Use of grape stalk, a waste of the viticulture industry, to obtain activated carbon

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ABSTRACT

Grape stalk is an organic waste produced in great amounts in the industrialization processes of grape. This work presents the results of studies carried out to use this waste as raw material to prepare activated carbon through the physical and chemical route. The physicochemical characterization of this material suggests the presence of unusually high levels of ashes. Metal content was determined and high levels of potassium, sodium, iron, calcium and magnesium in carbonized and raw grape stalk were exhibited. This characteristic made difficult physical activation at high temperatures. A leaching step was included before the activation with steam, and adsorbents with surface areas between 700 and 900 m^2/g were obtained. Physical activation was also performed at lower temperatures using carbonized grape stalk without leaching, leading to the development of some grade of porosity, with an area of 412 m^2/g. These results would indicate the catalytic effect of the minerals present in this raw material. Chemical activation using phosphoric acid as activating agent seemed to be a very efficient method as final products with BET areas between 1000 and 1500 m^2/g were obtained.

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1. Introduction

Industrial activity generates important amounts of wastes which, in most of cases, produce serious environmental problems. As industrial wastes go on increasing, finding ways to recycle these materials has become an important field of research.

Grape stalk is an organic waste from agricultural industry which is produced in great amounts in the industrialization processes of grape (wine, concentrated must, raisin, etc.). Its accumulation in industrial plants, besides occupying space, usually attracts insects and rodents. In order to avoid these problems, grape stalk usually spread on the plantations, but it alters the chemical composition of soils and, consequently, the life of the plants. For these reasons, finding alternatives for their employment will be of great utility.

Stalk is the skeleton of the grape bunch and consists of lignified tissues with a high content of fibers such as lignin, cellulose, hemicellulose [1], which provides a high carbon content. This characteristic was the basis to consider this waste as an adequate raw material to obtain activated carbon, which is considered the universal adsorbent to remove a great variety of substances in many liquid or gaseous phase processes. This material exhibits a well developed porous structure. Moreover, the chemical nature of its surface is very important for specific applications.

Activated carbon can be obtained from almost any material with high carbon content, including a lot of industrial wastes. Among these, cellulosic or lignocellulosic materials are the most frequently used, such as wood residues, fruits shells and stones (coconut, olive, apricot, peach, etc.), rice husk, olive cake and cane bagasse [2–4].

The activation process involves a partial gasification of the carbonized raw material under carbon dioxide and/or steam atmosphere (physical activation), or the impregnation of the carbonaceous material with a chemical compound followed by thermal treatment (chemical activation).

The kind of carbonaceous precursor used and the activation method selected, strongly influences both the product properties (surface area, pore size distribution, surface functionality, etc.), and the activation process yield [5].

This work presents the results of studies about the valorization of a viticultural industry waste (grape stalk), using it as a raw material to prepare activated carbon. The physicochemical properties of this material and synthesis routes used in order to obtain products with well developed porous structure are discussed.

The use of grape stalk for a few applications, such as raw material to improve compost by means of its addition to other agroindustrial wastes [6,7] or for the extraction of antioxidant compounds (phenolics) [8], has been studied. However, the authors have not found

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E-mail address: mfs@unsj.edu.ar (M.F. Sardella).

Table 1
Leaching assay conditions.

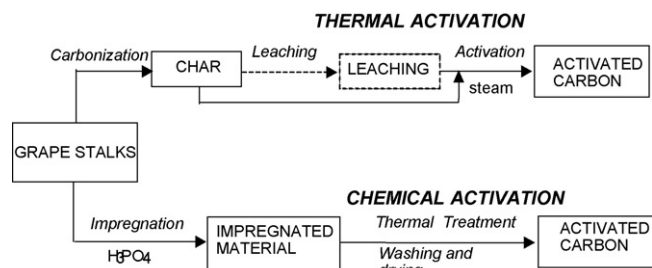| Assay	Leaching agent first step	T (K)	t (h)	Leaching agent second step	T (K)	t (h)
L1	H_2O	298	24	–	–	–
L2	H_2O	371	1	–	–	–
L3	H_2O	298	24	HCl	298	1
L4	H_2O	371	1	HCl	298	1
L5	HCl	298	1	–	–	–
L6	HCl	298	1	H_2O	298	24
L7	HCl	298	1	H_2O	371	1

T: temperature; t: time.

Fig. 1. Experimental work scheme for activated carbon production.

previous studies about the use of grape stalk to produce activated carbon.

2. Experimental

2.1. Materials

The lignocellulosic material studied here constitutes the skeleton of the grape wine bunch (*Vitis vinifera* L.). The grape stalk used in this work came from different kinds of grapes (Torrontés, Syrah, Chardonnay, Merlot, Malbec) and were provided by Bodegas y Viñedos Nesman, a winery from San Juan, Argentina. From the heap of this material stored in industrial plant, a representative sample was taken.

Analytical grade reagents, H_3PO_4 (85 and 99.99 wt% purity), NaOH (97 wt% purity) and HCl (36.5–38 and 99.99 wt% purity), from Cicarelli, Argentina, were used.

2.2. Methods

2.2.1. Activated carbon preparation

Activated carbon was prepared by physical and chemical activation. Fig. 1 shows a general scheme of the activation protocols adopted.

2.2.1.1. Physical activation. Grape stalk, as received, was heated in the absence of oxygen, at a rate of 1.4 K/min, from room temperature up to 773 K and kept at that temperature for 2 h. This step was carried out in a stainless steel carbonization retort electrically heated.

The carbonized material was weighed and separated into two fractions. One of them was directly activated and the other one submitted to leaching treatments before the activation step. An experimental schedule, under different operation conditions, was planned.

For the leaching step, static assays were performed in two stages. The first one with distilled water at room temperature and at 371 K, and the other one with hydrochloric acid (5 wt%) at room temperature. Leaching was carried out for periods of 1 and 24 h. In all cases, a grape stalk mass/liquid volume ratio of 0.067 g/mL was used. In Table 1 the operation conditions of the experimental schedule are shown. Leached solids were washed with distilled water and dried at 378 K.

Carbonized materials and those carbonized and leached, were activated with steam at high temperatures. This step was carried out in a stainless steel reactor (30 mm internal diameter and 300 mm length), in an electrically heated furnace with temperature control.

A measured flow of water was pumped by means of a Masterflex peristaltic pump through a heat exchanger electrically heated and temperature controlled in order to generate steam. The reactor was also connected to a nitrogen supply system, used to maintain an inert atmosphere until the reaction temperature was reached.

In all the assays, the reactor was loaded with 20 g of carbonized material or carbonized and leached one, according to the experimental schedule. The thermal treatment consisted in heating at 15 K/min, under nitrogen atmosphere (flow rate: 300 mL/min), from room temperature up to reaction temperature. When this temperature was reached, inert gas was replaced by steam (0.57 mL/min or 1.7 g/(g h)).

The experimental schedule for physical activation was developed as detailed in Table 2. Symbols A and L were used to identify samples activated and leached, respectively. Assays A1–A6 refer

Table 2
Thermal activation conditions using steam at 1.7 g/(g h) and characterization results.

Assay	Temperature (K)	Time (min)	Burn off (wt%)	BET area (m^2/g)	Micropore volume (cm^3/g)
A1	873	165	18	165	0.08
A2	923	165	32	186	0.09
A3	973	165	45	412	0.18
A4	1023	165	59	255	0.12
A5	1073	105	70	105	0.05
A6	1153	105	100	–	–
AL1	1153	105	100	–	–
AL2	1153	105	100	–	–
AL3	1153	105	53	748	0.28
AL4	1153	105	72	923	0.41
AL5	1153	105	58	812	0.31
AL6	1153	105	75	906	0.34
AL7	1153	105	78	737	0.27

Table 3
Chemical activation conditions using H_3PO_4 and characterization results.

Assay	Activation conditions			Activation yield (wt%)	BET area (m^2/g)	Micropore volume (cm^3/g)
	Temperature (K)	Time (min)	Acid concentration (wt%)			
Q1	843	60	30	66	1000	0.46
Q2	793	60	30	72	1033	0.48
Q3	793	60	50	71	1676	0.77
Q4	843	60	50	74	1466	0.67

to activation conditions for carbonized materials without previous leaching. Assays AL1–AL7 refer to operation conditions for carbonized and leached materials (assays L1–L7 of Table 1).

2.2.1.2. Chemical activation. Chemical activation assays were carried out using raw grape stalk as received and phosphoric acid as activating agent. A very important variable in this activation way is the impregnation ratio (mass of impregnating agent/mass of precursor). For the assays with grape stalk, two impregnation ratios (H_3PO_4 mass/grape stalk mass) were used: 3.37 and 4.22 g/g, equivalent to 0.15 and 0.26 g of retained phosphorus/g of precursor, respectively. This parameter expresses the mass of phosphorous (P) element that remains in the material after the impregnation and drying steps.

Grape stalk samples were impregnated with phosphoric acid for 24 h. Then, they were drained and kept in oven at 383 K for 24 h. The dried samples were thermally treated at two temperatures, 793 and 843 K, in the absence of oxygen for 1 h. The activated carbons obtained were washed with distilled water until neutrality and dried in oven for 24 h. In Table 3 a summary of the experimental assays carried out with this methodology is shown.

2.2.2. Characterization

Grape stalk was characterized by proximate analysis, according to ASTM standards, and elemental analysis (Carlo Erba EA 1108 CHNS-O). For the last, samples were previously dried in oven at 378 K until constant weight.

Metal contents (sodium, magnesium, calcium and iron) of both, grape stalk and liquids from leaching steps were determined by atomic absorption spectrometry (AA-100 Perkin Elmer). For the determination of metal content in raw grape stalk, the material was converted into ashes and then dissolved with an aqueous solution of HCl 23 wt%. This solution was then heated until dryness and the solid residue dissolved with an aqueous solution of HCl 4 wt%. All the analysis were replicated three times.

Thermogravimetric analysis (TGA-50 Shimadzu) was performed on raw and carbonized grape stalk and on samples L1–L7, from room temperature to 1173 K, with a heating rate of 5 K/min, under nitrogen atmosphere (flow rate: 50 mL/min), and particle size between 0.50 and 0.30 mm.

Nitrogen adsorption–desorption studies at 77 K were carried out in an automatic volumetric sorption analyser Quantachrome® Autosorb-1, after outgassing during 24 h at 373 K under vacuum. BET specific surface areas of the samples were determined from these data, in the range of relative pressures 0.03–0.30. Micropore volumes were calculated by applying Dubinin Radushkevich method. DFT method was used for the estimation of pore size distribution (PSD), with -3 and -1 as regularization parameters.

Table 4
Grape stalk analysis.

Proximate analysis (wt%)	
Ash (db)[a]	10
Moisture[b]	16
Volatile matter (db)[c]	51
Fixed carbon	23
Elemental analysis (wt%) (db)	
C	46.1
H	5.7
N	0.4
S	0.0

db: dry basis.
[a] Ref. [11].
[b] Ref. [12].
[c] Ref. [13].

Scanning electron microscopy (515 Philips) was also carried out. Each sample was dried under air atmosphere at 343 K, fixed to the stub with a carbon based painting and covered with a sputtering of Pt. The observation was done under vacuum (1×10^{-4} Torr).

3. Results and discussion

3.1. Grape stalk characterization

The results of the proximate and elemental analysis of grape stalk are shown in Table 4. Ash content is higher than the values for other activated carbon raw materials like eucalyptus wood (nearly 1%) and stones of different fruits (lower than 1%) [9,10].

When physical activation under standard conditions was used, considering as such those adequate for most of the lignocellulosic materials (1153 K, 105 min and 1.7 g steam/(g solid h)), grape stalk was totally transformed in ash (assay 6). Due to this fact, and taking into account the analytical results which revealed high metal contents, a leaching step previous to physical activation was included, in order to reduce the ash content and to identify potential interferences in the activation process.

3.2. Leaching

Proximate analysis of carbonized grape stalk before and after the leaching step is shown in Table 5 (assay L4).

When leaching was included between carbonization and activation steps, ash content decreased and consequently the fixed carbon content raised to more than 70%, which is suggested as adequate for industrial application purposes. Potassium, iron, sodium, magnesium, and calcium contents in grape stalk, carbonized grape stalk and in the liquids produced in the leaching steps, as mass percentage, are shown in Table 6.

Table 5
Carbonized grape stalk analysis.

Sample	Moisture (wt%)	Ash (wt%)	Volatile matter (wt%)	Fixed carbon (wt%)
Carbonized grape stalk	9	25	16	50
Carbonized and leached grape stalk (L4)	8	3	17	71

Table 6
Metal content in grape stalk, carbonized grape stalk, eucalyptus wood and leaching liquids.

Sample	K (%)[a]		Na (%)[a]		Fe (%)[a]		Ca (%)[a]		Mg (%)[a]	
	M	SD	M	SD	M	SD	M	SD	M	SD
Eucalyptus wood [10]	0.04	0.060	1.20	0.01	0.060	0.060	0.77	0.04	0.06	0.01
Grape stalk[b]	4.46	0.03	1.42	0.01	0.02	0.00	1.53	0.08	0.37	0.00
Carbonized grape stalk[b]	12.19	0.50	1.99	0.02	0.04	0.080	2.81	0.08	0.67	0.02
Liquid from L1[c]	5.09	0.03	0.31	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Liquid from L2[c]	9.88	0.09	0.89	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Liquid from L3[c]	6.72	0.02	0.51	0.00	0.01	0.00	1.53	0.01	0.10	0.00
Liquid from L4[c]	11.40	0.32	1.66	0.02	0.01	0.00	1.67	0.02	0.10	0.00
Liquid from L5[c]	3.28	0.02	0.29	0.01	0.01	0.020	1.40	0.04	0.06	0.01
Liquid from L6[c]	4.07	0.01	0.37	0.01	0.01	0.00	1.55	0.11	0.07	0.00
Liquid from L7[c]	6.31	0.05	0.63	0.04	0.01	0.050	1.75	0.07	0.08	0.02

M: mean value; SD: standard deviation.
[a] Mass percentage (wt%).
[b] db.
[c] Percent of metal extracted from carbonized material.

Eucalyptus wood analysis is also shown in order of comparison. The analyzed elements represent more than 70% of the ash mass of both, the raw and the carbonized grape stalk. There is a high content of potassium and remarkable levels of calcium and sodium. Important differences can be pointed out if these contents are compared with a typical raw material, as eucalyptus wood.

Leaching with water at boiling point temperature, followed by acid leaching (assay L4) yielded the best extraction of metal ions, especially sodium and potassium.

It can be concluded that leaching is an effective operation to reduce the mineral content, and simultaneously to increase the fixed carbon content, which reaches 71% in sample L4.

Thermogravimetric studies were carried out for the samples detailed in Table 1.

DTG curves for some representative samples are shown in Fig. 2. For raw grape stalk, mass loss due to humidity removal is observed up to 450 K. Slight differences are observed for the other samples, basically due to the strength in which water molecules are bond. At temperatures higher than 450 K, organic matter decomposition, evolution of volatile substances from inorganic compounds and secondary decomposition of the pyrolysis products occurred [14,15].

The main peak for raw grape stalk placed at 420–770 K, would indicate the presence of hemicellulose, cellulose and lignin, as some references state [16].

Single peaks appeared at 940 K for the raw and carbonized materials and for the carbonized materials leached only with water. For samples L3–L7 these peaks flattened and appeared at tempera-

Fig. 2. Rate of weight loss vs temperature.

tures slightly lower. This could be associated to the elimination or decomposition of inorganic compounds when the carbonized materials were leached with hydrochloric acid solutions. For these samples, a slight mass loss, which started at 770 K, is attributed to the secondary decomposition of the pyrolysis products.

3.3. Physical activation

The results of the characterization of activated carbons obtained from carbonized materials, with and without leaching, under different operation conditions are shown in Table 2.
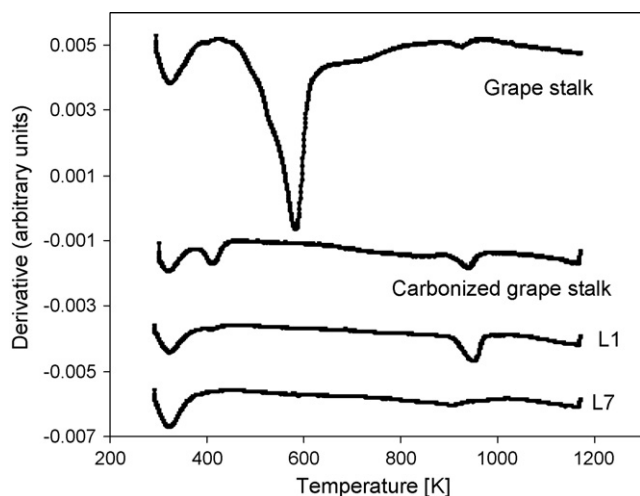
3.3.1. Activation of the carbonized sample

It can be observed that in the assay performed at 1153 K (A6), only ash was obtained (burn off 100%). Under the hypothesis that the alkaline metals (K and Na) present in this material catalyze the carbon gasification, five additional assays (A1–A5) at lower activation temperatures (873, 923, 973, 1023 and 1073 K) were carried out, using the carbonized material without leaching. Lower activation temperatures lead to final products with higher porosity, with a maximum of 412 m^2/g corresponding to assay A3, which was carried out at 973 K. The high inorganic content in the grape stalk could catalyze the gasification, leading to the generation of wider pores at higher temperatures [17]. This observation is confirmed by the BET areas of samples A4 and A5, lower than the one of sample A3. And at the typical temperature, sample A6 only ash was obtained. At temperatures below 973 K (samples A1 and A2), lower activation temperatures yielded activated carbons with lower surface areas. This is attributed to a low progress of the gasification reaction. Fig. 3 shows how the BET area changes with temperature and burn off.

Another characteristic of grape stalk is the sinterization of the carbonized non-leached material during the activation reaction, which is attributed to the presence of alkaline metals and silica. This phenomenon makes difficult the interaction between the solid and the activation gas.

3.3.2. Activation of leached carbonized samples

The results shown in Table 2 indicate that carbonized and leached materials yielded activated carbons with textural properties comparable with those of commercial adsorbents, except those treated only with water. Samples AL3–AL7, which were leached with acid and water, showed BET areas similar to commercial activated carbons. Leaching with water at boiling temperature followed by acid seems to be the most effective combination to obtain activated carbons by physical activation (sample AL4). This is attributed to the better removal of mineral matter with the consequent increase of fixed carbon.
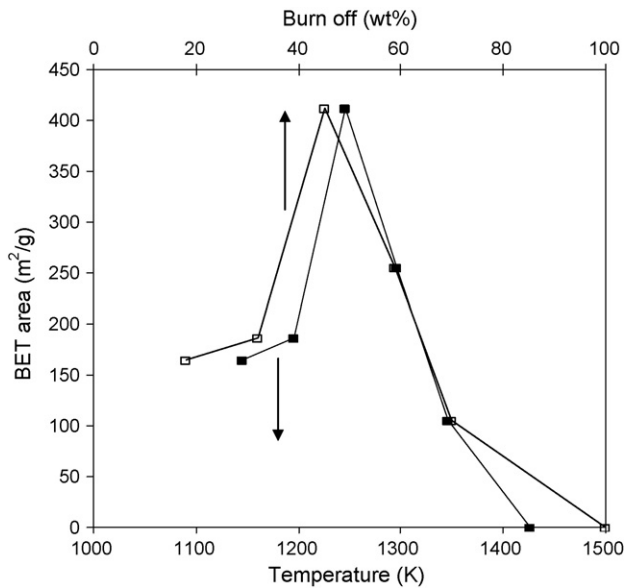
Fig. 3. BET area variations as a function of temperature (solid symbols) and burn off (open symbols).

Pore size distributions, obtained from the nitrogen adsorption–desorption isotherms carried out at 77 K, modelled by the Density Functional Theory (DFT), from the adsorption points, corresponding to samples AL4–AL6, are shown in Fig. 4.

Carbons AL5 and AL6 are essentially microporous materials, with an important contribution of narrower than 15 Å wide pores in both cases. DFT curve for sample AL6 is quite similar to that of AL5, but for AL6 the adsorbed volumes are higher, which is in agreement with the difference in BET area exhibited in Table 2. Sample AL4 shows a wider pore size distribution compared to those of AL5 and AL6, with a higher development of mesopores.

3.4. Chemical activation

The results of the chemical activation of grape stalk, using phosphoric acid as activating agent, are presented in Table 3. Activation yield was defined as the ratio between activated carbon mass and raw material mass, multiplied by 100.

BET surface area values were higher, in all cases, than those obtained by physical activation, and higher than $1000 \, m^2/g$, suggesting higher microporosity. It is important mentioning that lesser amounts of impregnant agent than those used by other researchers [18] led to adsorbents with well developed porous structure.
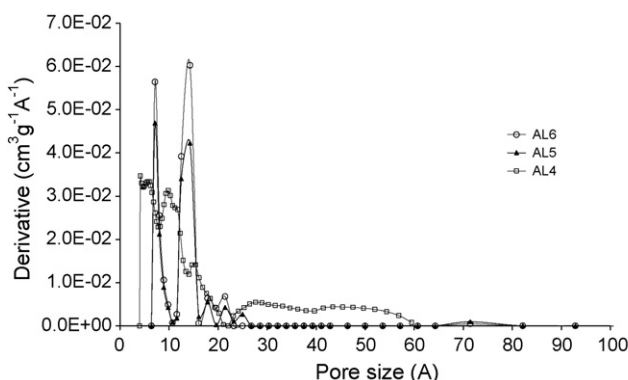

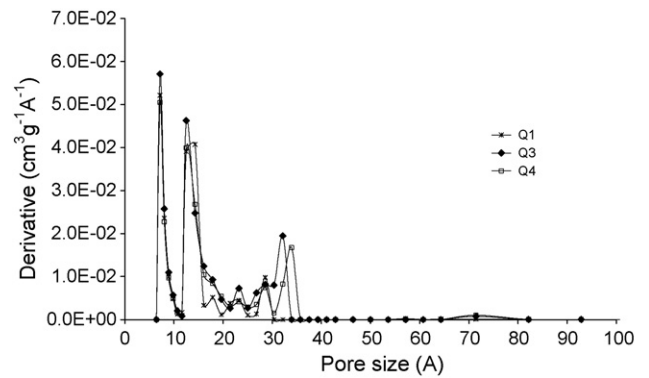**Fig. 4.** Pore size distribution by DFT for samples AL4–AL6.

Fig. 5. Pore size distribution by DFT for samples Q1, Q3 and Q4.

When 30 wt% phosphoric acid was used, the temperature at which the thermal treatment of the impregnated material was carried out seems to have no influence on the microporous volume. When 50 wt% acid was used, a higher activation temperature led to lower BET areas. An explanation for these results is that under more severe conditions a widening of pores occurs, leading to lesser microporous volumes, as it is shown in Table 3 (samples Q3 and Q4). This could be due to the thermal decomposition of phosphate and polyphosphate bridges of Q4 carbonaceous structure, caused by the higher temperature of the assay [19]. Pore size distributions corresponding to activated carbons from assays Q1, Q3 and Q4 (Fig. 5) confirm these statements.

3.5. Comparison of physical and chemical activation results

Nitrogen adsorption–desorption isotherms at 77 K of those samples with the highest BET surfaces areas obtained by physical and
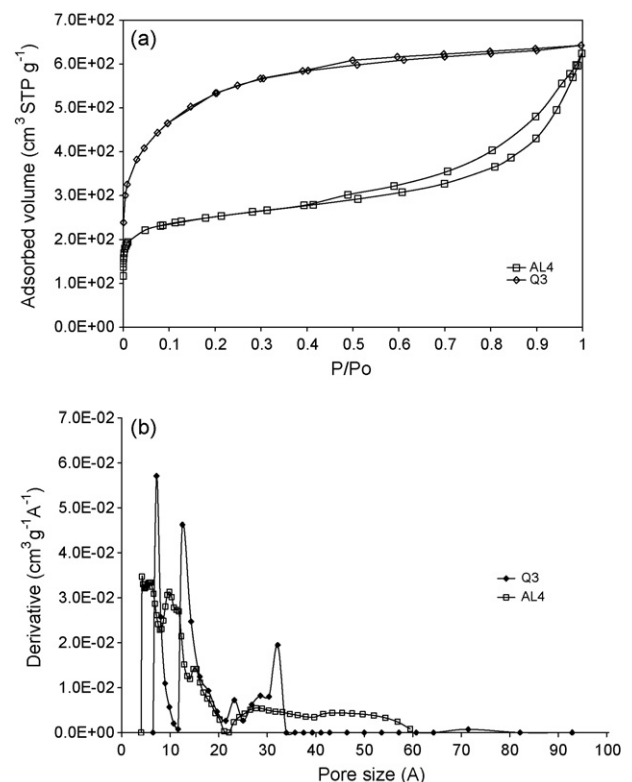

Fig. 6. Nitrogen adsorption isotherm (a) and pore size distribution (b) of physically and chemically activated carbons (samples AL4 and Q3).
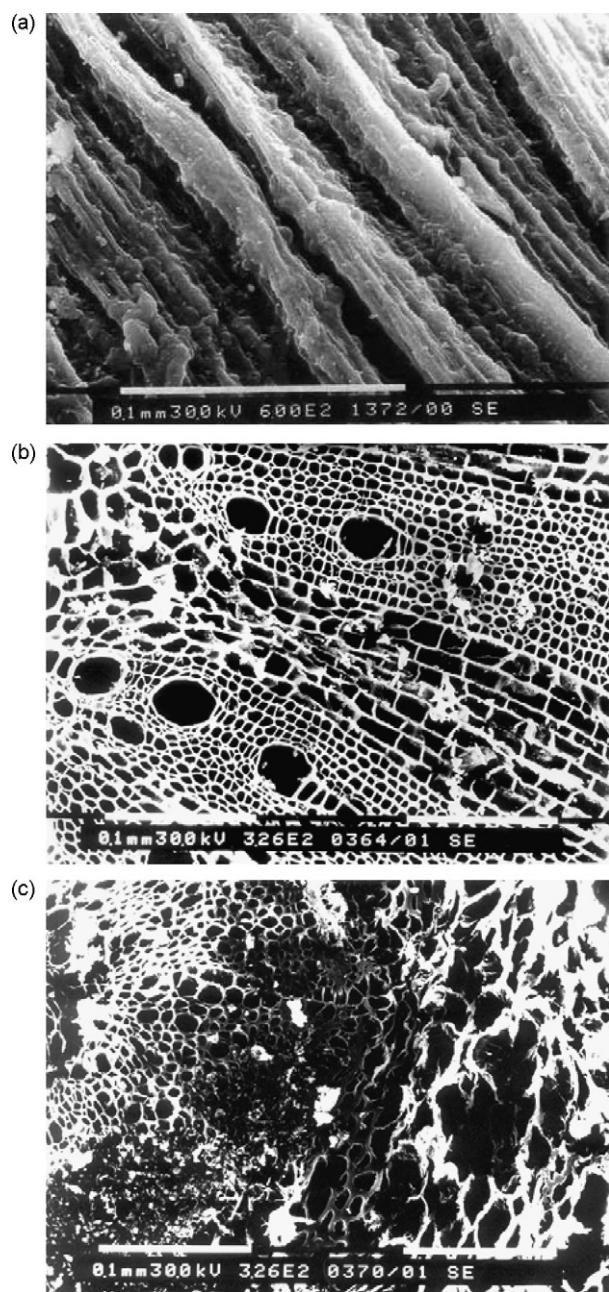
(a)

(b)

(c)

Fig. 7. SEM images of samples AL4 (a and b) and Q2 (c).

chemical activation (samples AL4 and Q3, respectively) are shown in Fig. 6. It can be seen that the isotherm shape is very different for each one. There is a greater microporosity development in Q3, which is indicated by the higher nitrogen volume adsorbed at low relative pressure (P/P_0) and the knee shape, whereas AL4 presents higher mesoporous volume.

From the nitrogen adsorption isotherms the mean pore connectivity can be also analyzed. This property plays an important role in the diffusion of adsorbate molecules into the porous structure.

According to the model proposed by Seaton [20] and improved by Liu and Seaton [21,22], based on the use of the percolation theory, the net connectivity is related with the hysteresis loop shape. A relevant aspect is the delay in the vaporization of nitrogen from the porous structure. The higher the relative pressure at which desorption starts, the higher the mean pore connectivity of the solid. From this analysis, the adsorbent prepared by physical activation

(AL4) had a higher mean pore connectivity than the one prepared by chemical activation (Q3).

SEM images are shown in Fig. 7. Fig. 7a exhibits the external surface of steam activated carbonized grape stalk (AL4), and Fig. 7b a cross-section of the same sample. In these images it can be seen that grape stalk basic structure longitudinal fibers were not altered, and that the pores preserved the fibers cellular order. Chemical activation (Q1 sample) produced a more random porosity distribution (Fig. 7c), which can be attributed to the modification of the cellular structure by the acid activation agent.

The comparison between both synthesis routes indicated that the chemical activation is more effective than the physical one. Firstly, it has less steps, as phosphoric acid could produce the leaching of mineral compounds simultaneously with the activation. Second, the process yield is about 66–74%, higher than that of the physical method, that can be estimated in 10%.

4. Conclusions

Grape stalk, an abundant waste of viticulture industry, can be used as raw material to produce activated carbon. Because of its high ash content, an adequate activation route is required.

Steam physical activation requires a leaching step of the carbonized material, previous to the activation step. By leaching, about 70% of the mineral material is removed, and the fixed carbon content raises to similar values to those of other materials used to prepare activated carbon. Final products with surface areas between 700 and 900 m^2/g were obtained. Alkaline metals present in the raw material would catalyze carbon gasification, allowing the porosity in non-leached carbonized materials could be developed at lower temperatures than that theoretically established for this reaction (1073 K) [5].

Chemical activation of grape stalk, using phosphoric acid as activating agent is an efficient activation method as final products with BET areas between 1000 and 1500 m^2/g are obtained.

The comparison of those activated carbons with the higher surface area prepared by physical and chemical methods showed that the one prepared by physical activation had a higher mean pore connectivity than the one prepared by chemical activation.

The results showed that chemical synthesis route is more effective to obtain activated carbons with a well developed porosity, because it includes only one step, higher process yields and products with BET areas above 1000 m^2/g. For these reasons, the chemical method seems to be more adequate for industrial applications.

Acknowledgements

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