One-step Steam Pyrolysis Preparation and Characterization of Spherical Carbon Adsorbents Obtained from Ion-exchange Resins

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ABSTRACT: Using the single-set steam pyrolysis of Dowex 50 WX-2 (a polystyrene–divinylbenzene resin), Spherical Carbon Adsorbents (SCAs) were prepared. The porous structure of the materials obtained was easily controlled by varying the heating rate, allowing carbons having a controlled ratio of micropores to mesopores to be obtained. These materials are promising for the adsorption of phenol from aqueous solutions. Moreover, due to the relatively small amount of irreversibility exhibited in such adsorption, they could find potential use in environmental protection.

1. INTRODUCTION

Recently, different new methods of preparation of activated carbons with controlled porosity from ion-exchange resins as the source of spherical carbon adsorbents (SCAs) have been reported by Nakagawa et al. (1999), Kocirik et al. (2001), Miura et al. (1991), Antonetti et al. (2000), Bratek et al. (2002) and Grzegorczyk et al. (2006). Amongst other conclusions, it was deduced that the presence of cations in the source material, as well as the pyrolysis conditions employed, determine the structure and properties of the resulting SCAs. Nakagawa et al. (1999) have reported that carbons prepared from resins with di- or tri-valent cations maintain their sharp pore distributions, whereas those prepared from resins with univalent cations lose most of their porosity. The main reason for this drastic difference is that di- or tri-valent cations can form ionic cross-links connecting two or three functional groups in the resins, with these cross-links acting as pillars to stabilize the pores during the carbonization process. Grzegorczyk et al. (2006) observed a similar pillaring effect and claim that the spherical shape is not preserved during the carbonization of samples exchanged with univalent cations (i.e. the H+- or Na+-forms).

On the other hand, the one-step steam pyrolysis process has been used successfully by Sentorun-Shalaby et al. (2006), Gergova and Eser (1996) and Girgis et al. (2002) for the preparation of activated carbons from different carbon precursors such as apricot stones, peanut hulls and agricultural wastes. In addition, other lignocellulosic materials such as cherry stones or almond, walnut and coconut shells, and grape seeds have been used as carbon sources in one-step steam pyrolysis and activation processes.

The present study was directed towards the characterization of a newly produced polymer-based spherical activated carbon. The major purpose of this work was to prove that the spherical shape of ion-exchange resins obtained from cross-linked sulphonated styrene and divinylbenzene copolymers (in the H+-form) can be preserved during steam pyrolysis processes. Thus, we have

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studied the effect of the heating rate (HR) on the characteristics of the SCAs thereby prepared. The carbons obtained exhibited a very well developed porous structure and have been tested as adsorbents in the adsorption of phenol from aqueous media.

2. EXPERIMENTAL

The resin used in this study was a commercial Dowex 50 WX-2 material (Fluka AG, Germany) composed of a sulphonated polystyrene framework structure cross-linked with divinylbenzene (2 wt%). The resins were spherical in shape with a size in the 100–200 mesh range. The wet resins were heated in the presence of steam (10 vol%) in argon from room temperature up to the desired temperature (900°C) for 3 h in a horizontal tube furnace under atmospheric pressure. For such purposes, HR values of 5°C/min (DW_14), 7.5°C/min (DW_16), 10°C/min (DW_19) and 12.5°C/min (DW_18) were employed. The yields of the processes relative to the dry resins were in the range of 20–30%. Table 1 summarizes the synthesis procedure and the results of elemental analyses.

The structural parameters of the materials were determined via N₂ adsorption isotherms measured at −196°C using an ASAP 2010 (Micromeritics Instrument Corp., Norcross, GA, U.S.A.) gas sorption analyzer. The resulting data were analyzed by the BET and Nguyen and Do (2000) models. The concentrations of acidic and basic groups in the carbons were determined according to the Boehm method. The microstructures of the carbons were examined using scanning electron microscopy [LEO electron microscope (1430VP) at high vacuum (10⁻⁴ Pa)]. Phenol adsorption (initial concentration C₀ = 10⁻³ mol/dm³) from aqueous solutions (pH = 7.0) was studied in order to test the sorption capacity of the produced SCAs. This was undertaken in a flow reactor connected on-line to a UV–vis spectrophotometer (JASCO V-550, Japan) using the maximum absorption wavelength of 270 nm.

Measurements of the adsorption kinetics were performed at 21 ± 0.2°C employing a flow rate of phenol solution of 400 mL/h. Two adsorption/desorption cycles were carried out for all the samples studied in order to estimate the amount of irreversibly adsorbed phenol.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atmosphere</th>
<th>Conditions</th>
<th>Elemental analysis (% mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>DW_14</td>
<td>H₂O/Ar</td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5°C/min</td>
<td></td>
</tr>
<tr>
<td>DW_16</td>
<td>H₂O/Ar</td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.5°C/min</td>
<td></td>
</tr>
<tr>
<td>DW_18</td>
<td>H₂O/Ar</td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.5°C/min</td>
<td></td>
</tr>
<tr>
<td>DW_19</td>
<td>H₂O/Ar</td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10°C/min</td>
<td></td>
</tr>
</tbody>
</table>
3. RESULTS AND DISCUSSION

Figure 1 shows some typical SEM images of the SCA sample denoted as DW_16. The micron-sized spheres depicted were produced within the size range of 10–60 µm irrespective of the carbonization procedure employed. Figure 1(b) shows the surface morphology of the sample, where a sponge-like consistency is visible on the surface. This was responsible for the very well developed macro- and meso-porosities of the carbons produced. The cross-section shows that such a consistency also occurred within the spherical particles. Hence it is clear that, contrary to the conclusions of Nakagawa et al. (1999) and Grzegorczyk et al. (2006), in our opinion it is possible to produce activated carbons with a spherical shape from sulphonated polystyrene–divinylbenzene resins (in the H+-form) which exhibit a promising textural structure. As mentioned by Nakagawa et al. (1999) and Grzegorczyk et al. (2006), the HR strongly influences the structure of the SCA produced. The data depicted in Figure 2 show that the higher the HR value, the larger the

![Figure 1](image)

Figure 1. Scanning electron micrographs of (A) the DW_16 sample and (B) the cross-section of the SCA sample.

<table>
<thead>
<tr>
<th>SCA</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_{\text{tot}}$ (cm$^3$/g)</th>
<th>$V_{\text{micro}}$ (cm$^3$/g)</th>
<th>Surface functional groups (mmol/g)</th>
<th>Diffusion coefficient* $(10^{10}$ cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;C–OH Basic Ads_I Des_I Ads_II Des_II</td>
<td></td>
</tr>
<tr>
<td>DW_14</td>
<td>1000</td>
<td>0.522</td>
<td>0.364</td>
<td>0.1998 0.6238 4.21 3.50 6.84 3.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5492 (189.1) (96.0) (97.8) (92.3)</td>
<td></td>
</tr>
<tr>
<td>DW_16</td>
<td>1020</td>
<td>0.528</td>
<td>0.375</td>
<td>0.3996 0.5492 3.73 3.11 6.12 2.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(179.1) (92.5) (91.6) (79.3)</td>
<td></td>
</tr>
<tr>
<td>DW_19</td>
<td>1307</td>
<td>0.928</td>
<td>0.480</td>
<td>0.2997 0.6241 6.67 5.23 8.64 4.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(169.0) (116.2) (117.6) (116.6)</td>
<td></td>
</tr>
<tr>
<td>DW_18</td>
<td>1431</td>
<td>1.205</td>
<td>0.530</td>
<td>0.3497 0.7992 7.89 6.03 9.44 5.71</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(196.7) (151.9) (148.5) (141.5)</td>
<td></td>
</tr>
</tbody>
</table>

*$a$The effective diffusion coefficient was determined according to Timofiejev’s relationship: $D_e = 0.308R^2(\pi^2t_{0.5})^{-1}$, where $R$ is the mean SCA radius (30 µm) and $t_{0.5}$ is the time necessary for $a/a_{\text{max}} = 0.5$.

*Maximum values for adsorption and desorption (in mg/g C) for each cycle are reported in parentheses.
Figure 2. Nitrogen adsorption isotherms at –196°C for SCAs (see Table 2) and the pore-size distribution curves for the most microporous and mesoporous samples. Data points in both parts of the figure relate to the following samples: +, DW_14; ∆, DW_16; ○, DW_19; ◇, DW_18.
mesoporosity contribution in the samples. Small differences in the structural parameters are recorded for samples DW_14 and DW_16 (HR = 5°C/min and 7.5°C/min, respectively). Increasing the value of HR to 10°C/min and 12.5°C/min resulted in a considerable increase in the BET surface area (Table 2), which was greater than those reported by Nakagawa et al. (1999), Miura et al. (1991) and Bratek et al. (2002) for other SCAs (250–1140 m²/g).

The pore volume also increased with increasing HR value, with a remarkable development of mesopores as shown by the data recorded in Figure 2. Figure 3 displays the kinetic curves for the

![Figure 3. Kinetic curves for the phenol adsorption/desorption cycles undertaken on the carbons studied. The data points relate to the following steps: +, first adsorption; Δ, second adsorption; ○, first desorption; ○, second desorption.](image-url)
adsorption/desorption cycles studied to demonstrate the time scale of the process. The diffusion coefficients listed in Table 2 were calculated from these curves. This increase in mesoporosity caused an increase in the value of the phenol diffusion coefficient [Figure 4a)]. Interestingly, the second adsorption cycle was always faster than the first; however, the increase in mesoporosity led to a decrease in such differences. For this series of SCAs, the adsorption capacity towards phenol was ca. 180–190 mg/g C on the most microporous materials, viz. DW_14 and DW_16 (HR = 5°C/min and 7.5°C/min, respectively). The lowest adsorption capacity was obtained for the DW_19 sample (ca. 170 mg/g C). An increase in HR resulted in an increase in its adsorption capacity, with the value approaching that of 200 mg/g C as recorded for sample DW_18 (12.5°C/min). This capacity is in the upper range of that recorded for the majority of commercial activated carbons [they are usually in the range 100–290 mg/g as reported by various workers (Terzyk 2003; Lu and Sorial 2004, 2007; Tai and Jou 1999; Juang et al. 2006)].

As the adsorption capacity appeared to pass through a minimum as the mesoporosity of the SCA increased, the differences in adsorption capacity between the first and second adsorption cycle decreased with increasing HR value. This effect could be promising in any applications of the studied carbons, since typical adsorbents applied in water filter beds usually lose their adsorption capacities due to irreversible effects, especially as a result of chemisorption, a phenomenon which has been studied in detail by Moreno-Castilla (2004). We have tried to establish correlations between the value of the calculated effective diffusion coefficient and different parameters characterizing the carbon structure and surface properties. However, we found no correlation with the surface functional group contents, probably because the concentrations of surface functional groups were similar. However, we have established a correlation with the pore volumes. Thus, one of the present authors has mentioned previously (Terzyk 2003) that some workers have implied that the adsorption of phenol is mainly controlled by the porous structure, while others have thought otherwise. The correlations presented in Figure 4 show that both the adsorption capacity as well as the diffusion coefficient show a linear dependence on the \( V_{\text{micro}}/V_{\text{tot}} \) ratio.

These results show that the adsorption of phenol on the SCAs tested was controlled to a greater extent by the structural properties rather than by the acid–base properties of the surface (the latter were not drastically different for the various samples studied). Hence, in the case studied, it may be presumed that the process of pore diffusion dominated during phenol adsorption.

\[
\begin{align*}
0.3 & \quad 0.4 & \quad 0.5 & \quad 0.6 & \quad 0.7 & \quad 0.8 & \quad 0.9 \\
1.2E-009 & \quad 1E-009 & \quad 8E-010 & \quad 6E-010 & \quad 4E-010 & \quad 2E-010
\end{align*}
\]

(a) Plots of the variation in the effective diffusion coefficient, \( D_e \), calculated for adsorption and desorption versus the ratio of the micropore volume to the total pore volume of the samples studied. The data points relate to the following adsorption (ADS) and desorption (DES) steps: +, ADS_I; ○, DES_I; △, ADS_II; ⊙, DES_II. (b) Plot of the ratio of the adsorption values in the first and second cycles (ADS_I/ADS_II) versus the ratio of the micropore volume to the total pore volume of the samples studied.

Figure 4. (a) Plots of the variation in the effective diffusion coefficient, \( D_e \), calculated for adsorption and desorption versus the ratio of the micropore volume to the total pore volume of the samples studied. The data points relate to the following adsorption (ADS) and desorption (DES) steps: +, ADS_I; ○, DES_I; △, ADS_II; ⊙, DES_II. (b) Plot of the ratio of the adsorption values in the first and second cycles (ADS_I/ADS_II) versus the ratio of the micropore volume to the total pore volume of the samples studied.
4. CONCLUSIONS

In summary, Spherical Carbon Adsorbents (SCAs) have been prepared via the single-step steam pyrolysis of Dowex 50 WX-2 (a polystyrene–divinylbenzene resin). The porous structures of the materials thus obtained could be controlled readily by the heating rate (HR), leading to carbons having controlled ratios of micropores to mesopores. The resulting carbons are promising materials for the adsorption of phenol from aqueous solutions. Moreover, due to the relatively small amount of irreversibility in such adsorption processes, these carbons could have a potential use in environmental protection.

ACKNOWLEDGEMENT

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