INFLUENCE OF ACTIVATION ATMOSPHERE USED IN THE CHEMICAL ACTIVATION OF ALMOND SHELL ON THE CHARACTERISTICS AND ADSORPTION PERFORMANCE OF ACTIVATED CARBONS

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ABSTRACT

The aim of this work was to compare the effect of different activating atmospheres on the final properties and adsorption performance of activated carbons. Almond shell based activated carbons have been obtained by chemical activation with phosphoric acid. Two sets of activated carbons were prepared. First set was prepared under inert atmosphere at different impregnation ratios, temperatures and times of activation. Second set of activated carbons was prepared at the same activating conditions except the activating atmosphere using and oxidant one. Activated carbons prepared under both activation atmospheres were characterized by elemental analysis (EA), thermogravimetry (TGA), temperature programmed desorption (TPD), point zero charge (PZC), Boehm titration and N₂ physisorption. To study the adsorption performance of the activated carbons toluene adsorption-desorption isotherms were determined gravimetrically. The results obtained confirm that the activating atmosphere has a strong influence on the final characteristics of the activated carbons. Activated carbons with higher oxygen content and more negative surface charge have been obtained by changing the activating atmosphere by an oxidant one. Surface area is also higher for activated carbons prepared under oxidant atmosphere. However toluene adsorption capacity is lower for activated carbons prepared under oxidant atmosphere due to their surface chemistry.

KEYWORDS: activated carbons, activation atmosphere, chemical activation, adsorption, air pollution control, agricultural waste.
1. INTRODUCTION

Activated carbons are one of the most versatile adsorbents to be used for the effective removal of volatile organic compounds in gas streams [1]. The adsorption capacity of an activated carbon depends on the porosity [2,3], mainly on the microporosity, and on the surface chemistry [4].

Depending on the characteristics of the adsorbates, activated carbons can be designed by using the appropriate precursor and optimizing the preparation conditions, this is known as tailoring concept [5]. Main parameters affecting the characteristics of activated carbon are impregnation ratio, activation temperature, activation time and activating atmosphere.

Activated carbons can be produced from a large variety of raw materials by chemical or physical activation [6]. Advantages of the chemical activations compared to the physical activation are the lower activation temperature and the shorter activation time. The chemical activation involves the impregnation of the raw material with a chemical agent and the heat treatment of the mixture to carbonize the material. Different activated agents can be used in the chemical activation but phosphoric acid permits the preparation of activated carbons with lower activation temperatures [7,8]. Phosphoric acid promotes the depolymerization, dehydration and redistribution of constituent biopolymers [9] during the pyrolytic decomposition of lignocellulosic materials.

Activated carbons with a large development of porosity can be prepared from lignocellulosic wastes by chemical activation with phosphoric acid [10-14]. The preparation of activated carbons by chemical activation with phosphoric acid under inert atmosphere, usually N₂, has been studied by several authors [8,11,15-17]. Although the effect of the phosphoric acid on the activation of activated carbons is well
The effect of the atmosphere during the heat treatment has only been studied by few authors [18-21]. Puziy et al. [12] obtained activated carbons with a higher oxygen content when an air atmosphere is used instead of N₂ atmosphere. Porosity of activated carbons is also affected by the activating atmosphere; the use of an oxidant atmosphere instead of an inert atmosphere produce activated carbon with larger surface areas [12,19-22] and an increase in mesopore volume [21,23] due to the widening of the pores during the activation process. It can be explained in terms of the aromatization process during heat treatment. The presence of oxygen inhibits the aromatization process, reducing the influence of the phosphoric acid in both promoting the development of porosity and reducing the extent of contraction produced during the heat treatment [18].

The present work compares the characteristics of activated carbons obtained by chemical activation of almond shells as well as their toluene adsorption performance of two series of activated carbons prepared with the same activation conditions except the activating atmosphere: either under N₂ or 8%O₂/N₂ atmosphere.

2. MATERIAL AND METHODS

2.1 Preparation of activated carbons

Raw material chosen for the preparation of activated carbons was almond shell from Vera del Moncayo, Zaragoza (Spain). Dry shells were crushed and sieved at 0.2-1 mm. The chemical activation was carried out by impregnation of the almond shell with (ortho)-phosphoric acid of 89 wt. % followed by one-step carbonization-activation under N₂ or in 8%O₂/N₂ atmosphere.
Impregnation ratio (defined as: weight of phosphoric acid / weight of precursor),
activation temperature and activation time were selected according to a previous work [15]. In that work, a total of 12 activated carbons were prepared under N2 atmosphere. The activation conditions which led to activated carbons with higher toluene adsorption capacities [24] were selected to prepare the new activated carbons under 8%O2/N2 activating atmosphere.

Before activation, the almond shell is mixed with a determined amount of phosphoric acid of 89 wt % concentration to reach the impregnation ratios in the range 0.5-1.5. The suspension was shaken at room temperature during 1 h. The impregnated samples were further thermally treated at different activation temperatures under a flow of 250 cm3/min either of 8%O2/N2 (which was kept during both heating and cooling), and maintained at the selected temperature during a time ranging from 30 to 120 min. Solid pyrolysis residues were water washed in Soxhlet until pH>6. The resulting activated carbons were dried at 100°C until constant weight and stored under Ar. The activated carbons included in this study are given in Table 1.

2.2 Characterization of activated carbons

Activated carbons were characterized by elemental analysis, thermogravimetry (TGA) temperature programmed desorption coupled to mass spectrometry (TPD-MS), point of zero charge (PZC), Boehm titration and nitrogen adsorption at -196 °C. Ultimate analysis of the activated carbons was carried out in a Thermo Flash 1112 microanalysis apparatus. Oxygen content was obtained by difference.
Thermogravimetric (TG) curves were obtained in a TA Instruments thermobalance. Approximately 20 mg of sample was placed in a Pt crucible and was heated at 10ºC/min up to 1000ºC under a flow of Ar. The TPD runs were carried out with a custom build set-up, consisting of a tubular quartz reactor placed inside an electrical furnace connected to a quadrupole mass spectrometer from Pfeifer. TPD experiments were carried out by heating the samples in Ar flow up to 1100 ºC at a heating rate of 10 ºC/min, and recording the amount of CO and CO$_2$ evolved at each temperature with the mass spectrometer. The calibrations for CO and CO$_2$ were carried out by standards diluted in Ar. For each experiment 0.5 g of activated carbon was placed in a horizontal quartz tube reactor under a stream of 30 ml/min of Ar.

The immersion technique [25] was used to determine the point of zero charge of the samples. Suspensions of 0.7 g of activated carbon were put in contact with 10 ml of NaNO$_3$ 0.1 M at different pH values. Initial pH values were obtained by adding an amount of HNO$_3$ or NaOH solution taking the NaNO$_3$ solution to pH≈3, pH≈6 and pH≈10. The suspensions were agitated for 24 h in a shaker at 250 r.p.m. at room temperature and filtered. The pH of the filtered solutions were measured. The final values for the PZC were the average of the three pH values.

The selective neutralization method was used to evaluate the acidic character of the surface of the activated carbons according to Boehm’s procedure [26]. The amounts of various acidic oxygen functional groups (carboxyls, lactones, phenols and carbonyls) were measured by selective neutralization using bases of different strength. Approximately 0.5 g of each sample was mixed with 50 ml of a 0.1 N solution of a base (NaOH, Na$_2$CO$_3$, NaHCO$_3$, NaOC$_2$O$_5$). The suspension was shaken for 24 h at room temperature. After that time, the solution was filtered and an aliquot was taken. The
amount of each base neutralized by the activated carbon was determined by back-
titration using HCl 0.1 N solution.

The nitrogen adsorption at -196 ºC was carried out in a Micromeritics ASAP 2020
automatic adsorption apparatus. The samples were initially outgassed at 150 ºC and up
to a vacuum of 10⁻⁶ mm Hg. The volume of adsorbed nitrogen was measured from a
relative pressure of 10⁻⁷ up to 0.995. The isotherms were analysed using different
methods such as the BET method [27] for determination of surface area, the BJH
method [28] for determining the volume of mesopores and t-plot for determining the
volume of micropores [29]. The total pore volume was taken from the measurement of
adsorbed nitrogen at a relative pressure of 0.995.

2.3 Toluene adsorption

The adsorption-desorption isotherms of toluene were determined gravimetrically using
an automatic adsorption apparatus (VTI Co). The temperature of the sample, 25 ºC, was
monitored during the experiment and a pressure transducer monitored the pressure of
the system. For each experiment 80 mg of activated carbon was taken. Initially the
sample was outgassed at 150 ºC and up to a vacuum of 10⁻⁶ mm Hg. After cooling to 25
ºC toluene was introduced in the system to obtain the adsorption and desorption
isotherms.

3. RESULTS AND DISCUSSION

3.1 Characterization of samples
Elemental analysis and yield of activated carbons (calculated as 100 x mass of AC / mass precursor) is included in Table 2. Activated carbons show a low content in nitrogen and a negligible amount of sulfur. Activated carbons prepared under oxidant atmosphere and at lower activation temperatures (400ºC) show a higher amount of oxygen [12]. Activated carbons prepared at low and intermediate impregnation ratio show higher yields [30,31]. It can be attributed to the decomposition of the polymeric structures of the activated carbons during the activation stage that release most elements different from carbon (N, H and O). Activating agent employed permits the dehydration, depolimerization and the redistribution of the constituent polymers, and the conversion of aliphatic groups to aromatics, increasing the yield of the activated carbons. Higher impregnation ratios produce a higher elimination of tars of the pores decreasing the yield [17]. Different activation atmospheres provided different yields [12], obtaining higher results of yield for activated carbons prepared under oxidant atmosphere and low activation temperatures. This can be attributed to the inhibition of the activating agent in presence of air [18]. Figure 1 shows DTG curves for activated carbons obtained under inert and oxidant atmospheres. Lignocellulosic wastes are mainly compound of hemicellulose, cellulose, lignin and other polymers [32]. Hemicellulose decomposes at low temperatures (310 ºC) while cellulose decomposes at higher temperature (at around 380 ºC) [33,34]. Lignin starts to decompose at low temperature (220 ºC) and at low rate up to about 900 ºC overlapping with the temperatures of decomposition of hemicellulose and cellulose [35]. The addition of chemicals to the precursor and the thermal treatment carried out
result in a variation in the temperature of decomposition in function of the employed conditions [33,36] shifting degradation to considerably higher temperatures [37].

The temperature used to prepare the activated carbons is higher than the decomposition temperature of hemicellulose and cellulose therefore the curves of DTG obtained do not present the processes corresponding to their decomposition, except for the activated carbons AT400R15t30 and AT400R15t30-ox, due to the short time of activation employed.

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The activated carbons prepared at lower temperatures (400-467 ºC) present a broad band around 550 ºC, which can indicate that the degradation process of the lignin has been incomplete. The higher bands obtained for activated carbons prepared under oxidant atmosphere indicate that this process has been more incomplete than for the activated carbons prepared under inert atmosphere.

The band at about 800 ºC becomes more intense and it is shifted to higher temperatures of decomposition at increasing temperature of activation. This band can indicate that the crosslinking process to produce aromatic units becomes more important for activated carbons prepared under inert atmosphere due to the higher bands obtained. The oxidant atmosphere inhibits the production of aromatic units in the activation stage.

At the temperature of activation of 600ºC the crosslinking process has started during activation of the samples and during TGA experiments this process is completed at temperatures around 900 ºC.

During the thermal decomposition of activated carbons the surface oxygen complexes are desorbed as CO and CO$_2$ at specific temperatures. It has been proposed that CO$_2$ evolves from carboxylic groups and their derivatives, such as lactones and anhydrides, while CO is mainly a decomposition product of quinones, hydroxyquinones and phenols [38,39].
Profiles of CO and CO\textsubscript{2} evolution are given elsewhere [40]. Since then, it can be summarized that the preparation of activated carbons under oxidant atmosphere results in the formation of more stable functional groups in the surface. These results can be compared with the results obtained in DTG curves.

The amounts of CO and CO\textsubscript{2} evolved up to 1100ºC in TPD experiments are reported in Table 3. For all samples studied the amount of CO evolved during the thermal treatment is higher than the amount of CO\textsubscript{2}. For activated carbons prepared under N\textsubscript{2} atmosphere, increasing the activation temperature the amount of CO evolved increases but there is no relationship with the amount of CO\textsubscript{2}. Activated carbons prepared under oxidant atmosphere show higher amounts of CO evolved than activated carbons prepared under inert atmosphere, except for the activated carbons prepared at lower activation time AT400R1t30-ox and AT600R1t30-ox. This result could be explained in terms of the low activation time used. The aromatization process is inhibited under oxidant atmosphere, as it has been shown above, but low activation times enhance this inhibition.

The point of zero charge (PZC) is a very important parameter characterizing the acid-base behaviour of the solids. In sorption studies is an useful parameter that permits to hypothesize on the ionization of functional groups in the surface of activated carbons and their interactions with adsorbates. PZC is defined as the value of pH at which the charge of the solid surface is zero [41]. At this pH, the charge of the positive surface sites is equal to that of the negative ones.

PZC of the activated carbons can be seen in Table 3. All samples have noticeably acid properties with PZC values between 1.69 and 4.54. This can be explained by the formation of acidic groups at the carbon surface as a result of the activating agent. It can be observed that with the same preparation conditions activated carbons prepared under
oxidant atmosphere show a lower $pH_{PZC}$. It can be explained by the formation of a higher amount of oxygenated surface groups on the activated carbons in presence of an oxidant atmosphere. Both, under inert and in oxidant atmospheres, the value of $pH_{PZC}$ decreases at increasing the activation temperature.

Differences in the values of $pH_{PZC}$ are a consequence of different preparation conditions, confirming that, by carefully selecting the conditions of preparation, it is possible to prepare activated carbons with different acidity levels and oxygen surface groups distribution [42].

The selective base neutralization method gives information only on the oxygen surface functionality of the carbons. Despite that not all the oxygen known to be on a carbon surface can be measured by titration techniques, Boehm titration [26] was used to obtain the amount of acidic sites on the activated carbon surface. Some oxygen could be bonded within the graphene layers (in-ring) and hence would be non-reactive, and some carbonyl groups may not be able to react with the alkaline solutions. Figure 2 reports the results from Boehm titration. Main contribution to the surface chemistry corresponds to carbonyls type groups, while the low content in phenolic groups respect to the contribution of carbonyls groups has been described previously for activated carbons from lignocellulosic materials activated with phosphoric acid [43]. Assuming that carboxyls and lactones evolve CO$_2$ in TPD experiments and phenols and carbonyls evolve as CO in TPD experiments, Boehm titration results follow the same trend obtained from TPD experiments.

The characterization of porosity of samples obtained by the analysis of the N$_2$ physisorption is included in Table 4 and the isotherms obtained are shown in Figure 3. The percentage of microporosity was obtained as the ratio between total micropore
volume, calculated applying the Dubinin-Radushkevich equation [44] to the adsorption branch of the N₂ isotherm and the volume adsorbed at relative pressure of 0.995 [2].

For the activated carbons prepared under N₂ atmosphere, lower activation temperatures (400-467 ºC), intermediate impregnation ratios (1.0-1.17) and intermediate activation times (45-75 min) result in highest surface area BET. This is also confirmed taken into account the values of micropore and mesopore volumes. This is in agreement with others research works that prepare activated carbons from lignocellulosic wastes by chemical activation with H₃PO₄ and obtain higher BET surface areas at activation temperatures of 400-450 ºC [11,13,45] and with intermediate impregnation ratios [10,46].

All activated carbons prepared under oxidant atmosphere show higher BET surface area than those activated carbons prepared as same conditions under inert atmosphere. This has been reported by other authors that obtain activated carbons with higher BET surface area by changing an inert atmosphere by an oxidant one [12,16,21,22,47]. The BET surface area of activated carbons prepared under oxidant atmosphere is a function of the BET surface area of the activated carbons prepared under inert atmosphere [48].

The reproducibility of the preparation method used was tested previously [15], showing a slightly variation, for example a difference of 1% in the BET surface area or 0.8% in the carbon content.

3.2 Toluene adsorption

The static adsorption isotherms for toluene at 25 ºC are shown in Figure 4. The experimental adsorption capacity, defined as the amount at the plateau of the isotherm, is higher for the samples prepared at lower temperatures (400-467 ºC), for both inert
and oxidant atmosphere. Toluene adsorption capacities for activated carbons prepared under inert atmosphere are slightly higher than for those activated carbons prepared at the same activating conditions under oxidant atmosphere. This can be explained by the higher amount of oxygenated groups present on the surface of activated carbons prepared under oxidant atmosphere which have a negative influence on the toluene adsorption capacity [14,49]. Samples with lower adsorption capacity are the samples prepared at 533 °C, which are the samples with the lower impregnation ratio, and the sample prepared at 600 °C. The adsorption capacities for each activated carbon are included in Table 4.

Activated carbons show high toluene adsorption capacities, higher than 60% (wt/wt). These values are higher than the adsorption capacities reported by other authors [4,50-53].

The experimental adsorption isotherm data were fitted to the Langmuir model [54]. The parameters of limiting value for toluene adsorption ($W_m$) and constant value (K) obtained are resumed in Table 5. The Langmuir isotherm expressed relatively well the adsorption of toluene, indicating the dependence on both physical and chemical adsorption. $W_m$ has a good correlation with the experimental results obtained for toluene adsorption. Values of K can be related with the development of the microporosity of the activated carbons.

Comparing the amount of toluene adsorbed with BET surface area it can be concluded that there is not a direct correlation between both values. Activated carbons with higher values of BET surface area do not show the higher adsorption capacities. In spite of BET surface area is a very important parameter in toluene adsorption there are another factors with a high influence on the toluene adsorption capacity. Surface chemistry is an important characteristic of activated carbons which gives different adsorption sites.
From Table 3 and Figure 4, it is evident that the activated carbons have different polarity coming from the different type and amount of surface groups. However, comparing the amount of surface groups and toluene adsorption capacity it is clear that there is not relationship. This fact can be explained in terms of a compromise between textural properties and surface chemistry.

The heterogeneity of the activated carbon surface could give preferred sites for the adsorption. This heterogeneity should be a compromise between adsorption potential distribution in micropores and surface chemistry.

The heterogeneity of the surfaces can be studied by inspection of the deviation from linearity of the D-R model applied to either n-hexane or toluene isotherms at high relative pressures [55]. When a polar adsorbate is adsorbed onto a surface containing polar sites there is a thermal effect on the orientation of the molecule on the adsorbent. So the distribution of the adsorbed volumes with -ΔG for such a system should not represent solely of the physical nature of the surface but will also be markedly affected by its chemical nature.

Present case, all the toluene isotherms modeled by D-R equation exhibit a positive deviation at the highest relative pressures (low log \( \frac{p_0}{p} \)). At the lowest relative pressures, the adsorption capacities are strongly influenced by electronic properties of the adsorbate and also with the energy of interaction with the adsorbent. This fact is in line with adsorption capacities being associated with strong interaction between adsorbent and adsorbate at the early stages of adsorption, corresponding to primary micropore filling. During the later stages of adsorption, as micropores of bigger size are being filled, at higher relative pressures, the adsorption capacities are determined mainly by molecular size, the hydrophilic character of the adsorbate and polarity. The importance of these properties indicates that polar as well as
non-polar interactions between adsorbate molecules play a key role in the adsorption mechanism at this stage. At high relative pressures range the adsorption capacity is affected by both mechanisms [55]. These positive deviations at high relative pressures (low log²p₀/p) from the D-R equation indicate that the adsorption process is dominated by surface heterogeneity rather than volume filling of micropores. The role played by both the chemical nature of the surface and the microporosity in the deviation of the D-R plots may be quantified by calculating the slope of the portion of the plot corresponding to high relative pressures (low log²p₀/p) responsible of the deviation from linearity.

The amount of toluene adsorbed is plotted as a function of the D-R slope at low log²p₀/p in Figure 5. It can be observed that there is a maximum of adsorption capacity at intermediate values of D-R slope. This fact can indicate that there is a compromise between porosity and surface chemistry, existing an optimum value to reach high toluene adsorption capacity. High values for D-R slope deviation imply high surface heterogeneity which can involve accessibility problems to the microporosity because the high concentration of surface sites. Low values for D-R slope deviation can imply lower concentration of adsorption sites, leading to lower toluene adsorption characteristics.

**CONCLUSION**

The results of this study indicate that activating atmosphere during phosphoric acid chemical activation of almond shell has a strong influence on the characteristics and toluene adsorption capacity of the activated carbons. Activated carbons with higher surface area can be obtained by changing an inert activating atmosphere by an air
atmosphere. The surface chemistry of activated carbons can be modified by using an oxidant atmosphere, resulting in activated carbons with higher contents in oxygenated surface groups and surface negative charge. Toluene adsorption capacity is lower for activated carbons prepared under air atmosphere in spite of their higher surface area. This can be attributed to the surface chemistry of the activated carbons. A compromise between textural properties and surface chemistry has been found in terms of surface heterogeneity defined as the deviation of linearity of D-R plot, obtaining maximum of adsorption capacity at intermediate values of D-R slope.

**Acknowledgements**

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**References**


[40] A. Martínez de Yuso, Development of activated carbons from lignocellulosic wastes for toluene and h-hexane adsorption and recovery, University of San Jorge, Spain, 2012.


Table 1. Preparation conditions of the activated carbons and labelling of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (ºC)</th>
<th>IR(^1)</th>
<th>Time (min)</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT400R1t75</td>
<td>400</td>
<td>1</td>
<td>75</td>
<td>N(_2)</td>
</tr>
<tr>
<td>AT400R15t30</td>
<td>400</td>
<td>1.5</td>
<td>30</td>
<td>N(_2)</td>
</tr>
<tr>
<td>AT467R117T45</td>
<td>467</td>
<td>1.17</td>
<td>45</td>
<td>N(_2)</td>
</tr>
<tr>
<td>AT533R083t60</td>
<td>533</td>
<td>0.83</td>
<td>60</td>
<td>N(_2)</td>
</tr>
<tr>
<td>AT600R1t30</td>
<td>600</td>
<td>1</td>
<td>30</td>
<td>N(_2)</td>
</tr>
<tr>
<td>AT400R1t75-ox</td>
<td>400</td>
<td>1</td>
<td>75</td>
<td>8%O(_2)/N(_2)</td>
</tr>
<tr>
<td>AT400R15t30-ox</td>
<td>400</td>
<td>1.5</td>
<td>30</td>
<td>8%O(_2)/N(_2)</td>
</tr>
<tr>
<td>AT467R117T45-ox</td>
<td>467</td>
<td>1.17</td>
<td>45</td>
<td>8%O(_2)/N(_2)</td>
</tr>
<tr>
<td>AT533R083t60-ox</td>
<td>533</td>
<td>0.83</td>
<td>60</td>
<td>8%O(_2)/N(_2)</td>
</tr>
<tr>
<td>AT600R1t30-ox</td>
<td>600</td>
<td>1</td>
<td>30</td>
<td>8%O(_2)/N(_2)</td>
</tr>
</tbody>
</table>

\(^1\) Impregnation ratio: amount phosphoric acid (g) / amount almond shell (g)
Table 2. Ultimate analysis of activated carbons (% in dry basis).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>Yield</th>
</tr>
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<tr>
<td>AT400R1t75</td>
<td>75.20</td>
<td>2.42</td>
<td>0.31</td>
<td>n</td>
<td>22.07</td>
<td>68.4</td>
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<tr>
<td>AT400R15t30</td>
<td>72.40</td>
<td>3.13</td>
<td>0.49</td>
<td>n</td>
<td>23.98</td>
<td>69.2</td>
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<td>70.00</td>
<td>2.72</td>
<td>0.30</td>
<td>n</td>
<td>26.98</td>
<td>70.6</td>
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<td>0.38</td>
<td>n</td>
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<td>72.9</td>
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<td>2.05</td>
<td>0.42</td>
<td>n</td>
<td>29.06</td>
<td>73.2</td>
</tr>
<tr>
<td>AT400R1t75-ox</td>
<td>61.91</td>
<td>1.84</td>
<td>0.54</td>
<td>n</td>
<td>35.71</td>
<td>80.9</td>
</tr>
<tr>
<td>AT400R15t30-ox</td>
<td>60.35</td>
<td>3.31</td>
<td>0.45</td>
<td>n</td>
<td>35.89</td>
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<td>AT467R117t45-ox</td>
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<tr>
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<td>0.43</td>
<td>n</td>
<td>25.92</td>
<td>69.3</td>
</tr>
</tbody>
</table>

1 By difference

2 Mass of activated carbon/mass of precursor x 100

n: negligible
Table 3. Total amount of CO and CO$_2$ evolved up to 1100ºC in TPD experiments and pH$_{PZC}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO (mmol/g)</th>
<th>CO$_2$ (mmol/g)</th>
<th>pH$_{PZC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT400R05t120</td>
<td>2.17</td>
<td>1.32</td>
<td>4.04±0.39</td>
</tr>
<tr>
<td>AT400R15t30</td>
<td>1.80</td>
<td>0.75</td>
<td>4.54±0.10</td>
</tr>
<tr>
<td>AT467R117t45</td>
<td>2.18</td>
<td>1.18</td>
<td>3.39±0.14</td>
</tr>
<tr>
<td>AT533R083t60</td>
<td>2.23</td>
<td>0.39</td>
<td>2.36±0.11</td>
</tr>
<tr>
<td>AT600R1t30</td>
<td>3.04</td>
<td>0.45</td>
<td>1.89±0.05</td>
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<tr>
<td>AT400R1t75-ox</td>
<td>9.68</td>
<td>0.66</td>
<td>2.19±0.03</td>
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<tr>
<td>AT400R15t30-ox</td>
<td>1.43</td>
<td>0.60</td>
<td>2.07±0.02</td>
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<td>AT467R117t45-ox</td>
<td>7.76</td>
<td>0.54</td>
<td>2.04±0.02</td>
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<tr>
<td>AT533R083t60-ox</td>
<td>9.54</td>
<td>0.61</td>
<td>1.74±0.01</td>
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<tr>
<td>AT600R1t30-ox</td>
<td>3.38</td>
<td>0.46</td>
<td>1.69±0.02</td>
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<tr>
<td>Sample</td>
<td>$S_{BET}$ (m²/g)</td>
<td>$V_{meso}$ ¹ (cm³/g)</td>
<td>$V_{micro}$ ² (cm³/g)</td>
</tr>
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<td>-----------------</td>
<td>------------------</td>
<td>-----------------------</td>
<td>-----------------------</td>
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<tr>
<td>AT400R1t75</td>
<td>1128±50</td>
<td>0.385</td>
<td>0.259</td>
</tr>
<tr>
<td>AT400R15t30</td>
<td>789±34</td>
<td>0.268</td>
<td>0.176</td>
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<td>0.181</td>
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<td>AT533R083t60</td>
<td>891±36</td>
<td>0.341</td>
<td>0.194</td>
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<tr>
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<td>980±38</td>
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<td>AT600R1t30-ox</td>
<td>1122±50</td>
<td>0.400</td>
<td>0.103</td>
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</table>

1 BJH method

2 t-plot method

3 According to Lillo-Rodenas et al., 2005
<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental (mmol/g)</th>
<th>Wm (mmol/g)</th>
<th>K (cm$^3$/g)</th>
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<tbody>
<tr>
<td>AT400R1t75</td>
<td>6.612</td>
<td>6.540</td>
<td>1.21</td>
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<td>7.156</td>
<td>7.436</td>
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<td>AT467R117t45</td>
<td>6.924</td>
<td>6.891</td>
<td>0.94</td>
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<td>AT533R083t60</td>
<td>4.954</td>
<td>4.949</td>
<td>1.51</td>
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<tr>
<td>AT600R1t30</td>
<td>6.471</td>
<td>6.504</td>
<td>0.8</td>
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<td>AT400R1t75-ox</td>
<td>6.372</td>
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<td>AT467R117t45-ox</td>
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<td>5.804</td>
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<td>AT600R1t30-ox</td>
<td>5.759</td>
<td>5.628</td>
<td>1.25</td>
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</table>

Table 5. Maximum adsorption capacity for toluene (mmol/g).
FIGURE CAPTIONS

Figure 1. DTG curves for decomposition of low temperature activated carbons.

Figure 2. Results from Boehm titration.

Figure 3. Nitrogen adsorption isotherms.

Figure 4. Toluene adsorption isotherms.

Figure 5. Amount of toluene adsorbed as a function of the D-R slope at low log²p₀/p.
Figure 3

Nitrogen adsorption (cm$^3$/g)

P/P$_0$

AT400R1t75
AT400R15t30
AT467R117t45
AT533R083t60
AT600R1t30

Nitrogen adsorption (cm$^3$/g)

P/P$_0$

AT400R1t75-ox
AT400R15t30-ox
AT467R117t45-ox
AT533R083t60-ox
AT600R1t30-ox
Figure 4

Adsorbed toluene (mmol/g)

$P/P_0$

Adsorbed toluene (mmol/g)

$P/P_0$

- AT400R1t75
- AT400R15t30
- AT467R117t45
- AT533R083t60
- AT600R1t30

- AT400R1t75-ox
- AT400R15t30-ox
- AT467R117t45-ox
- AT533R083t60-ox
- AT600R1t30-ox
Figure 5

![Graph showing adsorbed toluene (mmol/g) against DR slope (at low log²p₀/p).]