Activated carbon from cherry stones by chemical activation.

Influence of the impregnation method on porous structure

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A B S T R A C T

Cherry stones are utilized as a precursor for the preparation of activated carbons by chemical activation with phosphoric acid (H₃PO₄). The activation process typically consists of successive impregnation, carbonization and washing stages. Here, several impregnation variables are comprehensively studied, including H₃PO₄ concentration, number of soaking steps, H₃PO₄ recycling, washing of the impregnated material, and previous semi-carbonization. The choice of a suitable impregnation methodology opens up additional possibilities for the preparation of a wide variety of activated carbons with high yields and tailored porous structures. Microporous activated carbons with specific surface areas of ~800 m² g⁻¹ are produced, in which > 60% of the total pore volume is due to micropores. High surface areas of ~1500 m² g⁻¹ can be also developed, with

micropore volumes being a 26% of the total pore volume. Interestingly, using the same amount of H_3PO_4 , either carbons with surface areas of 791 and 337 $\text{m}^2 \text{g}^{-1}$ or only one carbon with a surface area of 640 $\text{m}^2 \text{g}^{-1}$ can be prepared. The pore volumes range very widely between 0.07-0.55, 0.01-0.90 and 0.09-0.79 $\text{cm}^3 \text{g}^{-1}$ for micro-, meso- and macropores, respectively.

Keywords: Cherry stones, H_3PO_4 activation, impregnation method, activated carbon, porous structure.

1. Introduction

Activated carbon (AC) is an extremely versatile adsorbent with a wide range of uses and applications, including adsorption from the liquid or gas phase for separation, purification, catalysis and pollution control processes [1]. The key factor for the use of AC in such processes lies in the synthesis of low cost adsorbents with an appropriate porous structure, which depends on the starting material and method of preparation [1-3]. AC precursors include a great variety of agricultural wastes as shells, seeds, and so on [4-6]. AC can be prepared by physical or chemical activation methods. In chemical activation, an appropriate agent such as phosphoric acid, zinc chloride or potassium hydroxide is used. Phosphoric acid is the preferred one, not only because of its activating action but also for environmental and health reasons. That is why the preparation of AC with H_3PO_4 has been extensively investigated [1-3, 7-11]. A wide range of AC precursors and H_3PO_4 concentrations has been applied under different carbonization conditions. The concentration of the H_3PO_4 solution determines the size of the phosphorus species present in the impregnation solution and thereby the size of

the pores created as a consequence of the activation process. The presence of large size phosphorus species in a concentrated solution gives rise to large pore sizes [2]. The carbonization temperature controls the physicochemical changes occurring in the H_3PO_4 -impregnated product, which are responsible for the creation of porosity [9, 11, 12]. Carbonization under nitrogen atmosphere has been widely employed [1, 2, 9], while argon [13], carbon dioxide [14], N_2/O_2 synthetic mixtures [15], self-generated atmospheres [16, and citations therein] and air [17] have also been used.

The present study deals with the preparation of AC from cherry stones, which is an agricultural industry waste locally generated in large quantities, by the method of chemical activation with H_3PO_4 . Our research group has previously reported the preparation of AC by conventional physical, chemical and surface-modification methods [12, 18, 19]. However, certain process variables have not received sufficient attention in the literature, even though a careful design of the AC fabrication protocol can substantially save energy and reactants and lead to final products with improved properties. Accordingly, using two H_3PO_4 aqueous solutions of very different concentrations, the main objective of the present work was to investigate the foreseeable influence of the impregnation method of cherry stones on the porous structure of AC. The impregnation strategies were devised with a view to controlling the degree of association of H_3PO_4 not only in the impregnation solution but also during the impregnation process. The textural characterization of the samples was undertaken by gas physical adsorption (N_2 , $-196\text{ }^\circ\text{C}$; CO_2 , $0\text{ }^\circ\text{C}$), mercury porosimetry and density measurements.

2. Experimental

2.1. Materials and reagents

The starting cherry stones (CS) were furnished by “Agrupación de Cooperativas Valle del Jerte” (Cáceres, Spain). First CS were air-dried and analyzed. Data on the ultimate and proximate chemical analyses are listed in Table 1. The biopolymer composition is: hemicelluloses, 14.7%; cellulose, 29.4%; and lignin, 30.7%. Accordingly, the empirical formula is $\text{CH}_{1.52}\text{O}_{0.62}\text{N}_{0.006}$ [20]. Then, CS were milled and sieved until the particle size was between 1 and 2 mm. As a conditioning treatment, CS were soaked overnight in dilute H_2SO_4 (5% v/v), thoroughly rinsed with distilled water until neutral pH and oven-dried at 120 °C for 24 h. Similar conditioning treatments are frequently used for the improvement of wettability and towards applications in the removal of inorganic impurities and oils [1, 13, 21, 22]. Phosphoric acid of 85 % PA-ACS-ISO grade was used. Both inorganic acids (H_2SO_4 , H_3PO_4) were purchased from Panreac in reagent grades.

2.3. Preparation of the ACs

The overall process of AC preparation by chemical activation with H_3PO_4 consisted of three stages of impregnation, carbonization and washing, as described elsewhere [23], and summarized in Table 2. The detailed description of such procedures is given below.

2.3.1. Impregnation

Two H_3PO_4 aqueous solutions containing 16 g H_3PO_4 /100 mL water and 144.5 g H_3PO_4 /100 mL water (i.e., the commercial product) were used as stocks, the concentrations of these solutions being similar to those used in previous studies [1]. In a typical impregnation experiment, 25 g of CS (or low-temperature charred CS) and 100

mL of H_3PO_4 solution were heated in a beaker at 85 °C for 2 h under steady magnetic stirring and the resulting heterogeneous mixture was oven-dried at 120 °C for 24 h. As a whole three series of impregnated products were prepared (Table 2). Regarding series 1, the impregnation of CS was carried out not only with the aforementioned dilute H_3PO_4 solution (sample D) but also with a 5.33 g H_3PO_4 /100 mL water solution once, twice and three times (samples DL1, DL2 and DL3, respectively). For comparison with DL2, a 10.66 g H_3PO_4 /100 mL water solution was also used for the preparation of DI1. Therefore, the total amount of H_3PO_4 brought into contact with AC along the impregnation process was the same for DL2 and DI1 (10.66 g) and for DL3 and D (16 g); for DL1 it was as low as 5.33 g. Impregnation was also carried out by first soaking CS in the dilute stock solution of H_3PO_4 and by then removing the supernatant by filtration (sample DF), washing the residual solid with distilled water (sample DFW) and impregnating fresh CS with such a supernatant (sample DRL). For series 2, the impregnation of CS was performed with the 144.5 g H_3PO_4 /100 mL water solution and with over-concentrated solutions prepared from it by oven-drying at 120 °C for 2-24 h (samples C0-24). In the case of series 3, two chars prepared by heating CS at 200 or 300 °C for 2 h in N_2 atmosphere (flow = 100 mL/min) (S200, S300) were impregnated with both stock solutions of H_3PO_4 (samples S200D, S300D, S200C, S300C).

To the best of our knowledge, as investigated here, the above-described impregnation strategies have not been previously reported in the literature [1, 7, 24, 25].

2.3.2. Carbonization and washing

In the carbonization stage, approximately 8 g of impregnated product was placed in a ceramic crucible and heat-treated in a cylindrical horizontal furnace from room temperature to 500 °C in N_2 atmosphere. Heating rate was 10 °C/min and soaking time

at maximum heat treatment temperature was 2 h [2]. After this time had elapsed, the resulting heat-treated product was washed thoroughly with distilled water for two days in a Soxhlet extractor, oven-dried at 120 °C for 12 h, weighed and stored in shut tight plastic containers. The obtained ACs were designated by adding an ending A to the notations used for the impregnated products, e.g., D as DA, DL3 as DL3A, C0 as C0A, and so on. For comparison purposes, raw CS were also carbonized under the same heating conditions as for the impregnated products.

2.4. Textural characterization of ACs

The textural characterization of the samples was accomplished by gas physical adsorption (N₂ at -196 °C and CO₂ at 0 °C), mercury porosimetry, and density measurements. N₂ and CO₂ adsorption isotherms were measured in Autosorb-1 (Quantachrome) and ASAP 2020 (Micromeritics) instruments, respectively. A given amount of sample, depending on its adsorption capacity, was degassed at 250 °C for 12 h under a pressure lower than 10⁻³ Torr prior to effecting adsorption measurements. Mercury intrusion curves were measured using an Autoscanner 60 porosimeter (Quantachrome) working with 0.3–0.4 g of sample; Hg contact angle was 140° and its surface tension 480 erg/cm². The mercury density (ρ_{Hg}) was calculated from the mass and volume of sample, as obtained by weighing and knowing the previously calibrated volume for the sample holder and the tabulated mercury density as a function of temperature. Helium density (ρ_{He}) was measured in a Quantachrome stereopycnometer, using about 3 g of sample. Measurements were effected with time until constancy in the ρ_{He} value was obtained.

3. Results and discussion

3.1. Yields

Previously reported data [23] showed that the yield of the processes of impregnation (Y_i), carbonization (Y_c) and washing (Y_w) is strongly dependent on the impregnation method. As a guide, the variation range is between 3.0 and 99.1 wt% for Y_i , 25.1 and 66.9 wt% for Y_c and 19.4 and 97.8 wt% for Y_w (Table 2). Specifically, Y_i as a rule increased when the concentration of the impregnation solution increased. However, the fact that Y_i for S200DA is higher than for not only DA but also for S300CA indicates that factors other than the concentration of the H_3PO_4 solution influenced the extent to which the impregnation process occurred. By contrast, Y_i could not be obtained for S300CA because S300 showed a reduced tendency to impregnation in the presence of a high H_3PO_4 content, as seen below.

3.2. Textural characterization of the samples

3.2.1. By gas physical adsorption

3.2.1.1. Samples DA and C0A

Since DA and C0A were prepared by impregnation of CS with the H_3PO_4 stock solutions, the results obtained in the textural characterization of this couple of samples are dealt with first, mainly for comparison purposes. The N_2 adsorption isotherms at -196 °C determined for DA and C0A are plotted in Figs. 1 and 2, respectively. According to the isotherm shapes [26, 27], DA is an essentially microporous AC and C0A is a mesoporous AC. Furthermore, porosity is very heterogeneous in C0A, with larger size pores being predominant in this AC. Data in Table 3 corroborate that the degree of development of the porosity analyzed by N_2 adsorption is larger for C0A than for DA, particularly in the mesopore region as V_{me-na} is $0.04 \text{ cm}^3 \text{ g}^{-1}$ for DA and $1.12 \text{ cm}^3 \text{ g}^{-1}$ for

C0A. Also notice that both W_{0-na} and S_{BET} are much higher for C0A than for DA. Comparison of W_{0-na} and W_{0-cda} for both samples points to a less restricted N_2 adsorption in C0A [28], which is consistent with the presence of wider microporosity in this sample.

3.2.1.2. Series 1

From the shape of the N_2 adsorption isotherms measured for the ACs of series 1 and for the carbonized product prepared from CS in Fig. 1 it becomes apparent that these carbonaceous materials are essentially microporous carbons. As compared to DA, microporosity and narrow mesoporosity are more heterogeneous in DRLA and especially in DL3A. Conversely, the carbonized product and DFA, DL1A and DFWA almost exclusively contain narrower pores that are further more uniform in size. The relative position of the adsorption isotherms along the y-axis indicates that the process of N_2 adsorption occurred in the order of $DL3A > DLRA > DA > DL2A > DI1A > DFWA > DFA \approx DL1A > \text{carbonized product}$. In fact, as shown in Table 3, W_{0-na} and V_{me-na} are markedly higher for DL3A and DRLA than for DA and for the rest of the samples. It should be mentioned that even for DL1A and DFA activation of the impregnated products occurred to some extent. In brief, it may be stated that the impregnation of CS in more than a stage and using the residual liquid after a previous soaking step of CS gave rise to important developments of microporosity and narrow mesoporosity made up of varying size pores. Furthermore, the effects on pore sizes and volumes were stronger as the number of impregnation stages increased in the preparation of the impregnated products. In relation to the effectiveness of the method of AC preparation, it should be also noted that the cumulative amount of H_3PO_4 loaded on CS after the three impregnation stages in the preparation of DL3A (i.e., 5.35 g) was

significantly smaller than for DA (i.e., 7.30 g) (González-Domínguez et al., 2015). As a final comment it should be mentioned that the presence of higher volume of wider pores in DL3A than in DA, despite using more dilute solutions in the impregnation of CS for DL3A, strongly advocates for a more favorable association and concentration of H_3PO_4 in CS with the increase in the number of heat-treatments effected at low temperatures in the impregnation of CS. Somehow, it may also apply to DRLA as the residual liquid used in the preparation of this sample was heat-treated twice at 85 °C in the soaking step in the presence of two different samples of CS.

Further information about microporosity of the samples is provided by adsorption of CO_2 at 0 °C (the isotherms have been omitted for the sake of brevity). As seen in Table 3, $W_{0\text{-cda}}$ is higher than $W_{0\text{-na}}$ for DL1A and DFA which demonstrates occurrence of restricted diffusion of N_2 at -196 °C in micropores of the samples because of the presence of narrow microporosity or constrictions in pore entrances [28]. It is compatible with a small degree of activation in the preparation of the samples, because of a very low content of activating agent in the impregnated products (i.e., the mass increase produced after the impregnation of CS was 1.20 g for DL1A and 1.34 g for DFA; [23]). The presence of wider micropores in the samples with the increase in the degree of impregnation of CS becomes evident from the behavior exhibited by DI1A, for which $W_{0\text{-cda}} = W_{0\text{-na}}$. For the rest of the ACs, $W_{0\text{-cda}}$ is lower than $W_{0\text{-na}}$ and therefore microporosity must be wider and heterogeneous [28]. Finally, it is also worth mentioning that $W_{0\text{-cda}}$ and $W_{0\text{-na}}$ are higher for DL3A and DRLA than for DA, as expected.

As estimated as usual by the BET method from the N_2 adsorption isotherms at -196 °C (see Table 3), S_{BET} is 640 $\text{m}^2 \text{g}^{-1}$ for DA and ranges between 123 $\text{m}^2 \text{g}^{-1}$ for DL1A and 837 $\text{m}^2 \text{g}^{-1}$ for DL3A. The S_{BET} values show that with dilute H_3PO_4 solutions,

using the same amount of activating agent but different impregnation strategies, either two ACs (DFA or DFWA and DRLA) with S_{BET} 134 or 337 and 791 $\text{m}^2 \text{g}^{-1}$ or only an AC (DA) with S_{BET} 640 $\text{m}^2 \text{g}^{-1}$ can be prepared, which gives one idea of the economic benefits of the recycling method in the impregnation of CS.

3.2.1.3. Series 2

As for C0A, the N_2 adsorption isotherms measured for samples C2A-C24A in Fig. 3 are characteristic of mesoporous solids. Furthermore, they show that mesoporosity is very heterogeneous and is made up of mainly large size pores, in particular for C0A, C2A and C6A. Moreover, for C12A and C24A the content of larger mesopores significantly decreases. On the other hand, it should be noted that microporosity is similarly developed for all samples, except for C2A. In general, as expected, $W_{0-\text{na}}$ and $V_{\text{me-na}}$ are quite similar for most samples. It is worth mentioning that $W_{0-\text{na}}$ is 0.54 $\text{cm}^3 \text{g}^{-1}$ for C0A and 0.45 $\text{cm}^3 \text{g}^{-1}$ for DL3A and therefore only somewhat higher for C0A than for DL3A, which indicates that ACs with not very different microporosity developments can be prepared with both dilute and concentrated H_3PO_4 solutions. On the other hand, $W_{0-\text{na}}$ is nearly twofold higher than $W_{0-\text{cda}}$, which is consistent with the fact that the samples prepared with concentrated H_3PO_4 solutions possess a wide pore size distribution in the micropore range, therefore embracing not only narrow but also wide porosity. S_{BET} ranges between 1203 $\text{m}^2 \text{g}^{-1}$ for C2A and 1491 $\text{m}^2 \text{g}^{-1}$ for C0A, being about 1440 $\text{m}^2 \text{g}^{-1}$ for the rest of the samples.

For this series of samples, Y_i first increased from 93.8 wt% for C0A to 99.1 wt% for C2A, then decreased to 87.4 wt% for C6A and finally increased again to 88.2 wt% for C12A and 93.4 wt% for C24A [23]. Therefore, regardless of whether the concentrated H_3PO_4 solution or an over-concentrated solution prepared from it was

used, impregnation was a highly effective treatment to incorporate H_3PO_4 to CS. Probably, the process was favored by both the aggregation of H_3PO_4 inherent to the high concentration of the impregnation solution and by the molecular condensation of H_3PO_4 produced while oven-drying at 120 °C, respectively occurring before and after soaking at 85 °C. By H_3PO_4 molecular condensation with elimination of one or more water molecules, polyphosphoric acids of general formula $\text{H}_{n+2}\text{P}_n\text{O}_{3n+1}$, with n up to 17 are formed as a complex mixture of linear molecules of various chain lengths [29-33]. In connection with the condensation process of H_3PO_4 it is worth noting that when the concentrated H_3PO_4 solution was separately oven-dried at 120 °C the volume of liquid decreased by $\sim 10\%$ at most, instead of at least [23]. When oven-drying for a long time period and the resulting liquid was used in the impregnation of CS, stirring was progressively more hindered and on the surface of a very viscous liquid a solid phase was readily visible during the soaking step. After oven-drying at 120 °C for 24 h, a sponge-like compact mass was ultimately formed. Mass transference of a solid phase from the bulk of the impregnation liquid to the lignocellulosic substratum would promote the loading and concentration of activating agent on CS with the consequent effects on the impregnation yield and porous structure of AC.

3.2.1.4. Series 3

For these samples, Y_i was 94.0 wt% for S300DA, which is much higher than 45.6 wt% for DA [23]. In the impregnation of the S300 with the concentrated H_3PO_4 solution, it was detected the presence of a residual liquid in S300 after oven-drying at 120 °C for 24 h and consequently it was necessary to separate such a liquid by filtration before the residual solid was oven-dried again to dryness [23]. Therefore, it was not possible to obtain Y_i for S300CA, as commented above. As revealed by the N_2

adsorption isotherms in Fig. 4, the micro- and mesoporous structures of these samples are also greatly influenced by the charring temperature of CS, with the strongest changes with respect to the samples prepared by the usual method occurring when heating at 300 °C. Textural data in Table 3 show that W_{0-na} is by far lower for S300DA than for DA and for S300CA than for C0A. Furthermore, in S300CA microporosity must be narrow, constricted or blocked in S300CA as W_{0-cad} is smaller than W_{0-na} for this sample. On the other hand, V_{me-na} is $1.40 \text{ cm}^3 \text{ g}^{-1}$ for S200CA, which is markedly higher than for the rest of the ACs (i.e., at most V_{me-na} is as high as $1.27 \text{ cm}^3 \text{ g}^{-1}$ for C12A). The enhanced development of mesoporosity produced for S200CA must be highlighted because it may be relevant with a view to preparing carbonaceous adsorbents with a well-developed porosity in the mesopore range. By contrast, the low V_{me-na} for S300DA and very especially for S300CA as compared to DA and C0A, respectively, is worth noting. S_{BET} is $1491 \text{ m}^2 \text{ g}^{-1}$ for C0A and $1489 \text{ m}^2 \text{ g}^{-1}$ for S200CA. However, S_{BET} is greatly smaller for S300DA and S300CA than for DA and C0A.

When investigating the thermal behavior of CS by TG-DTG analysis, it was found that this lignocellulosic material thermally degrades with a mass loss of 8.28 wt% between 30 and 200 °C and of 17.93 wt% between 200-300 °C. These effects of weight loss were associated with the removal of moisture and a small fraction of volatile components and of low thermal stability biopolymers of CS, such as hemicelluloses [34-37]. Accordingly, the high yield for S300DA and the greatly decreased amount of H_3PO_4 loaded on S300 for S300CA together with the decreased micro- and mesoporosity for the two ACs prepared from S300 must be somehow connected with the partial devolatilization of CS during the preparation of S300. Probably, the changes originated in the chemical composition of CS affected the behavior of S300 in the wetting and swelling processes after its contact with the impregnation solution. It may

be assumed that as a result of the devolatilization of CS a network of narrow and blocked pores (i.e., the so-called incipient porosity) was formed which acted as a molecular sieve with respect of H_3PO_4 , in such a way that only the H_3PO_4 chemical species with a sufficiently small size were able to enter such pores. Of course, small H_3PO_4 species were predominant in the dilute H_3PO_4 solution, unlike in its concentrated solution where larger size H_3PO_4 molecular aggregates were more abundant. Regardless of the concentration of the impregnation solution, the trend along the impregnation process should be to an increase in the size and content of H_3PO_4 chemical species because of molecular condensation and thereby to a more forbidden access to narrow porosity present in S300. On the other hand, the fact that the great increase produced in the amount of H_3PO_4 loaded on S300 with the dilute H_3PO_4 solution is not reflected by an increase in the activation action of H_3PO_4 suggests that, because of the absence of mainly hemicelluloses from CS, H_3PO_4 in part at least physically adsorbed on the surface of S300 pores and thereby was removed from the impregnated S300 during the carbonization process in the preparation of S300DA, which also holds for S300CA. From these results it becomes clear that the biopolymer composition of the chars prepared from CS and the dependent interaction with H_3PO_4 played a prominent role in the activation process of S300 with H_3PO_4 during the preparation of S300DA and S300CA.

For comparison purposes, in Fig. 4 the values of S_{BET} obtained for the prepared ACs are presented against the impregnation amount of H_3PO_4 [23]. It can be observed that the variation of S_{BET} is not totally linear, which proves its dependence on the impregnation method.

3.2.2. Mercury porosimetry

The curves of mercury intrusion obtained for the ACs are plotted in Figs. 5-6 and the derived values of $V_{\text{me-mp}}$ and $V_{\text{ma-mp}}$ are compiled in Table 3. Regarding mesoporosity, the results obtained by mercury porosimetry are usually in good qualitative agreement with those of N_2 adsorption. Thus, it is shown that the development of mesoporosity is greater for DL3A and DRLA than for DA, which is worth mentioning. Furthermore, mesoporosity is heterogeneous in DA, DL3A and DRLA. For a number of ACs, however, the relative development of mesoporosity depends on the method used on its analysis. As an illustrative example, $V_{\text{me-na}}$ and $V_{\text{me-mp}}$ are 1.40 and 0.79 cm³ g⁻¹ for S200CA and 1.20 and 0.90 cm³ g⁻¹ for C6A.

The method of impregnation not only has a marked influence on micro- and mesoporosity, as described above, but also on macroporosity. This porosity region is well-developed in most ACs, particularly in DFWA, C0A-C24A, S200CA, S300DA and S300CA. Conversely, macroporosity is more poorly developed for DA, DRLA and S200DA. Also notice (see Figs. 5 and 6) that the pore size distribution in the macropore range is homogeneous for most ACs belonging to series 1 and 3, including S300CA, and heterogeneous for the ACs of series 2 and also for S200CA. In the former ACs the pores with radii in the range 2000-4000 Å are predominant. Larger macropores are only present in C24A and S200CA.

In connection with the high volume of macropores in ACs such as DFWA it should be recalled here that in the preparation of this sample the degree of impregnation of CS was very small since, after removing the residual liquid and washing with distilled water, the mass increase was as low as 0.48 g [23], and therefore it is likely that macroporosity originated in the pyrolysis rather than in the activation of the hardly impregnated product. In any event it should be mentioned that $W_{0\text{-na}}$ and S_{BET} are relatively high for DFWA (i.e., 0.18 cm³ g⁻¹ and 337 m² g⁻¹; Table 3), which is a proof

of the activating action of H_3PO_4 . In the case of C24A, the development of wide porosity may be connected with phase transitions occurring during the over-concentration of the H_3PO_4 commercial solution for longer time periods. With regard to S200CA, the porosity enlargement as compared to C0A seems to indicate that H_3PO_4 somehow concentrated in S200 because of an irreversible release of water and/or volatile matter from CS during the preparation of S200.

3.2.3. By density measurements

From the determined mercury density (ρ_{Hg}) and helium density (ρ_{He}) (data in Table 3) the total pore volume (V_T) and total porosity (ε) of the ACs were calculated by the expressions:

$$V_T = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}} \quad (1)$$

$$\varepsilon = 100 \cdot \left(1 - \frac{\rho_{Hg}}{\rho_{He}} \right) \quad (2)$$

the obtained V_T and ε values being listed in Table 3. Alternatively, the total pore volume (V_T') was also estimated as the sum of W_{0-na} , V_{me-mp} and V_{ma-mp} . The values of V_T together with those of W_{0-na} , V_{me-mp} and V_{ma-mp} (i.e., V_T') are plotted together in Fig. 6. As can be seen, as a rule the agreement between V_T and V_T' is pretty good, despite being determined and calculated by different methods. Also, from Fig. 7 it becomes clear that in the present study ACs with quite similar and very different pore volumes in the three porosity regions are prepared. Given as porosity percentages with respect to V_T' , W_{0-na} , W_{me-mp} and V_{ma-mp} are in turn 26%, 36% and 38% for S200CA and as high as 67 % for DA, 46 % for C6A and 63 % for DFWA. By replacing V_{me-pm} with V_{me-na} in

the calculation for C6A, $V_{\text{me-na}}$ is then 53 %. ϵ varies widely between 30.8 % for DL1A and 80.2 % for S200CA.

4. Conclusions

In the present study, from CS and using different impregnation methods, a wide range of ACs have been prepared by chemical activation with H_3PO_4 and texturally characterized by gas physical adsorption (N_2 , -196°C ; CO_2 , 0°C), mercury porosimetry, and helium and mercury density measurements. Obtained results show that, in general, the impregnation method exerts a great influence on the porous structure of AC. It has been found that:

- Using more dilute solutions of H_3PO_4 and effecting the impregnation in various stages or with the residual liquid after the soaking step in the impregnation process of CS, enhanced developments of micro-, meso- and macroporosity are obtained. The mesopore volume is as high as $0.13 \text{ cm}^3 \text{ g}^{-1}$ for DL3A and $0.16 \text{ cm}^3 \text{ g}^{-1}$ for DRLA. This is an outstanding finding as mesoporosity increases are usually associated with the use of concentrated H_3PO_4 solutions in impregnation treatments.
- With the aforesaid residual solution two ACs with BET surface areas 137 or 337 and $791 \text{ m}^2 \text{ g}^{-1}$ instead of only one with BET surface area $640 \text{ m}^2 \text{ g}^{-1}$ can be prepared, using the same amount of H_3PO_4 .
- Macroporosity is more sensitive to the removal of the residual liquid after the soaking step and especially to the subsequent washing of the remaining product with distilled water. The generation of macropores has been associated with pyrolysis of H_3PO_4 -poorly impregnated CS rather than with the activating action of H_3PO_4 during the carbonization process.
- Micro- and mesoporosity are heterogeneous and macroporosity is homogeneous.

- Using concentrated H_3PO_4 solutions, AC with high pore volumes in the regions of micro-, meso- and macropores are prepared. Preconcentration significantly influences the pore size distribution and pore volumes in the regions of large meso- and macropores.
- The effect of the previous charring of CS on the porous structure of AC depends on temperature and concentration of the impregnation solution. Charring at 200 °C gives rise to ACs with increased developments of porosity, whereas the opposite may be applied when heating at 300 °C.
- ACs with very large macropores are only prepared using the concentrated H_3PO_4 solution either after overconcentration for 24 h or in the impregnation of S200.
- ACs with variety of porous structures are prepared. For different ACs, the volumes of micro-, meso- and macropores may be as high as 67%, 46% and 63%, respectively. Conversely, porosity may be made up of 26% of micropores, 36% of mesopores and 38% of macropores. BET surface areas vary between 123 and 1491 $\text{m}^2 \text{g}^{-1}$.

The operational strategies studied in this work can be applied to the efficient preparation of activated carbons with tailored porosities for specific applications.

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Conflict of interest

The authors declare no conflict of interest.

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Table headings

Table 1. Chemical analyses of CS.

Table 2. Impregnation methods and yields: m = mass of H_3PO_4 per impregnation; N = number of impregnations; t = oven-drying time in Series 2; T = charring temperature in Series 3; Δm = mass increment of CSs after impregnation; Y = yield; n-d = non-determined.

Table 3. Characterization of the ACs by gas adsorption, mercury porosimetry and density measurements: textural data and density values.

Figure Captions

Figure 1. N_2 adsorption isotherms at -196°C for ACs of series 1 and the carbonized product prepared from CS.

Figure 2. N_2 adsorption isotherms at -196°C for ACs of series 2.

Figure 3. N_2 adsorption isotherms at -196°C for ACs of series 3.

Figure 4. Plot of S_{BET} against the H_3PO_4 mass used in the impregnation of CS and of chars prepared from CS.

Figure 5. Curves of the cumulative pore volume against pore radius (mercury porosimetry) for ACs of series 1.

Figure 6. Curves of the cumulative pore volume against pore radius (mercury porosimetry) for ACs of: a), series 2; b), series 3.

Figure 7. Plot of total pore volumes obtained for all ACs.

Table 1. Chemical analyses of CS.

Ultimate	wt. %	Proximate	wt. %
Carbon	49.00	Moisture	5.41
Hydrogen	6.37	Volatile matter	71.72
Nitrogen	0.24	Ashes	0.24
Oxygen	44.15	Fixed carbon	22.62

Table 2. Impregnation methods and yields: m = mass of H₃PO₄ per impregnation; N = number of impregnations; t = oven-drying time in Series 2; T = charring temperature in Series 3; Δm = mass increment of CSs after impregnation; Y = yield; n-d = non-determined.

Series	Sample	m (g/100 mL)	N	Filtered	Washed	t (h)	T (°C)	Δm (g)	Y (%)
1	D	16	1	-	-	-	-	7.30	45.6
	DL1	5.33	1	-	-	-	-	1.20	22.5
	DL2	5.33	2	-	-	-	-	1.85	34.7
	DI1	10.66	1	-	-	-	-	4.43	41.6
	DL3	5.33	3	-	-	-	-	2.30	43.1
	DF	16	1	Yes	-	-	-	1.34	8.4
	DFW	16	1	Yes	Yes	-	-	0.48	3.0
	DRL	Reutilized	1	-	-	-	-	10.9	n-d
2	C0	144.5	1	-	-	0	-	135.54	93.8
	C2	n-d	1	-	-	2	-	143.20	99.1
	C6	n-d	1	-	-	6	-	126.29	87.4
	C12	n-d	1	-	-	12	-	127.45	88.2
	C24	n-d	1	-	-	24	-	134.96	93.4
3	S200D	16	1	-	-	-	200	9.09	56.8
	S300D	16	1	-	-	-	300	15.04	94.0
	S200C	144.5	1	-	-	-	200	132.80	91.9
	S300C	144.5	1	-	-	-	300	94.36	n-d

Table 3. Characterization of the ACs by gas adsorption, mercury porosimetry and density measurements: textural data and density values.

Samples	N ₂			CO ₂		Mercury				
	adsorption			adsorption		porosimetry		Densities		
	W _{0-na} ^a	V _{me-na} ^b	S _{BET} ^c	W _{0-cda} ^a	V _{me-mp} ^d	V _{ma-mp} ^e	ρ _{Hg}	ρ _{He}	V _T	ε ^f
	(cm ³ /g)	(cm ³ /g)	(m ² /g)	(cm ³ /g)	(cm ³ /g)	(cm ³ /g)	(g/cm ³)	(g/cm ³)	(cm ³ /g)	(%)
DA	0.35	0.04	640	0.25	0.08	0.09	1.02	1.78	0.42	42.7
DL1A	0.07	0.01	123	0.15	0.01	0.21	1.17	1.69	0.26	30.8
DL2A	0.29	0.04	512	0.23	0.06	0.18	0.99	1.73	0.43	42.8
DI1A	0.20	0.02	351	0.20	0.03	0.22	0.96	1.72	0.46	44.2
DL3A	0.45	0.05	837	0.29	0.13	0.15	0.83	1.79	0.65	53.6
DFA	0.08	0.02	134	0.16	0.03	0.23	0.96	1.68	0.45	42.9
DFWA	0.18	0.03	337	0.18	0.03	0.36	0.84	1.44	0.50	41.7
DRLA	0.40	0.08	791	0.23	0.16	0.09	0.82	1.75	0.65	46.9
C0A	0.54	1.12	1491	0.20	0.81	0.76	0.40	1.78	1.94	77.5
C2A	0.46	1.02	1203	0.16	0.73	0.61	0.43	1.65	1.72	73.9
C6A	0.54	1.20	1441	0.21	0.90	0.52	0.40	1.81	1.95	77.9
C12A	0.53	1.27	1440	0.18	0.84	0.58	0.42	1.73	1.80	75.7
C24A	0.53	1.25	1438	0.20	0.85	0.60	0.41	1.67	1.84	75.5
S200DA	0.36	0.04	660	0.23	0.10	0.08	0.93	1.76	0.51	47.2
S300DA	0.19	0.02	330	0.20	0.03	0.34	0.88	1.71	0.55	48.5
S200CA	0.55	1.40	1489	0.13	0.76	0.79	0.41	2.07	1.96	80.2
S300CA	0.33	0.05	596	0.22	0.07	0.39	0.76	1.80	0.76	42.2

^a Micropore volume by the Dubinin-Radushkevich equation [38].

^b Mesopore volume by the Barrett, Joyner and Halenda (BJH) method [39].

^c Specific surface area by the Brunauer, Emmett and Teller (BET) equation [40].

^d Mesopore volume from the difference between the cumulative pore volumes at the pore radii of 20 Å and 500 Å.

^e Macropore volume equal to the cumulative pore volume at the pore radius of 500 Å.

^f Total porosity as calculated by the expression (2).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

GRAPHICAL ABSTRACT