Scaled-up Cork-Derived Activated Carbon: Performance as Pharmaceuticals Adsorbent

Marta A. Andrade\textsuperscript{a}, Ana S. Mestre\textsuperscript{a}, Susana P. Silva\textsuperscript{a}, Ana P. Carvalho\textsuperscript{a}
\textsuperscript{a} Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 749-016 Lisboa, Portugal
\textsuperscript{b} Corticeira Amorim, S.G.P.S., S.A., Rua do Ribeirinho, 202, 4536-907 S. Paio de Oleiros, Portugal
mvandrade@fc.ul.pt

Introduction
Cork transformation is one of the most important and sustainable industries in the Portuguese and Mediterranean region economies, producing several materials beyond the traditional ones, from agglomerates to composites, applied in a series of end products. The manufacturing process originates a set of by-products, as is the case of granules of expanded corkboard, among many others.

Integrated in a previous QREN project, industrial expanded corkboard granules were explored as precursors for the preparation of activated carbons at the lab-scale which proved to perform as efficient adsorbents for pharmaceutical compounds from liquid phase [1]. In the present study we investigate the performance of the activated carbon obtained from the scale-up of the patented activation methodology [2]. The potentialities of this material in liquid phase assays are herein evaluated, aiming a future application in synthetic and real water matrices, in the context of project LIFE Impetus “Improving current barriers for controlling pharmaceuticals compounds in urban wastewater treatment plants”.

Materials and Methods
The preparation of carbon S800/Lab was reported elsewhere [1]. Briefly, granules of expanded corkboard (obtained from Amorim Isolamentos, Portugal) were used as precursor, being activated at 800 °C for 1 h, with steam generated in a bubblter half full with distilled water at 90 °C and carried to the sample by a N\textsubscript{2} flow in a quartz reactor placed in a vertical furnace (Thermolyne, model 21100). Carbon S800/Scale-up was obtained from the scale-up of this procedure, involving the preparation of 10 activation batches of 15 dm\textsuperscript{3} of expanded corkboard granules in a 50 dm\textsuperscript{3} rotating stainless steel reactor. The potentialities of the prepared activated carbons as liquid phase adsorbents were evaluated through screening assays with six pharmaceutical compounds: ibuprofen (Ibu), paracetamol (Para), acetylsalicylic acid (ASA), caffeine (Caf), clofibric acid (Clof), and lopamidol (Iop). The removal efficiencies, after a contact time of 24 h (6 mg of carbon for 9 cm\textsuperscript{3} of each pharmaceutical solution of 120 mg dm\textsuperscript{-3}), were determined using UV–vis spectrophotometry (Genesys 10S).

Results and Discussion
The nanotextural parameters of the activated carbons show that the scale-up has led to a less developed porous network. Actually, compared to lab-prepared carbon, sample
S800/Scale-up has half of the supermicropore volume and a quarter of the mesopore volume.

Table 1. Nanotextural properties of the studied activated carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( A_{\text{mic}} ) (m(^2)g(^{-1}))</th>
<th>( V_{\text{total}} ) (cm(^3)g(^{-1}))</th>
<th>( V_{\text{micro}} ) (cm(^3)g(^{-1}))</th>
<th>( V_{\text{meso}} ) (cm(^3)g(^{-1}))</th>
<th>( V_{\text{meso}} ) (cm(^3)g(^{-1}))</th>
<th>( V_{\text{mic}} ) (cm(^3)g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>S800/Lab</td>
<td>750</td>
<td>0.50</td>
<td>0.27</td>
<td>0.28</td>
<td>0.09</td>
<td>0.19</td>
</tr>
<tr>
<td>S800/Scale-up</td>
<td>590</td>
<td>0.44</td>
<td>0.05</td>
<td>0.18</td>
<td>0.10</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Regarding the results of the screening assays for the removal of the pharmaceutical compounds, the efficiencies obtained using both carbons are displayed in Figure 1. The performance of carbon S800/Scale-up for most of the pharmaceutical compounds is similar or slightly inferior regarding the lab-made carbon (S800/Lab).

Fig. 1. Removal efficiencies for 24 h of the mentioned pharmaceuticals by carbons S800/Lab and S800/Scale-up.

An accentuated negative impact of the scale-up of the process is reflected only in the case of clofibric acid and iopamidol removal. The lower removal for iopamidol is certainly related with the smaller volume of supermicropores and mesopores of carbon S800/Scale-up, that causes diffusional constrains to this molecule, since the presence of agglomeration was reported in the studied experimental conditions [3]. However, from the perspective of an application in environmental conditions, it is expectable that S800/Scale-up material may reach similar iopamidol removal to that of lab-made carbon, since in the concentration range detected in real samples iopamidol is present as a monomer.

Acknowledgements
The authors thank EU funding through the Project LIFE 14 ENV/PT/000739-LIFE Impetus, Fundação para a Ciência e Tecnologia for financial support to CQB (PEst-OE/QUI/UI0100/2014), and COMPETE, Adi - QREN Project WaterCork (nº 5523). ASM thanks FCT for the Post-doc grant SFRH/BPD/86693/2012. The authors thank Covione for the supply of iopamidol.

References