated by t-plot.

The mole fraction of gas produced during the activation process was measured in a gas chromatograph (DANI, Master GC). The analyses were performed using N_2 as the carrier gas at a flow rate of 3 mL min^{-1} in a Carboxen 1006 packed column. The temperature of the thermal conductivity detector (TCD) and of the oven was 100°C and 35°C, respectively.

Pyrolysis Process

Semi-continuous Pilot Screw Reactor

A semi-continuous pilot screw reactor was used for leather waste pyrolysis process. The reactor has a 2 m long screw conveyor with 195 mm of diameter and 195 mm of pitch. The bed was heated by the combustion gases from the LPG burner that flows in counterflow in a jacket around the screw conveyor. The char formed was deposited gravimetrically in a reservoir at the bottom of the reactor. Pyrolysis gases were separated in a flash separator, which has an external cooling belt to cool the gases and condensate the compounds of higher molar weight. Ferreira et al.[17] accurately described this reactor. The reactor was fed with 3.0 kg of leather waste and the pyrolysis test was carried out at 450°C. The velocity of the screw conveyor was of 0.169 rpm, which resulted in a residence time of approximately 30 minutes.

Char yield in the pilot reactor was calculated according to Equation 1.

$$Yp = \left(\frac{m}{M}\right) \times 100 \qquad \text{Equation 1}$$

where Yp is pyrolysis yield (%); m is the char mass obtained after pyrolysis reaction (g) and M is the mass of leather waste fed into the reactor (g).

Table I
Characterization of leather waste.

Parameters	Method	Results
Proximate analysis (wt%)		
Volatile matter	ASTM D-3176	76.78
Ash	ASTM D-3176	7.59
Fixed Carbon[a]	ASTM D-3176	15.63
Ultimate analysis (wt%)		
Chrome Cr_{total}	SMEWW	2.92
Sulfur	ASTM D-4239	1.98
Carbon	ASTM D-5373	42.12
Hydrogen	ASTM D-5373	5.75
Nitrogen	ASTM D-5373	16.28
Other analysis		
HHV (MJ kg^{-1})	ASTM D-5865	18.61

[a]By difference

In the pilot reactor, the fuel gas yield was measured by the difference between the mass of leather waste fed into the reactor and the sum of the char mass and bio-oil mass produced.

Demineralization and Physical Activation of Carbon

Char obtained in the pyrolysis process was demineralized with hydrochloric acid (HCl - 3 mol L^{-1}). The samples were kept under shaking conditions (100 rpm) at 35°C for 24 h. The demineralized char was rinsed with tap water until pH 6-7 and dried at 105°C for 24 h. The demineralized and non-demineralized char were activated for 4 and 6 h. Non-demineralized and demineralized char were activated in a tubular fixed-bed reactor, which is made up of a stainless steel tube AISI 310, with 85 mm of internal diameter and 129 cm of length. Electrical resistances heated the reactor. After the reactor had been fed with 300 g of char, the activation process was performed with N_2 and CO_2 in the heating step as described below. The reactor was heated to 900°C under N_2 or CO_2 atmosphere (0.8 L min^{-1}). In the first case, when the final temperature was reached, N_2 was replaced by CO_2 (0.8 L min^{-1}). After the activation time, N_2 was used again while the system was cooling until room temperature was reached. A factorial experimental design was used to evaluate the influence of char demineralization and activation time on the activated carbon surface (Table II).

The yield of carbon activation process was evaluated from the burn-off (BO), according to Equation 2.

$$BO = \frac{m_1 - m_2}{m_1} \times 100 \qquad \text{Equation 2}$$

where BO is burning-off (%); m_1 is the initial mass of char fed into the reactor (g) and m_2 is the mass of activated carbon obtained at the end of the reaction.

Table II
Factors and respective levels evaluated in the 2^k factorial experimental design for carbon activation.

Factors	Corresponding factor	Coded level	
		-1	+1
X_1	Residence time (h)	4	6
X_2	Demineralization	Yes	No

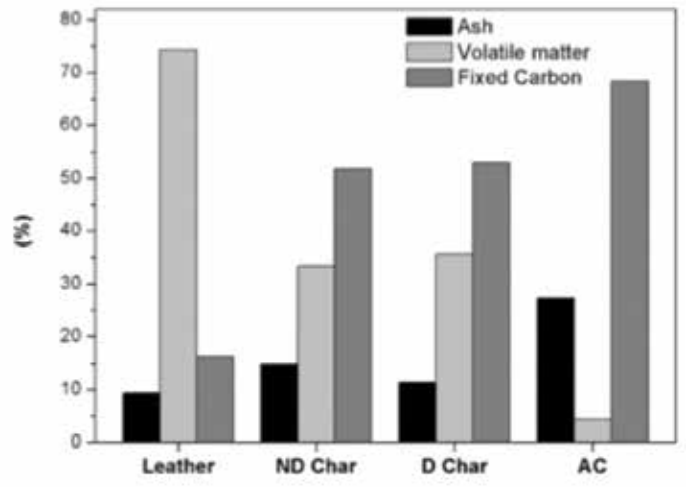

Figure 1. Ash, volatile matter and fixed carbon for the leather waste, non-demineralized char (ND char), demineralized char (D char), and activated carbon (AC).

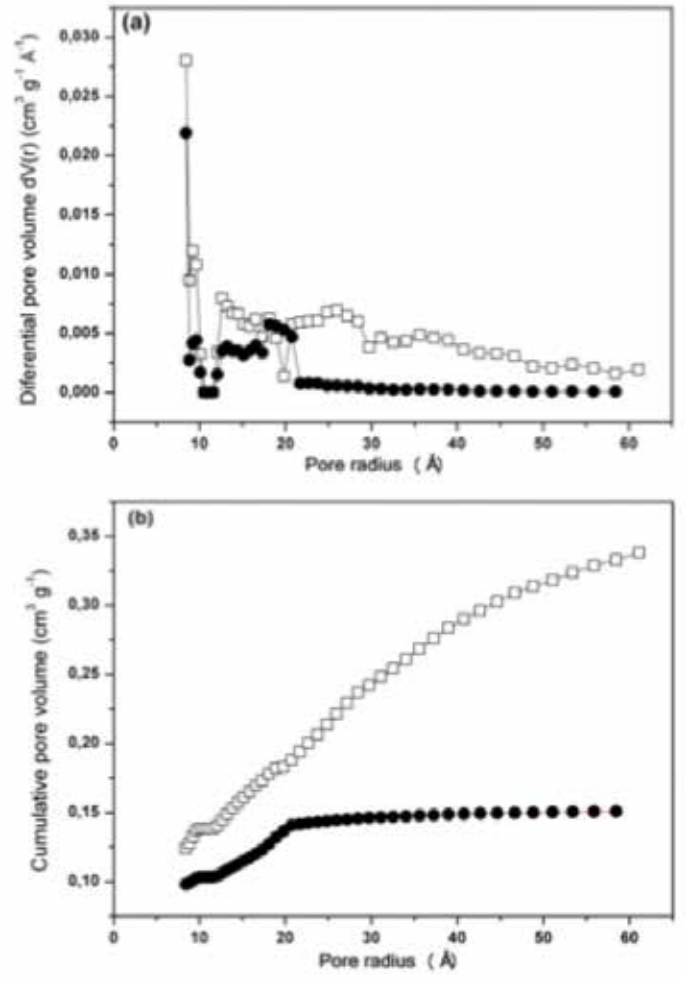

Figure 2. Pore size distribution (a) and cumulative pore volume (b) by DFT method obtained in the activation carbon process using N_2 (□) and CO_2 (●) in the reactor heating step.

Results and Discussion

Proximate Analysis of Char

Because of pyrolysis process, the ash and carbon content increased in the char samples. Activated carbon presented the same behavior after activation process (Figure 1). This phenomenon occurs due to the release of organic material and volatilization of hydrogen, oxygen and nitrogen. According to Gill *et al.*,[18] the high carbon content found in the leather waste used in the pyrolysis process makes this material highly suitable for activated carbon production. Furthermore, the char generated in the pyrolysis process can be used in pulverized coal injection (PCI) process, which is a promising technology.

Effect of Physical Activation Conditions on the Activated Carbon

The first test carried out in the process of carbon activation was the comparison between the N_2 and CO_2 atmospheres in the heating step. Char activation was performed for 3 h. BET surface area was higher for activated carbons produced in the N_2 atmosphere, 398.7 m^2g^{-1}, while for the CO_2 atmosphere, a surface area of 245.9 m^2g^{-1} was obtained. However, when evaluating pore distribution (DFT) (Figure 2), it is possible to observe that when N_2 was used to heat the reactor until 900°C, the pore volume was higher in the range of 20 Å. In other words, the mesopore volume was higher in this condition. The cumulative pore volume results support the above statement and clearly show the contribution of the mesopores.

Other tests were performed under CO_2 atmosphere at 900°C for 4 and 6 h. The results are presented in Table IV and are discussed based on the Pareto chart (Figure 3). The samples treated for 4 or 6 h presented different BET surface areas when char demineralization was carried out, but the activation time effect was not significant, as observed in the Pareto chart. However, statistical analysis confirmed that char demineralization

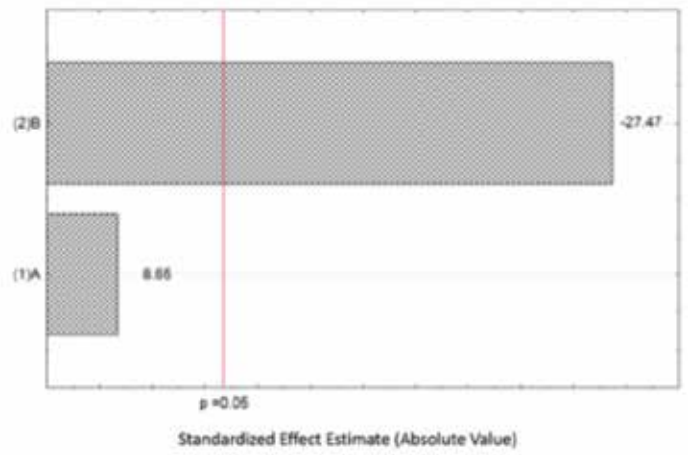

Figure 3. Pareto chart of the effects of time (1)A and demineralization (2)B on the BET surface area.

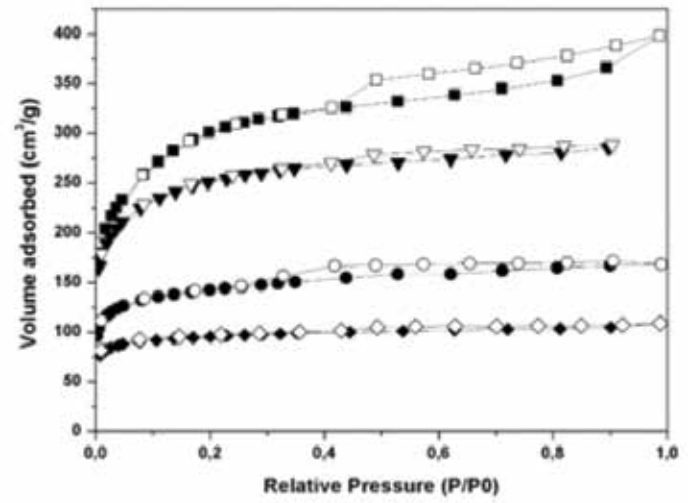

Figure 4. Adsorption isotherm of N_2 on activated carbon prepared at 900°C for 4 h – non-demineralized char (♦), demineralized (▼) and 6 h – non-demineralized char (●), demineralized char (▪).

Table III

Experimental design matrix (coded and real values) and burn-off, BET surface area and pore volume results.

	Codes		Values		BO (%)	S_{BET} (m^2g^{-1})	V_{total} (cm^3g^{-1})	V_{Micro} (cm^3g^{-1})	S_{Micro}	D_{Pore}
Run	X_1	X_2	X_1	X_2					(m^2g^{-1})	(nm)
1	-1	-1	4	Yes	70.0	757.9	0.446	0.285	520.7	1.23
2	-1	+1	4	No	64.7	293.3	0.168	0.125	241.7	1.23
3	+1	-1	6	Yes	82.8	927.4	0.616	0.302	554.1	1.17
4	+1	+1	6	No	58.3	427.7	0.265	0.152	273.3	1.16

X_1 – residence time, X_2 - Demineralization

significantly affected the surface area. A significant increase in the surface area was obtained when performing the demineralization at 35ºC, which differs this work from others that use boiling condition with HCL solutions. Yilmaz *et al.*[2] demineralized char samples using HCL solution (10 wt%) for 2 h at boiling condition. The demineralized samples presented higher BET surface area than the ones of non-demineralized char. This surface area increase can be explained by the removal of mineral material, which also decreases the ash content. Mukherjee and Borthakur[19] carried out coal treatment with HCl 10% and reached a demineralization degree of 28.1%. As previously observed in Figure 1, ash content of the char treated with HCl (3 mol L^{-1}) in a mild temperature condition reduced 23.6%, indicating that part of the mineral material was removed. The results obtained in this work corroborate the statement above, showing that the mineral content, mainly calcium and sodium concentration, was reduced (Table V). The removal of these mineral materials could be causing an increase in the char pores, which allows CO_2 to reach previously unreachable areas. N_2 adsorption/desorption analysis of char samples (before the activation process) proves that the demineralization step increased the surface area determined by BET. The values increased approximately 2.2 times, from 12.80 to 28.11 m^2g^{-1}, for the non-demineralized and demineralized char, respectively. The total pore volume increased from 0.023 to 0.083 cm^3g^{-1} for the same char samples.

Gases Produced During Carbon Activation

The gases produced during the activation process were collected and their molar composition was determined as shown in Table VI. Results prove that, during activation, the Boudouard reaction (Equation 3) successfully occurs. This reaction is used to explain CO_2 activation mechanism. In activation process, an increase in CO mole fraction was observed from 450ºC to 900ºC, while CO_2 was not detected until the isotherm reached 4.5 h. After this time, the carbonaceous material decreased its oxidant capacity and CO_2 was detected. The entire amount of CO produced during the activation process can be recovered and used as synthesis gas.

$$C + CO_2 = 2CO \qquad \text{Equation 3}$$

Textural Properties of the Activated Carbon

The nitrogen adsorption-desorption isotherms at 77 K of the demineralized and non-demineralized activated carbons are shown in Figure 4. The demineralization step increases the amount of N_2 adsorbed. According to the IUPAC classification, the activated carbon demineralized and activated for 6 h presented a mixture of types I and IV isotherms, and an important nitrogen adsorption at low P/P0, indicating a simultaneous presence of micro and mesoporous as described by Oliveira *et al.*[10] for activated carbon from leather waste. Furthermore, the slight rise of the isotherm near P/P0 ≈ 1 may indicate the presence of some macroporous in this structure. The sample demineralized and activated for 4 h presented a typical type I isotherm, which characterizes a microporous material. The volume adsorbed increased more significantly in

Table IV
Mineral analysis of the non-demineralized and demineralized char.

	Non-demineralized char	Demineralized char
Aluminum (g/kg)	4.090	2.320
Calcium (g/kg)	4.070	0.960
Iron (g/kg)	1.024	0.166
Phosphorus (%)	0.32	0.13
Magnesium (g/kg)	1.576	0.352
Potassium (g/kg)	0.128	0.051
Sodium (g/kg)	23.277	1.887

Table V
Molar composition of the gas produced during carbon activation.

	Mole Fraction of Gas			
	H_2	CH_4	CO	CO_2
Heating				
450ºC	0.383	0.193	0.396	nd
600ºC	0.416	0.021	0.557	nd
750ºC	0.210	nd	0.789	nd
900ºC	0.161	nd	0.838	nd
Isotherm 900ºC				
1.5 h	0.016	nd	0.983	nd
3.0 h	0.006	nd	0.986	nd
4.5 h	0.004	nd	0.895	0.100
6.0 h	0.005	nd	0.746	0.247

nd = not detected

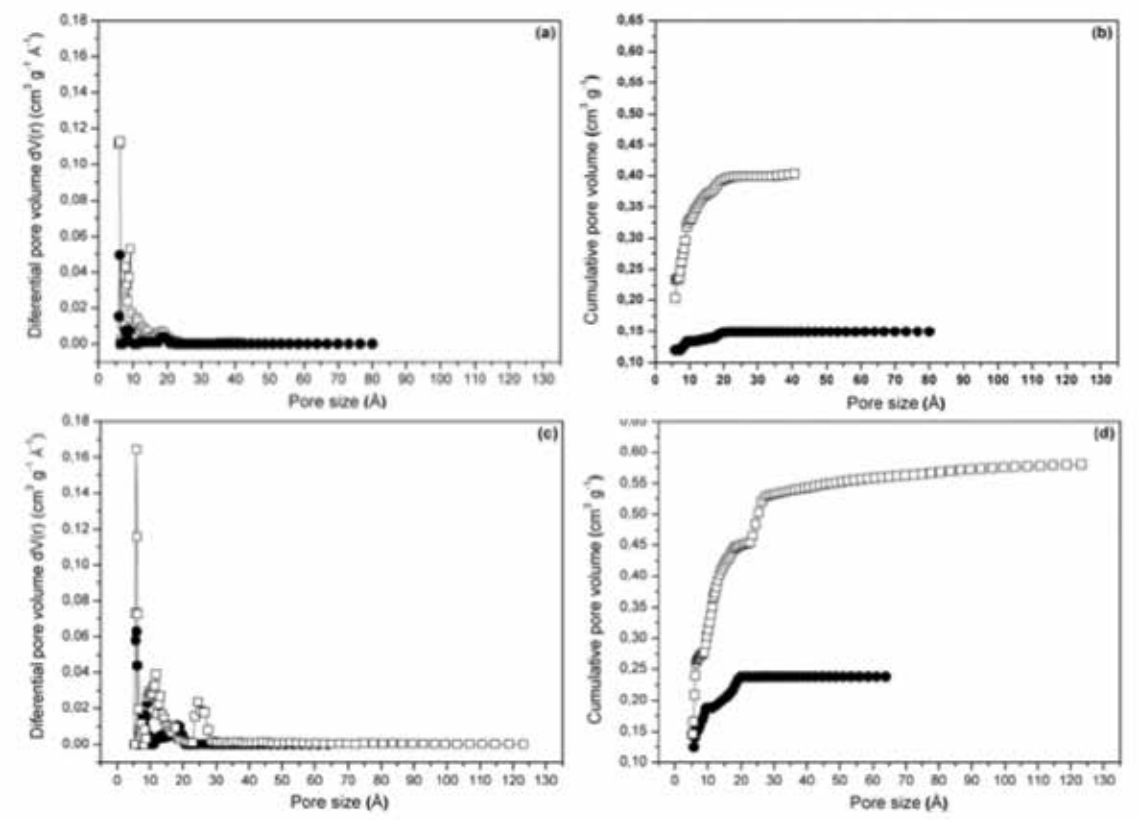

Figure 5. Pore size distribution and cumulative pore volume by the DFT method for non-demineralized samples (●) and demineralized samples (□) activated for 4 h (a, b) and 6 h (c, d).

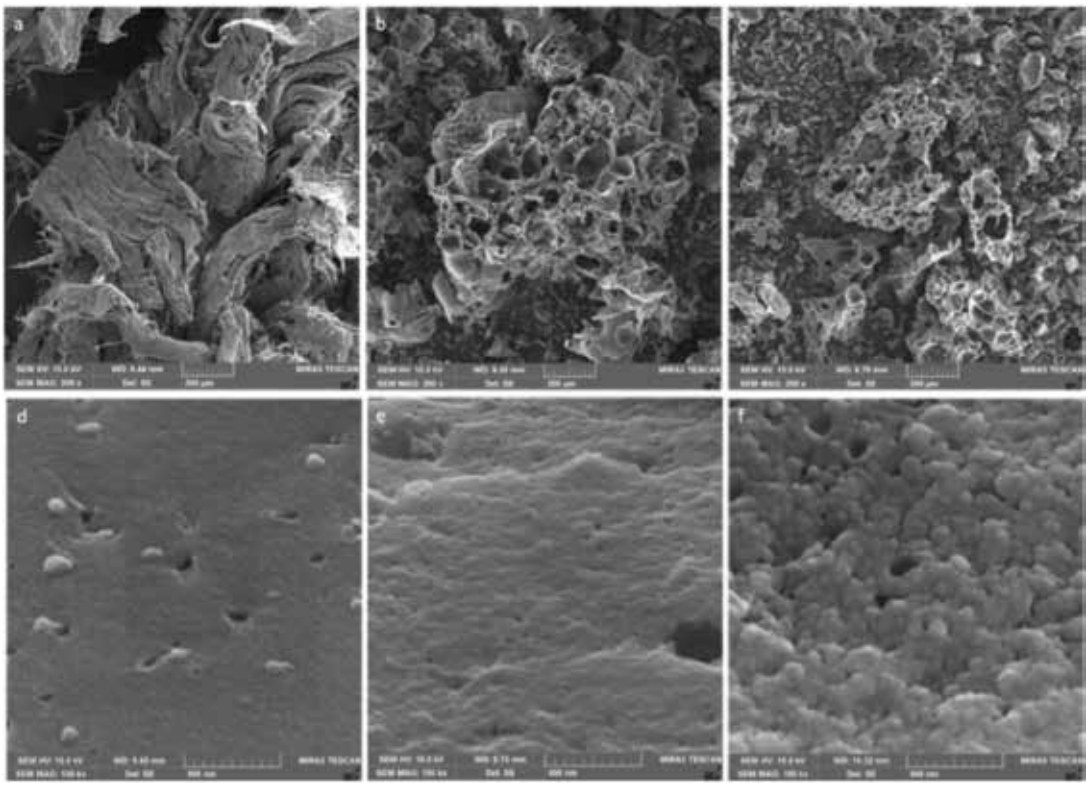

Figure 6. SEM micrographs of the leather waste at 200 x magnification (a), non-demineralized and demineralized char at 200 x magnification (b and c) and 150,000 x magnification (d and e), activated carbon treated for 6 h at 150,000 x magnification (f).

low relative pressures (P/P0 < 0.2). In the carbon activated for 4 h, the values of nitrogen adsorbed at P/P0 > 0.2 increased at a lower rate, tending to stabilize at P/P0 ≈ 0.99.

The hysteresis loop type H4, which is usually associated with capillary condensation, was observed near P/P0 ≈ 0.4 in demineralized samples activated for 4 and 6 h. It may indicate the presence of small mesopores structures.[20] The absence of a hysteresis curve between adsorption and desorption isotherms of the non-demineralized activated carbon may mean that the pores are tubular or wedge-shaped.[21]

The pore size distribution curve, calculated by the DFT method (Figure 5), shows clearly that the activated carbon obtained after the demineralization presented a higher cumulative pore volume in both activation times tested. Furthermore, the cumulative pore volume occurs mainly up to 20 Å, which is the microporous region.

Morphological Analysis

Figure 6 shows the FEG-SEM images of the leather waste and char obtained after pyrolysis process. Figure 6-a shows the fibers of collagen and, as reported by Sethuraman *et al.*,[22] they are coordinately bonded to the ion Cr^{3+} and covalently bonded to organic materials. After the pyrolysis process, chrome leather waste (Figure 6-b and c) became a porous material and the new structure resembles a honeycomb, as described by Bonelli[23] for nutshells after pyrolysis. Figure 6-d and Figure 6-e show that a significant change occurs in the demineralized char surface. The surface became more irregular and new pores or voids were formed. This result is in accordance with the BET surface area, previously discussed, and proves that the demineralization step is important to produce activated carbons with high surface areas. Figure 6-f shows the activated carbon surface, which presented a polygonal grain structure.

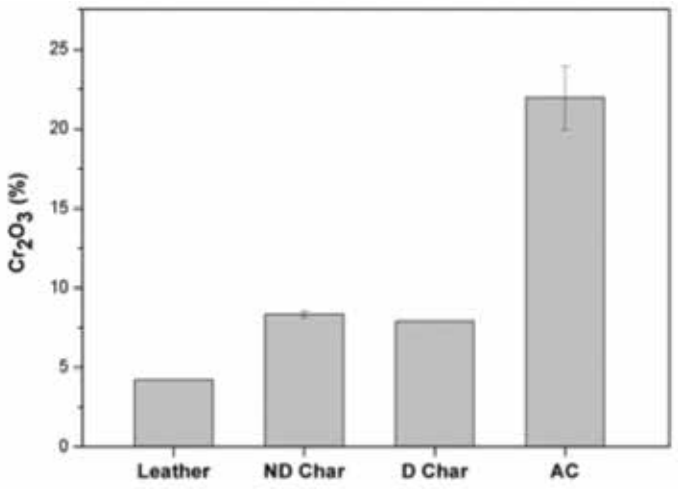

Figure 7. Amount of chromium in the samples of leather waste, non-demineralized (ND) char, demineralized (D) char and activated carbon (AC).

Table VI

Summary of the results for the textural analysis of activated carbon produced from leather waste.

References	Activation process	S_{BET} (m^2g^{-1})	V_{micro} (cm^3g^{-1})	D_{pore} (nm)
Present work	Physical - CO_2, 900°C, 6 h	927.4	0.302	1.17
Yilmaz *et al.*[2]	Physical - CO_2, 900°C, 10 h	799	-	-
Oliveira *et al.*[10]	Physical - CO_2, 850°C, 0.5 h	889	0.390	-
Kantarli and Yanik[3]	Physical - CO_2, 900°C, 3 h	796	0.197	3.06
	Chemical - $ZnCl_2$, 600°C	821	0.333	0.93
	Chemical - H_3PO_4, 600°C	670	-	5.08
Kong *et al.*[25]	Physical - steam, 850°C, 0.5 h	482	0.134	3.29
	Chemical - $H_4P_2O_7$, 450°C	495	0.186	2.67
Gil *et al.*[26]	Chemical - KOH, 750°C	1949	0.641	-
Lopez-Anton *et al.*[27]	Chemical - $ZnCl_2$, 750°C	1602	0.512	0.86

In addition, energy disperse X-ray spectroscopy (EDS) was performed for the samples of non-demineralized and demineralized char. The results indicated that chromium was not removed, as well as other elements that were not washed from the char surface. The approximate amount of Cr determined by EDS (peak at 5.4 keV) in the samples of non-demineralized char, demineralized char and activated carbon was 8.6%, 8.0%, and 18.0%, respectively. The other elements in the char samples were calcium, sodium, aluminum, magnesium, phosphorus, sulfur and chlorine.

Chromium Determination in Samples of Char and Activated Carbon

Chromium presence in the wet-blue leather waste was likely due to the use of chromium oxide in the tanning process. In the pyrolysis process, the material degradation occurs in a reducing environment. Therefore, the conversion of Cr^{3+} to Cr^{6+} is not favored. Chromium was not lixiviated from the char in the demineralization process. As shown in Figure 7, the Cr_2O_3 presented similar values, 7.9% and 8.3%, for the demineralized and non-demineralized char, respectively. The final Cr_2O_3 concentration in the activated carbon was 21.9%. The increase in this value in the activated carbon is due to the carbon consumed in the activation process. Oliveira et al.[24] observed that chromium on the surface of activated carbon obtained from leather waste is not leached in water. In the oxidation tests with methylene blue dye, the same authors showed that chromium in the activated carbon works as a catalyst during the process, indicating that its presence may play an important role in the methylene blue dye removal process.

Table VII presents relevant results for the carbon activation. As observed, there are few studies that use leather wastes in the production of activated carbon and that use physical activation process. The S_{BET} found in this work is coherent with the other works that use physical activation and 4% higher than the S_{BET} presented by Oliveira *et al.*[10] Pore diameter (1.17 nm) is lower than the ones observed by other authors, which contributes for the application of this activated carbon in separation processes.

Conclusions

The production of activated carbon from leather shaving wastes was carried out in this work and at least two general statements can be made: i) a chromium-rich waste, which can be a serious environmental issue, was turned into activated carbon that can be used in many adsorption processes; ii) the gases produced during the pyrolysis and the activation process can be used as fuel or synthesis gases. Furthermore, the demineralization step at a mild temperature (35ºC) was effective, which differentiates this work from the ones of other authors who performed demineralization at boiling condition. The activated carbon presented a good pore development in a microporous range and a high surface area, of 927.4 m^2g^{-1}.

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