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Microporous activated carbons from a bituminous coal

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A Spanish bituminous coal was used as raw material to prepare activated carbons both by CO_2 and by chemical activation. The activated carbons were characterized by adsorption of N_2 at 77 K, CO_2 at 273 K and benzene and cyclohexane at 303 K, as well as by mercury porosimetry and helium density. The microporosity of the activated carbons was evaluated by the Dubinin–Astakhov equation applied to the adsorption isotherms and the α-plot method applied to the N_2 adsorption data. All activated carbons studied were essentially microporous. The sample obtained by chemical activation with phosphoric acid had the widest micropores. The micropore volumes of activated carbons with medium to high activation determined by N_2 and CO_2 adsorption were quite similar, so both adsorbates measured the same type of micropores. Molecular sieve effects for benzene and cyclohexane were detected in activated carbons with low to medium activation. Copyright © 1996 Elsevier Science Ltd.

Microporous activated carbons are of commercial interest, being used as adsorbents, filters, catalyst supports, reactants and pigments and in numerous other applications. These activated carbons can be manufactured from a wide variety of raw materials, among which coals are widely used as feedstocks by carbonization followed by partial gasification or activation in steam or carbon dioxide at high temperatures to develop the porosity. Sometimes chemical activation has been used, normally with cellulosic materials and to a lesser extent with coals[1–8], involving reaction with a chemical reagent such as $ZnCl_2$ or phosphoric acid. High-surface-area carbons can be produced by heat treatment to temperatures of 673–1173 K.

In this work a Spanish bituminous coal was used to prepare microporous activated carbons. Activation of the demineralized coal was carried out both by CO_2 (after carbonization) and by phosphoric acid. The development of the microporosity was followed by adsorption of N_2 at 77 K, CO_2 at 273 K and benzene and cyclohexane at 303 K. The Dubinin–Astakhov method was applied to these activated carbons because, as shown in previous papers[9–11], this equation is more suited for activated carbons with a heterogeneous microporosity.

EXPERIMENTAL

A bituminous coal from Puertollano (Spain), whose proximate and ultimate analyses are given in *Table 1*, was used to prepare the activated carbons. For this purpose, the parent coal was demineralized with HCl and HF by a method described elsewhere[12]. The demineralized coal was pyrolysed in an N_2 flow at 1273 K for 30 min and activated in a CO_2 flow at 1123 K for different periods of time to achieve different degrees of activation. The activated carbons are referred to in the text as BP followed by a number indicating the percentage burnoff. The particle size of the activated carbons was between 0.15 and 0.25 mm. Activation time, percentage burnoff and ash yields of the activated carbons used are compiled in *Table 2*.

Another activated carbon was prepared by activation with phosphoric acid[13]. The procedure was as follows: 10 g of the demineralized bituminous coal was mixed with 10 g of phosphoric acid (75 wt% P_2O_5). This mixture was thoroughly stirred and heated in an air oven at 393 K for 24 h. The resulting solid was steam-activated at 1073 K for 24 h. The steam flow was obtained by pumping distilled water with a peristaltic pump (0.5 cm^3 min^{-1}) to a flask heated at 473 K and placed at the entrance of the furnace. The product was washed with distilled water until all phosphate was eliminated. This activated carbon is referred to in the text as BPQ.

All activated carbons were characterized by N_2 and CO_2 adsorption at 77 and 273 K respectively and benzene and cyclohexane adsorption at 303 K. The method has been described elsewhere[11,14]. From measurements of the He density and mercury porosimetry up to 400 MPa, using a Quantachrome Autoscan 60 porosimeter, the pore volumes given in *Table 2* were determined. Prior to gas adsorption or He density measurements, the samples were outgassed overnight at 383 K under a dynamic vacuum of $\sim$ 0.1 mPa.

Table 1 Analysis of parent coal (wt% db)

Proximate analysis
Volatile matter	28.8
Fixed carbon	47.5
Ash	23.7

Ultimate analysis
C	60.6
H	4.3
N	2.0
S	1.1
O (diff.)	8.3

Table 2 Activation time, burnoff, ash and porosity of the activated carbons from mercury porosimetry and He density

Sample	Activation time (h)	Burnoff (wt%)	Ash (wt%)	Pore volume $(cm^3 g^{-1})^a$		
				V_1	V_2	V_3
BP8	3	8.3	0.54	0.21	0.01	0.08
BP18	10	18.5	0.61	0.24	0.01	0.08
BP31	18	31.1	0.72	0.36	0.02	0.12
BP46	27	46.4	0.93	0.51	0.05	0.17
BP72	45	72.4	1.81	0.56	0.13	0.21

$^a V_1, \phi < 3.6\,nm; V_2, 3.6 < \phi < 50\,nm; V_3, \phi > 50\,nm$

RESULTS AND DISCUSSION

Nitrogen adsorption isotherms are given in *Figure 1*. The α-plots are shown in *Figure 2* and were constructed using the standard obtained for a heat-treated activated carbon from olive stones[15]. The value of the external surface, $S^\alpha_{ext(N_2)}$, was obtained from the slope of the linear part of the α-plot, and the micropore volume, $W^\alpha_{0(N_2)}$, from the intercept of the linear region. The values obtained for all activated carbons, together with the nitrogen surface area obtained from the BET equation, $S_{N_2(BET)}$, are compiled in *Table 3*.

The nitrogen adsorption isotherms are of type I, and up to sample BP31 are highly rectangular, indicating that the activated carbons are essentially microporous with very narrow microporosity[16]. At higher percentages of burnoff, samples BP46 and BP72, the knee becomes broader, which indicates the presence of wider micropores. The enlargement of the porosity with activation time seems to be restricted to the microporosity region, because the plateau of the isotherms is gently sloping even for the most activated sample, BP72. The highly microporous character of these samples is indicated by the small $S^\alpha_{ext(N_2)}$ values compared with the $S_{N_2(BET)}$ values given in *Table 3* and by the small values of
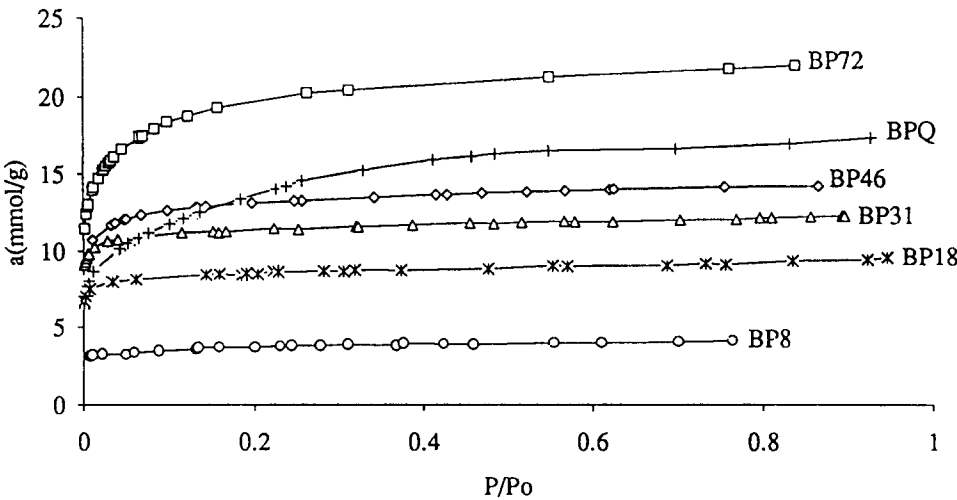
Figure 1 Nitrogen adsorption isotherms for activated carbons

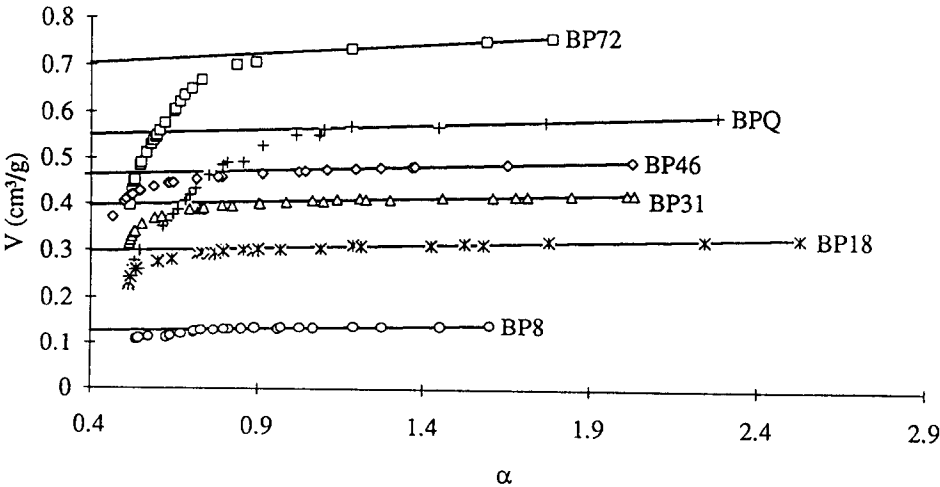**Figure 2** α-Plots from analyses of the nitrogen adsorption isotherms in *Figure 1*

Table 3 Nitrogen adsorption results from BET equation and α-plot methods and parameters of the Dubinin–Astakhov equation applied to nitrogen, carbon dioxide, benzene and cyclohexane adsorption[a]

	BP8	BP18	BP31	BP46	BP72	BPQ
$S_{N_2(BET)}$	306 ± 3	697 ± 6	924 ± 9	1078 ± 12	1632 ± 9	1074 ± 1
$W^{\alpha}_{0(N_2)}$	0.127 ± 0.002	0.292 ± 0.003	0.391 ± 0.001	0.455 ± 0.002	0.688 ± 0.003	0.572 ± 0.004
$S^{\alpha}_{ext(N_2)}$	22 ± 3	27 ± 3	29 ± 2	36 ± 2	69 ± 3	38 ± 7
$W_{0(N_2)}$	0.140 ± 0.002	0.309 ± 0.002	0.414 ± 0.001	0.487 ± 0.001	0.742 ± 0.002	0.583 ± 0.003
$E_{0(N_2)}$	28.6 ± 5.2	28.4 ± 1.4	25.6 ± 1.8	23.6 ± 0.5	18.0 ± 0.3	12.4 ± 0.1
$n_{(N_2)}$	1.31 ± 0.08	1.30 ± 0.04	1.26 ± 0.02	1.24 ± 0.02	1.20 ± 0.03	1.02 ± 0.04
$W_{0(CO_2)}$	0.209 ± 0.008	0.298 ± 0.012	0.422 ± 0.017	0.507 ± 0.008	0.691 ± 0.039	0.578 ± 0.033
$E_{0(CO_2)}$	22.9 ± 0.5	20.7 ± 0.6	18.0 ± 0.6	16.3 ± 0.2	14.1 ± 0.3	11.1 ± 0.4
$n_{(CO_2)}$	1.92 ± 0.06	1.67 ± 0.06	1.58 ± 0.05	1.56 ± 0.01	1.44 ± 0.03	1.17 ± 0.03
$W_{0(C_6H_6)}$	0.070 ± 0.001	0.189 ± 0.001	0.295 ± 0.001	0.390 ± 0.001	0.712 ± 0.007	0.598 ± 0.007
$E_{0(C_6H_6)}$	15.7 ± 0.3	27.4 ± 0.4	25.3 ± 0.4	23.3 ± 0.3	17.9 ± 0.3	11.9 ± 0.1
$n_{(C_6H_6)}$	1.80 ± 0.10	1.49 ± 0.03	1.38 ± 0.03	1.40 ± 0.03	1.39 ± 0.06	1.47 ± 0.07
$W_{0(C_6H_{12})}$	nil	0.116 ± 0.001	0.267 ± 0.001	0.388 ± 0.002	0.686 ± 0.004	–
$E_{0(C_6H_{12})}$	nil	22.2 ± 1.0	20.9 ± 0.3	21.1 ± 0.4	22.0 ± 0.6	–
$n_{(C_6H_{12})}$	nil	1.41 ± 0.11	1.40 ± 0.03	1.38 ± 0.05	1.37 ± 0.06	–

[a] The units are: S, $m^2\,\gamma^{-1}$; E_0, $kJ\,mol^{-1}$; W_0, $cm^3\,g^{-1}$

the volumes V_2 and V_3 compared with V_1 given in *Table 2*.

The Dubinin–Astakhov (DA) equation was applied to the N_2 and CO_2 adsorption data. The DA equation reads[17,18]

$$W = W_0 \exp\left[-\left(\frac{A}{\beta E_0}\right)^n\right] \tag{1}$$

where W is the amount adsorbed at a given relative pressure P/P_0; W_0 is the micropore volume, A is the differential molar work defined by $A = RT\,\ln(P_0/P)$, β is the affinity coefficient taken as 0.46 and 0.34 for CO_2 and N_2 at 273 and 77 K respectively[9,19] and E_0 is the characteristic adsorption energy. The value of n reflects the width of the energy distribution, which is related in a complex way to the pore size distribution[18,20–22]. Values of n between 1 and 4 are observed for most carbon adsorbents, with $n \geq 2$ for molecular sieve carbons or carbons adsorbents with highly homogeneous and small micropores[23–25], whereas $n < 2$ is found for strongly activated carbons and heterogeneous micropore carbons.

Equation (1) has three unknown parameters: W_0, E_0, and n. To calculate them, it was necessary to apply a computer programme with an iterative method to the experimental points, as has been used before[9]. The iterative method uses an approach based on minimizing the residual sum of squares, which in all cases was better than 10^{-5}. The final W_0, E_0, and n values were those that best fitted the DA equation to the experimental data points. The DA plots for CO_2 and N_2 adsorption are depicted in *Figures 3* and *4* respectively, and show that the experimental adsorption isotherms were very well fitted by the DA equation. To obtain the micropore volume, the liquid density of CO_2 at 273 K was taken[19] as $1.03\,g\,cm^{-3}$ and that of N_2 at 77 K as[20] $0.8086\,g\,cm^{-3}$.

The W_0, E_0, and n values obtained are compiled in *Table 3*, from which the following points can be deduced.

1. For sample BP8, $W^{\alpha}_{0(N_2)}$ and $W_{0(N_2)}$ are lower than $W_{0(CO_2)}$. This means that in this sample either there are constrictions at the entry of the micropores or the microporosity is so narrow that there is restricted diffusion of N_2 at 77 K. This behaviour has sometimes been found in carbonized
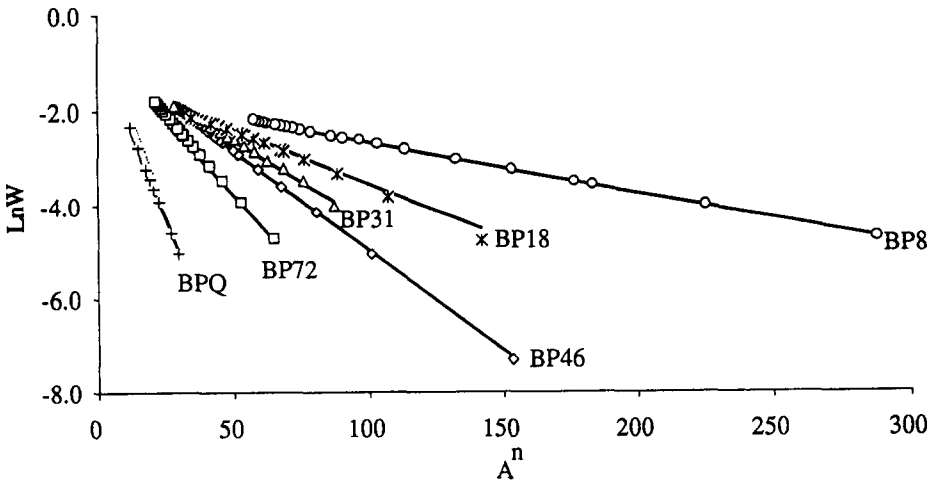

Figure 3 Dubinin–Astakhov equation applied to CO_2 adsorption data at 273 K
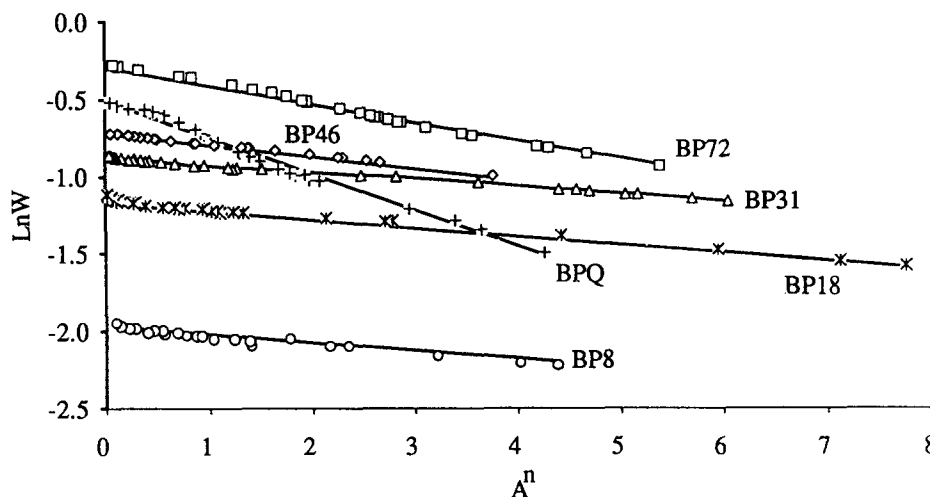
Figure 4 Dubinin–Astakhov equation applied to N_2 adsorption data at 77 K

materials and even in activated carbons with low burnoff[9,19]. Thus, restricted diffusion of N_2 at 77 K was also found for the demineralized and pyrolysed carbon BP, which had $S_{N_2(BET)} < 4 \, m^2 \, g^{-1}$ and $W_{0(CO_2)} = 0.165 \pm 0.017 \, cm^3 \, g^{-1}$, which indicates that practically all the microporosity was inaccessible to N_2 at 77 K. The activation of BP up to 8 wt% burnoff, to obtain sample BP8, did not completely remove the pore constrictions or widen the micropores, so BP8 still allows only restricted diffusion of N_2.

2. In sample BP18 both adsorbates, N_2 at 77 K and CO_2 at 273 K, have the same accessibility to the micropores, because $W^\alpha_{0(N_2)}$, $W_{0(N_2)}$ and $W_{0(CO_2)}$ are quite similar. This is due either to widening of the micropores or to removal of the constrictions.

3. It is noteworthy that from BP18 to BP72 the values of $W^\alpha_{0(N_2)}$, $W_{0(N_2)}$ and $W_{0(CO_2)}$ are also quite close, within experimental error. This is an important result which indicates that when the DA equation is applied to the adsorption isotherms of N_2 at 77 K and CO_2 at 273 K the micropore volumes, W_0, obtained are quite close if diffusion of N_2 is not restricted, indicating that both N_2 and CO_2 can measure the same type of micropores even in activated carbons with a high degree of activation. This is contrary to previous results[19] for highly activated carbons, in which the micropore volume obtained from N_2 at 77 K was higher than that obtained from CO_2 at 273 K. This was probably due to the use of the Dubinin–Radushkevich (DR) equation ($n = 2$ in Equation 1) to obtain these parameters instead of the DA equation, which is more suitable than the DR equation for highly activated carbons, due to their more heterogeneous micropore structure.

4. The values of $E_{0(CO_2)}$ and $E_{0(N_2)}$ decrease from BP8 to BP72 due to enlargement of the microporosity with increasing degree of activation. It is seen that $E_{0(N_2)}$ undergoes a large decrease from BP31 to BP46, which indicates marked widening of the microporosity when the activation increases from 31 to 46 wt% burnoff. This was previously shown by the widening of the knee of the N_2 adsorption isotherm for samples with greater activation than 31 wt% burnoff.

The DA equation was also applied to the adsorption

isotherms of benzene and cyclohexane at 303 K; the values of β in Equation (1) for benzene and cyclohexane were taken[14] as 1.00 and 1.04 respectively and their liquid densities[14] as 0.869 and 0.769 g cm^{-3} respectively. The experimental data points were also very well fitted by this equation, as in the case of CO_2 and N_2.

The values of W_0, E_0 and n are compiled in *Table 3*. It is seen that from BP8 to BP46, $W_{0(C_6H_6)}$ is smaller than either $W_{0(CO_2)}$ or $W_{0(N_2)}$. This is due to a molecular sieve effect for benzene, owing to its higher minimum dimension[14,26], 0.37 nm, than that[19] of either N_2, 0.30 nm, or CO_2 0.28 nm. However, for BP72 the three values of the micropore volume almost coincide, indicating that there is equal accessibility of the microporosity to CO_2, N_2 and benzene, due to widening during burnoff. This is also indicated by the larger decrease in $E_{0(C_6H_6)}$ from BP46 to BP72 compared with that from BP18 to BP46. The increase in $E_{0(C_6H_6)}$ from BP8 to BP18 is due to the increased activation in this range, making the pores more similar in size to the benzene molecule.

The minimum dimension of cyclohexane[14,26], 0.48 nm, is larger than that of benzene and therefore there is a molecular sieve effect for the cyclohexane–benzene couple from BP8 up to near the BP31 sample, with samples BP46 and BP72 showing equal accessibility to benzene and cyclohexane. It is interesting to note that $E_{0(C_6H_{12})}$ practically does not change from sample BP18 to BP72, which indicates that the microporosity accessible to cyclohexane does not change in width with the degree of activation.

The micropore size distribution, depicted in *Figure 5*, was constructed from the micropore volumes, W_0, obtained with CO_2, benzene and cyclohexane and the minimum dimension of these adsorbates. This figure clearly shows the enlargement of the porosity with the degree of activation of the sample BP and hence activated carbon BP72 shows only micropores wider than 0.48 nm.

The nitrogen adsorption isotherm of the activated carbon BPQ is depicted in *Figure 1* and the surface areas and microporosity volumes obtained with CO_2, N_2 and benzene are given in *Table 3*. The nitrogen adsorption isotherm is situated between those of BP46 and BP72, but its knee is considerably wider than even that of BP72. This means that BPQ has very wide micropores.
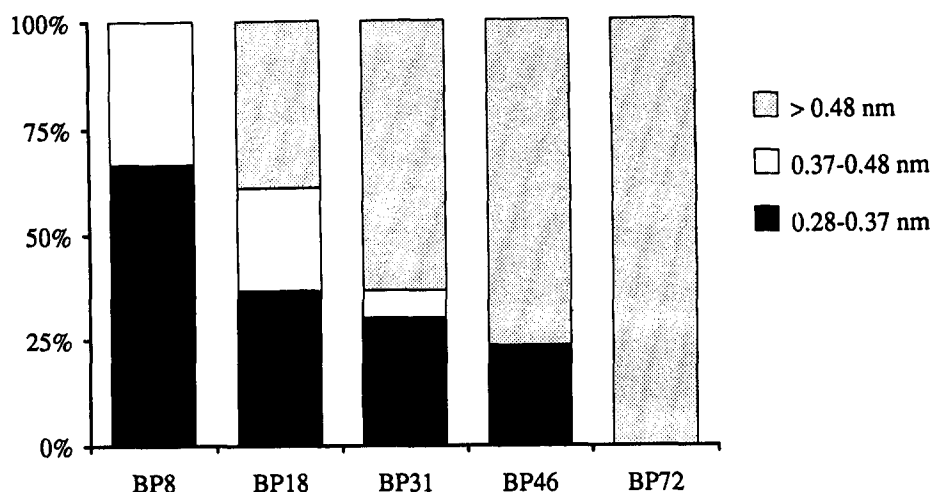
Figure 5 Micropore size distribution of activated carbons

However, the gradual slope of the plateau indicates that it does not have a large number of mesopores, which is confirmed by the smaller S_{ext}^{α} value compared with the $S_{N_2(BET)}$ value.

This sample shows the same surface areas as BP46, but its micropore volume is higher than that of the latter, and it also does not show a molecular sieve effect for benzene, since the micropore volumes for the three adsorbates N_2, CO_2 and C_6H_6 are quite similar. This means that activated carbon BPQ has a very wide microporosity, even wider than that of BP72, which is revealed by the smaller E_0 values for the three adsorbates in sample BPQ compared with those obtained with BP72.

CONCLUSIONS

Activated carbons obtained from the original bituminous coal either by CO_2 activation or by the phosphoric acid method were essentially microporous, even though the maximum activation degree attained by the first method was 72 wt% burnoff. The phosphoric acid activation method produced an activated carbon with the widest micropores of all those obtained.

The adsorption isotherms of N_2, CO_2, benzene and cyclohexane were very well fitted by the Dubinin–Astakhov equation, and it is worth pointing out that if there is no restricted diffusion of N_2, the micropore volumes obtained by application of the DA equation to the N_2 and CO_2 adsorption isotherms are quite similar even for highly activated carbons.

Activated carbons with a low to medium degree of activation show a molecular sieve effect for benzene and cyclohexane.

ACKNOWLEDGEMENT

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