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Benzene and toluene adsorption at low concentration on activated carbon fibres

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Abstract The present study analyses the preparation of activated carbon fibres (ACFs) by the so-called "physical" activation method with steam or carbon dioxide and their application for benzene and toluene adsorption at low concentration (200 ppmv). ACFs have been scarcely studied for the adsorption of these pollutants at low concentration in gaseous phase, despite their interesting features regarding adsorption kinetics, bed pressure drop, possibility of conformation and others. Our results have shown that the preparation method used is suitable to produce ACFs with high adsorption capacities for benzene and toluene at the low concentration used. The fibre morphology of the ACFs does not enhance their performance, which results to be similar to other non-fibrous activated carbons such as granular, pellets and powders. Such good performance of the ACFs, leading to benzene and toluene adsorption capacities as large as 31 g benzene/100 g ACF or 53 g toluene/100 g ACF, can be explained due to their large volume of narrow micropores (<0.7 nm) developed upon activation and their low content in surface oxygen groups. Our results have also shown very good agreement between the adsorption results derived from dynamic adsorption experiments and from adsorption isotherms. As the relative pressure of the organic compound increases the corresponding fraction of narrow micropore volumes filled by benzene and toluene increases. For a given low and comparable relative pressure, toluene always occupies a larger fraction of narrow micropores than benzene.

Keywords Activated carbon fibres · Adsorption · Volatile organic compounds · Porosity · Surface chemistry

1 Introduction

In the last two decades, great attention has been paid to the removal of volatile organic compounds (VOCs) at low concentration, since the presence of these pollutants is detrimental both for human health and environment, even at very low concentrations (Foster et al. 1992). Among the different VOCs, many studies have dealt with benzene and toluene removal at low concentration by activated carbons (ACs) (Benkhedda et al. 2000; Bouhamra et al. 2009; Cal et al. 1994; Cal et al. 1996; Cal et al. 1997; Chiang et al. 1999; Chiang et al. 2001; Chiang et al. 2001b; Chiang et al. 2002; Dimotakis et al. 1999; Foster et al. 1992; Huang et al. 2002; Huang et al. 2003; Noll et al. 1989; Ryu et al. 2002; Shin et al. 2002; Yun et al. 1998; Yun et al. 1999). Although these papers analysed different carbonaceous materials, no clear conclusions were established about the activated carbon parameters controlling VOC adsorption capacities at low concentrations.

In a previous work, we reported benzene and toluene adsorption results at 200 ppmv each in helium over ten different activated carbons in granular form, pellets and powders (Lillo-Ródenas et al. 2005). The referred study analysed systematically the effect of the porosity and surface chemistry of the adsorbents in the low concentration VOC adsorption capacity and highlighted the importance of both parameters (Lillo-Ródenas et al. 2005), putting emphasis on the need of developing the narrow micropore volume (pore

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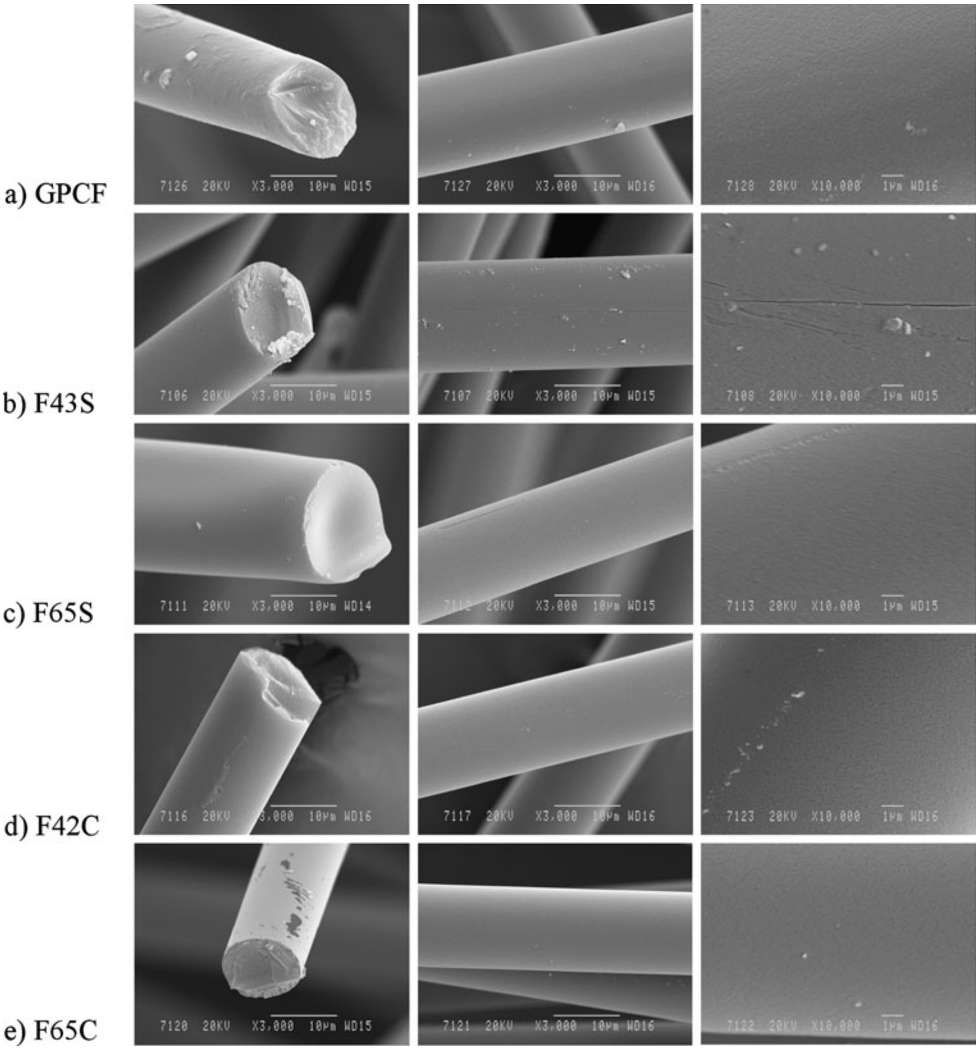

Fig. 1 Scanning Electron Microscopy Image of the GPCF used as precursor and the corresponding prepared ACFs. For each fibre, the first two images correspond to 3000× magnification (the scale bar corresponds to 10 μm), whereas the last image corresponds to 10000× magnification (the scale bar corresponds to 1 μm). Note that the number in the nomenclature of the fibres corresponds to the burn-off percentage and S is used when steam is the activating agent used, whereas C is used for carbon dioxide activation

size smaller than 0.7 nm). Moreover, the activated carbons prepared shown higher adsorption capacities, especially for toluene, than those previously reported in the literature in the same conditions (Lillo-Ródenas et al. 2005).

The present paper analyses benzene and toluene adsorption at low concentration on activated carbon fibres (ACFs) because these fibrous carbon materials present important advantages from the point of view of their high surface areas and micropore volumes (Das et al. 2004), low pressure drop in a bed (Zhang et al. 2010) and fast kinetics (Singh et al. 2002). Additionally, they can be handled or manufactured into different forms, such as ACF monoliths (Vilaplana-Ortego et al. 2002; Marbán et al. 2006), what makes them very interesting for practical applications. Although some works have been published about benzene and toluene adsorption at low concentration on ACFs (Cal et al. 1994; Foster et al. 1992; Huang et al. 2002; Yun et al. 1998; Zhang et al. 2010), a comparative study with other non-fibrous ACs, as well as a systematic study analysing the effect of the porosity and surface chemistry of these materials in VOC adsorption is still lacking. The present work, structured similarly to the previously mentioned one (Lillo-Ródenas et al. 2005), aims to compare the behaviour of ACFs with other non-fibrous ACs and to analyze the above mentioned advantages of these ACFs. For it, two series of ACFs have been prepared; one by carbon dioxide and one by steam activation at two comparable burn-off percentages in each series.

2 Experimental

2.1 Raw material

The ACFs were prepared from a commercial general purpose petroleum pitch-based carbon fibre (GPCF) from Kureha Chemical Industry, Japan, named T-101T. The mean diameter of these fibres is around 18 μm, and the typical diameters are between 14 and 20 μm. Figure 1 shows the morphology of the precursor, obtained from Scanning

Table 1 Nomenclature and preparation conditions of the ACFs prepared by steam or carbon dioxide activation

Sample	Activating agent	Burn-off (%)	Activation temperature (K)	Holding time (h)	Activating agent flow rate (ml/min)	N_2 flow rate (ml/min)
F43S	Steam	43	1093	0.92	40	150
F65S	Steam	65	1183	1.5	40	150
F42C	Carbon dioxide	42	1163	4.5	80	80
F65C	Carbon dioxide	65	1163	7	80	80

Table 2 Porous texture of the ACFs

Sample	BET (m^2/g)	V-DR-N_2 (cm^3/g)	V-DR-CO_2 (cm^3/g)	V-DR-N_2–V-DR-CO_2
F43S	1026	0.36	0.44	−0.08
F65S	1752	0.65	0.53	0.12
F42C	1095	0.48	0.48	0.00
F65C	1826	0.73	0.63	0.10

Electron Microscopy (SEM) images using JEOL JSM-840 equipment.

2.2 Steam activation

An amount of GPCF around 1 gram is placed into a stainless-steel reactor. The steam activation is carried out in a vertical furnace. The heating stage is performed at 20 K/min under nitrogen (150 ml/min) up to the maximum heat-treatment temperature. When this temperature is reached, a steam flow is added (40 ml/min), and the maximum temperature is held for different times. Finally, the samples are cooled down in nitrogen. Following this procedure, ACFs with two different burn-off percentages were prepared. Table 1 summarises the nomenclature and the preparation conditions of the ACFs.

2.3 Carbon dioxide activation

ACFs were prepared in a horizontal furnace for CO_2 activation. Around 1 gram of GPCF is placed in a ceramic crucible. The sample is heated up to 1163 K using a 10 K/min heating rate. At the maximum temperature, the nitrogen flow is switched to carbon dioxide flow, and the temperature is held for different times. Finally, the samples are cooled down in nitrogen. Following this procedure, that has been described before elsewhere (Alcañiz-Monge et al. 1994; Maciá-Agulló et al. 2004), ACFs with two different burn-off percentages were prepared. Table 1 summarises the nomenclature and the preparation conditions of the ACFs.

For both activating gases the activation conditions have been selected to achieve an appropriate development of porosity avoiding the external burn-off (Alcañiz-Monge et al. 1994; Alcañiz-Monge et al. 1997). The use of a vertical or horizontal reactor does not produce any difference provided that the appropriate activation conditions are used (Alcañiz-Monge et al. 1994; Alcañiz-Monge et al. 1997).

2.4 Characterisation of the ACFs

The morphologies of the prepared ACFs, obtained by SEM, are presented in Fig. 1. The porous texture of these ACFs has been characterised by physical adsorption of N_2 and CO_2 at 77 and 273 K, respectively, in an Autosorb-6 apparatus. Nitrogen adsorption has been used for determining the total volume of micropores, V-DR-N_2 (pore size smaller than 2 nm) whereas the adsorption of CO_2 at 273 K allows us to assess the narrow micropores, V-DR-CO_2 (pore size smaller than 0.7 nm) (Cazorla-Amorós et al. 1996; Cazorla-Amorós et al. 1998; Linares-Solano et al. 1998; Rodríguez-Reinoso and Linares-Solano 1988). Table 2 summarises the porosity characterisation of the ACFs.

The characterisation of surface oxygen groups present in the ACFs has been done by temperature programmed desorption (TPD) experiments. During the thermal decomposition of the surface complexes, CO_2 evolves from carboxylic groups and their derivatives, such as lactones and anhydrides, while CO is mainly a decomposition product of quinones, hydroquinones and phenols (Boehm 1994; Boehm 2002; Román-Martínez et al. 1993; Román-Martínez et al. 1995).

The experimental system for TPD experiments consists of a furnace coupled to a mass spectrometer (VG, Quadrupoles). A helium flow of 60 ml/min is used and the heating has been done at 20 K/min, up to 1173 K. The gases evolved as CO and CO_2 are analysed in the mass spectrometer. The quantification of CO and CO_2 groups on the ACFs

Table 3 Surface chemistry characterisation of the ACFs

Sample	CO (μmol/g ACF)	CO_2 (μmol/g ACF)	Total Oxygen (μmol/g ACF)
F43S	505	180	865
F65S	295	250	795
F42C	615	100	815
F65C	605	65	735

Table 4 Benzene and toluene adsorption capacities at 200 ppmv over the prepared ACFs

Sample	Benzene (g/100 g ACF)	Benzene (cm^3 liq/g ACF)	Benzene (cm^3 liq/cm^3 CO_2 micropores)	Toluene (g/100 g ACF)	Toluene (cm^3 liq/g ACF)	Toluene (cm^3 liq/cm^3 CO_2 micropores)
F43S	20	0.23	0.52	27	0.31	0.71
F65S	25	0.29	0.54	36	0.42	0.79
F42C	24	0.27	0.57	36	0.42	0.87
F65C	31	0.35	0.56	53	0.61	0.97

is included in Table 3, together with the total oxygen content obtained as $CO + 2CO_2$.

2.5 Benzene and toluene dynamic adsorption experiments

The system used to assess the adsorption of benzene or toluene consists of a BTRS reactor (fixed bed reactor with an internal diameter of 6 mm) coupled to a mass spectrometer (Balzers Thermocube). The samples have been outgassed before the adsorption experiments using a helium flow of 60 ml/min and a temperature of 523 K, which has been maintained for four hours. The adsorption experiments in this system have been carried out at 298 ± 1 K. The ACF bed contains around 0.075 grams of ACF. The exact weight of ACF used in each experiment was used for the calculations and it was measured with an accuracy of 0.001 g. The flow used during the experiments has been 90 ml/min. The gases for the adsorption tests contain 200 ppmv of VOC in helium and were provided from calibrated cylinders from Carburos Metálicos S.A.

By using this technique, the breakthrough curves, which represent the concentration of VOC in the outlet gas versus time, are obtained. From numerical integration of these curves, the adsorption capacity at 200 ppmv concentration and 298 K has been obtained. These values are presented in Table 4. For calculations of adsorption capacities in this table, benzene and toluene liquid densities of 0.874 and 0.865 g/cm^3, respectively, have been used.

2.6 Benzene and toluene adsorption isotherms

Benzene and toluene adsorption isotherms were obtained for sample F42C at 298 K using an ASAP 2020 from Micromeritics. The carbon sample (100 ± 1 mg) was outgassed to constant weight at 473 K. The liquids used to generate the vapours were fully degassed by repeated evacuation and vapour equilibration cycles of the liquid supply side of the vapour reservoir. The adsorption isotherms were fitted to the Toth isotherm, which is described by the following equation (Do 1998):

$$C_\mu = C_{\mu s}(bP)/\left[1 + (bP)^t\right]^{1/t}.$$

The parameters of this equation are $C_{\mu s}$ (saturated adsorbed concentration), b and t. C_μ corresponds to the adsorbed concentration (mmol/g) at each pressure P (mbar). Parameters b and t are specific for the adsorbate–adsorbent pair. The parameter t is usually lower than 1. When t reaches 1, the Toth isotherm reduces to the Langmuir isotherm.

3 Results and discussion

3.1 Characterisation of the ACFs

As mentioned, ACFs have been prepared from GPCF by steam and carbon dioxide activation. Figure 1 shows, at different magnifications, Scanning Electron Microscopy images of the ACFs prepared in this work. It can be seen, under the magnifications studied, that after steam and carbon dioxide activation the structure of the carbon fibres remains essentially unchanged, and no important defects appear on the surface of the fibres.

Figure 2 presents the N_2 adsorption isotherms at 77 K for these four ACFs and Table 2 summarises their porous texture characterisation. The N_2 adsorption isotherms and the porosity characterisation show that the ACFs prepared by

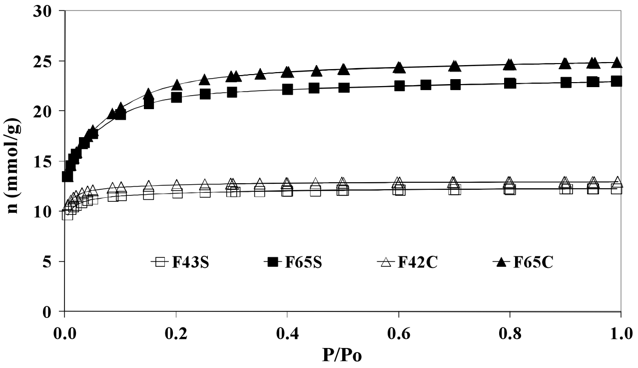

Fig. 2 Nitrogen adsorption isotherms at 77 K over the different ACFs

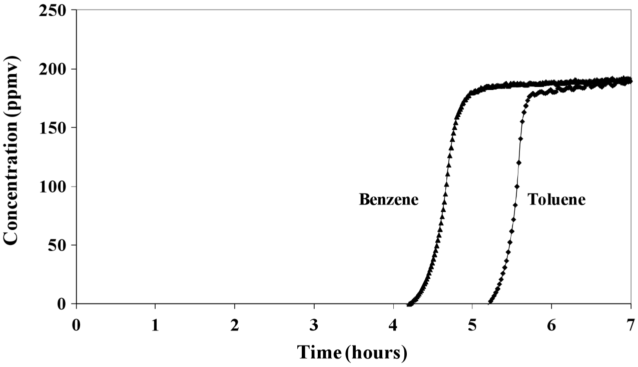

Fig. 3 Benzene and toluene breakthrough curves at 200 ppmv for F42C

either steam or carbon dioxide are essentially microporous (type I isotherms) (Rodríguez-Reinoso and Linares-Solano 1988). The microporosity of the samples at 42–43% burn-off degree (F43S and F42C) is very narrow, as reflected by the values of the difference V-DR-N_2–V-DR-CO_2, which are ≤ 0 (see Table 2). As expectable, the microporosity of the ACFs widens with the increase in burn-off, and therefore the values of the difference V-DR-N_2–V-DR-CO_2 are positive for both F65S and F65C (see Table 2).

The adsorption capacities for the ACFs prepared by steam and carbon dioxide activations are, for a given burn-off degree, very similar, although the latter produces slightly higher values.

The surface chemistry of the ACFs was characterised by TPD, as detailed in the experimental section. Table 3 compiles the total CO and CO_2 evolution, together with the total oxygen content of the ACFs, obtained as $CO + 2CO_2$. This table shows that no substantial differences are observed among the four different ACFs, and the total oxygen content remains essentially constant for all the samples. The small differences in the total oxygen content of the ACFs can be attributed to the different maximum heat-treatment temperatures and holding times in the preparation procedure. Thus, the larger amount of surface oxygen is present in sample F43S, which suffered a "mild" heat-treatment up to 1093 K, held for less than one hour. On the contrary, the lowest surface oxygen content is present in F65C, heat-treated up to 1163 K, temperature which was held for 7 hours.

Considering the absolute values in Table 3, it must be remarked that the content of surface oxygen groups of the ACFs is quite low, in comparison to most of those ACs analysed in a previous study (Lillo-Ródenas et al. 2005), but of the same magnitude as some ACs which suffered a subsequent heat-treatment step in inert atmosphere to reduce their surface oxygen content (Lillo-Ródenas et al. 2005).

Therefore, it should be emphasized that the procedure used in the preparation of the ACFs is suitable for the synthesis of adsorbents with low surface oxygen content, which can be useful for many applications. Moreover, no significant differences are observed between carbon dioxide and steam activation regarding surface chemistry, whereas in terms of porosity slightly higher porosity developments are achieved with carbon dioxide activation in comparison with steam for similar burn-off percentages.

3.2 Benzene and toluene dynamic adsorption experiments at 200 ppmv

The performance of the ACFs for benzene and toluene adsorption at 200 ppmv was studied using the conditions previously detailed. Thus, both benzene and toluene breakthrough curves were obtained for the four ACFs studied. As an example, Fig. 3 summarises the benzene and toluene breakthrough curves for a selected ACF (F42C). The amount of ACF used in each experiment is in the range of 0.075 grams, so that comparison between adsorption capacities can be done directly from the breakthrough curves. By numerical integration of this type of curves, benzene and toluene adsorption capacities at 200 ppmv were obtained. Table 4 summarises these data and shows that variable adsorption capacities for benzene and toluene can be achieved. Thus, Table 4 and Fig. 3 show that for a selected ACF, such as F42C, toluene adsorption capacity is higher than that for benzene. This is in agreement with the literature and can be explained, among other reasons, because of the higher relative pressure for toluene in relation to benzene (5.4×10^{-3} and 1.6×10^{-3}, respectively, at 298 K), although in both cases a constant 200 ppmv concentration was used.

Results from Table 4 show that benzene adsorption capacities vary from 20 to 31 g benzene/100 g of ACF, whereas toluene adsorption capacities as high as 53 g toluene/100 g of ACF are obtained.

If comparing these values with those from the literature for the adsorption of VOCs on ACFs, it can be seen that the benzene adsorption capacities achieved in the present work, as high as 31 g benzene/100 g of ACF, are slightly higher than the best results published obtained in the same conditions using ACFs, in the range of 26 g benzene/100 g of ACF (Cal et al. 1994). For toluene, the adsorption capacities achieved in the present study are much higher than the best values from the literature in the same conditions using ACFs (Yun et al. 1998). Thus, benzene and toluene adsorption capacities achieved by the ACFs prepared in this study should be highlighted.

Table 4 shows that VOC adsorption capacities are somewhat higher for the fibres activated with CO_2 than for steam. This may be due to the slightly higher porosity development for F42C and F65C, in comparison to F43S and F65S, respectively. The next section compares these results in more detail, analysing the effect of the porosity on benzene and toluene adsorption on the ACFs.

The comparison of benzene and toluene adsorption capacities of these ACFs with those values from a previous paper carried out with powder, granular and pellet ACs (Lillo-Ródenas et al. 2005) shows that the adsorption capacities achieved in this work are comparable to those obtained with highly activated powder ACs. Interestingly, in the case of ACFs these high benzene and toluene adsorption capacities can be reached with samples having lower porosity and surface area than those from (Lillo-Ródenas et al. 2005). Therefore, at a first glance we could conclude that the ACFs prepared in this study are interesting not only because of the advantages referred to in the introduction section (i.e. fast adsorption kinetics, low pressure drop and possibility of conformation), but also because they show high VOCs adsorption capacities at low concentration. The following sections will analyse this behaviour in more detail.

3.3 Effect of the porosity of the ACFs on the adsorption capacity

The results from Table 4 have shown that benzene and toluene adsorption capacities are different depending on the selected ACFs. Also, it can be observed that ACFs with very different surface areas and total micropore volumes, such as F65S and F42C, show very similar adsorption capacities for benzene and toluene. As we reported previously (Lillo-Ródenas et al. 2005), this anomaly (no relationship between VOC adsorption and N_2 adsorption data) can be explained considering that the narrow microporosity of the ACFs is the key factor that controls the low concentration VOC adsorption capacity. Figure 4 confirms the effect that the narrow porosity (assessed from CO_2 adsorption at 273 K) has on benzene and toluene adsorption at 200 ppmv.

Additionally, when observing the percentage of narrow micropores occupied by either liquid benzene or toluene (see Table 4), it is shown that liquid benzene occupies around half of the volume of narrow micropores of the ACFs. For toluene adsorption a larger percentage of the narrow micropore volume is occupied in comparison with benzene, although the narrow micropore volume is not totally filled with any of them, what explains that the available volume of narrow micropores is the key factor for low concentration VOC adsorption.

The fact that a worse regression coefficient is observed between toluene adsorption and the narrow micropore volume, in comparison with benzene in Fig. 4 (R2 is 0.77 for toluene and 0.95 for benzene), together with the fact that for toluene adsorption a larger fraction of narrow micropores are occupied than in the case of benzene seem to suggest that, for toluene adsorption at these conditions, not only the narrow micropore volume but also the total micropore volume have some influence on the adsorption capacity.

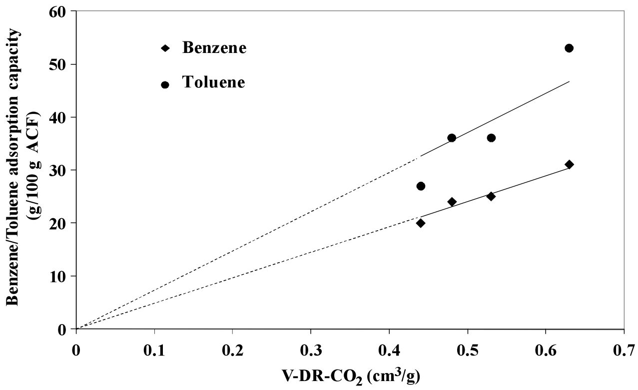

Fig. 4 Relationship between benzene or toluene adsorption capacity at 200 ppmv and the volume of narrow micropores (<0.7 nm) for the ACFs

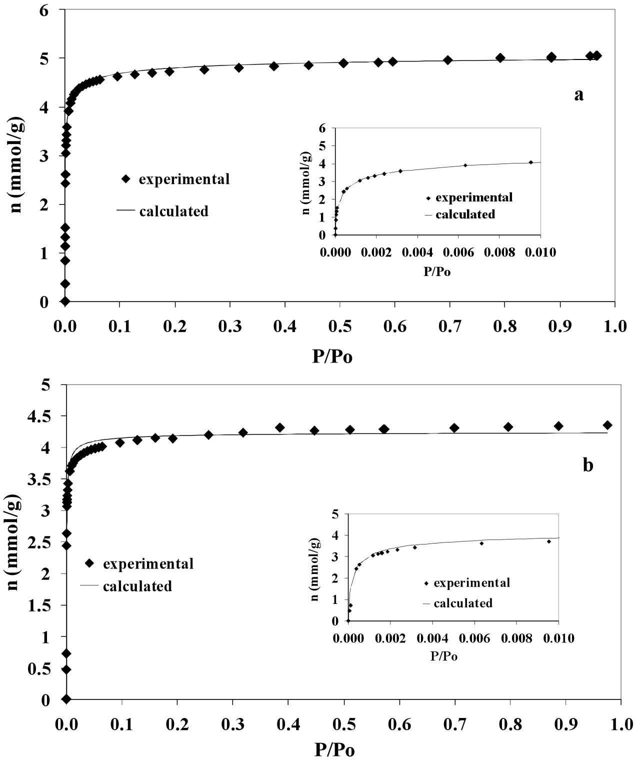

Fig. 5 Experimental adsorption isotherms for (**a**) benzene and (**b**) toluene on F42C at 298 K and data fitted to the Toth equation

For the 200 ppmv VOC concentration used, toluene relative pressure (5.4×10^{-3}) is more than three times larger than benzene relative pressure (1.6×10^{-3}). To study both adsorptives at similar relative pressures, two full benzene and toluene adsorption isotherms at 298 K were obtained for sample F42C, as shown in Fig. 5. Firstly, the shapes of the isotherms confirm the narrow microporous character of this ACF and, secondly, the maximum benzene and toluene adsorption capacities obtained (expressed as liquid) at the maximum pressure used (relative pressure =1) are, as expected, very coincident (0.45 cm^3 hydrocarbon/g ACF).

Figure 5 also plots the calculated isotherm, fitting the experimental data to the Toth equation, which shows a very good fitting from which the fitted parameters of this equation, $C_{\mu s}$, b and t, for benzene adsorption are 5.1925 mmol/g, 298.6724 mbar and 0.3887, respectively. For toluene adsorption, $C_{\mu s}$, b and t are 4.2577 mmol/g, 357.5582 mbar and 0.5825, respectively.

The benzene adsorption capacity at 200 ppmv (1.6×10^{-3} relative pressure) deduced from the Toth fitted isotherm is 25 g benzene/100 g ACF. This result agrees very well with the adsorption capacity at the same concentration calculated from the adsorption dynamic experiments. The toluene adsorption capacity at 5.4×10^{-3} relative pressure (200 ppmv concentration) calculated from the fitted isotherm is 34 g toluene/100 g ACF, what again fits very well with the values calculated from the dynamic adsorption experiments at the same conditions. These results highlight the validity of the comparison between results from both types of experiments.

From Fig. 5a, the benzene adsorption capacity value at the same relative pressure than toluene (5.4×10^{-3}) can be assessed. This value, deduced from the adsorption isotherm, is 30 g benzene/100 g ACF, which leads to a fraction of the narrow micropore volume occupied by liquid benzene of 0.72 cm^3 liquid benzene/cm^3 narrow micropores. Thus, as expected an increase in the relative pressure leads to an increase in the adsorption capacity, and hence to a larger fraction of narrow micropores occupied by liquid benzene.

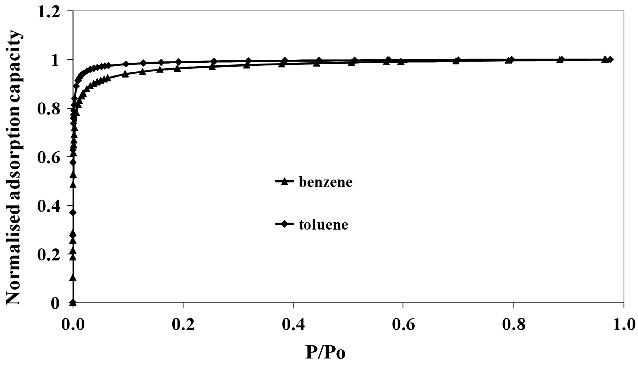

Fig. 6 Benzene and toluene adsorption isotherms for F42C normalised to the maximum adsorption capacity for each hydrocarbon

Figure 6 plots benzene and toluene adsorption isotherms (both normalised to the maximum adsorption capacity for each hydrocarbon), and shows the fact that larger ratios of toluene are adsorbed at low concentration in comparison to benzene at the same relative pressures, what is a consequence of the larger toluene adsorption potential.

Although at relative pressure 1 the liquid benzene and toluene uptake are similar, at the same low relative pressure of 5.4×10^{-3} the fraction of the narrow micropore volume occupied by benzene (0.72 cm^3 liquid benzene/cm^3 narrow micropores) is lower than that occupied for toluene (0.87 cm^3 liquid toluene/cm^3 narrow micropores). At 5.4×10^{-3} relative pressure, molar adsorption capacity for benzene is slightly higher than that for toluene, but toluene molar volume is much larger than benzene molar volume, which leads to a much larger fraction of narrow micropores occupied by toluene.

3.4 Effect of the surface chemistry of the ACFs

Figure 4 has shown that the narrow micropore volume has an important effect on the adsorption capacity of the ACFs.

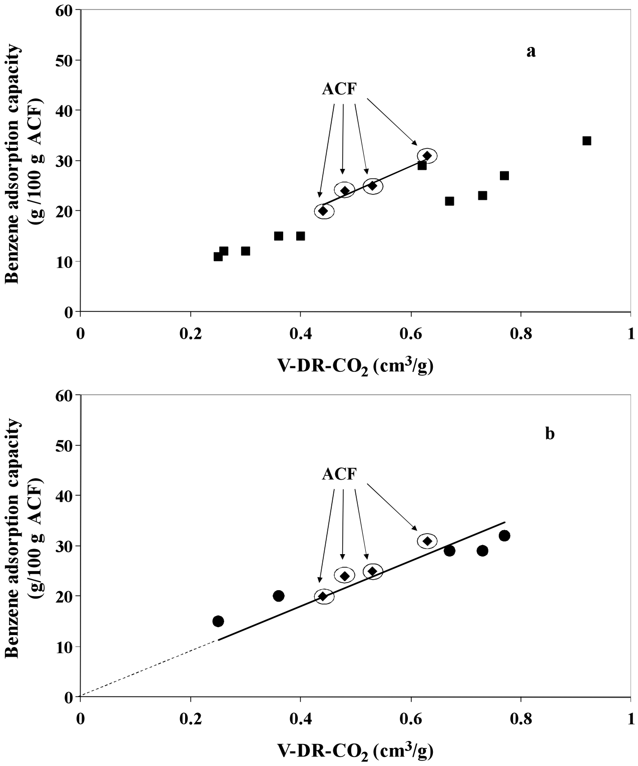

Fig. 7 Relationship between benzene adsorption capacity, at 200 ppmv, and the volume of narrow micropores characterised by CO_2 adsorption at 273 K for: (**a**) the ACFs prepared in the present work (*rhombus*) and pristine ACs from a previous study (Lillo-Ródenas et al. 2005) (*squares*) and (**b**) the ACFs prepared in the present work (*rhombus*) and ACs from the previous study (Lillo-Ródenas et al. 2005) that had been heat-treated to reduce the content in surface oxygen groups (*circles*)

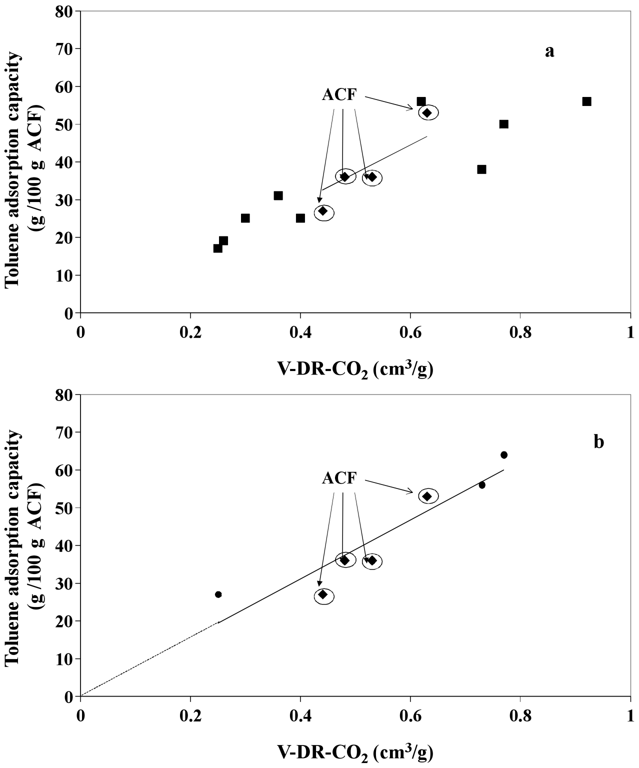

Fig. 8 Relationship between toluene adsorption capacity, at 200 ppmv, and the volume of narrow micropores characterised by CO_2 adsorption at 273 K for: (**a**) the ACFs prepared in the present work (*rhombus*) and pristine ACs from a previous study (Lillo-Ródenas et al. 2005) (*squares*) and (**b**) the ACFs prepared in the present work (*rhombus*) and ACs from the previous study (Lillo-Ródenas et al. 2005) that had been heat-treated to reduce the content in surface oxygen groups (*circles*)

However, when comparing the adsorption capacities of these ACFs with those of different pristine ACs prepared in a previous work (Lillo-Ródenas et al. 2005) (see Figs. 7a and 8a) it could be concluded, at a first glance, that ACFs prepared in the present work behave much better for adsorbing benzene and toluene at low concentration. In fact, much higher narrow micropore volumes are required in the ACs to achieve similar adsorption capacities as those in the ACFs. Before concluding so, and accordingly to (Lillo-Ródenas et al. 2005), another factor should be taken into account; the surface chemistry of the materials that are compared. In the activated carbons prepared in a previous study, the total content in surface oxygen groups varied in the range of 1700–4300 μmol/g, although typical values were around 2600 μmol/g. The total surface oxygen content in the ACFs prepared in this study is in the range 735–865 μmol/g, a much lower value. Therefore, the direct comparison of the VOCs adsorption capacities of the ACFs with those from the pristine ACs from a previous work (Lillo-Ródenas et al. 2005) is not very suitable, since the surface oxygen groups content of the materials differ strongly.

In this sense, we should compare the adsorption capacities of the ACFs prepared in the present study with those of ACs which had suffered a subsequent heat-treatment which strongly reduces their total oxygen surface group contents (Lillo-Ródenas et al. 2005), as it is shown in Figs. 7b and 8b. Interestingly, when the surface oxygen content of the adsorbent is taken into account, the behaviour of the ACFs is similar to that of other types of activated carbons (Lillo-Ródenas et al. 2005) and the adsorption capacity for the ACFs fits well the tendency followed for heat-treated ACs previously studied (Lillo-Ródenas et al. 2005). Hence, the advantage of the ACFs especially observed in Fig. 7a, and also in Fig. 8a is only due to their low oxygen contents and neither to their different morphology, nor to a different type of narrow microporosity.

All these results confirm the importance of porosity and surface chemistry of the activated carbons in the low-concentration VOCs adsorption, and highlight the applicability of the ACFs for this application, since these materials can be prepared with a high narrow micropore volume and a very low surface oxygen groups content, being both parameters of special interest to maximize the low concentration VOC adsorption capacities.

4 Conclusions

The present study has analysed the preparation of ACFs and their application to the adsorption of low concentration gaseous volatile organic compounds, due to the advantages of this type of materials for such application. For this purpose, the so-called “physical” activation method with steam or carbon dioxide were the chosen methods and, selecting different temperatures and holding times, samples with different burn-off percentages have been prepared. Our results show that ACFs with surface areas ranging from 1000 to 1800 m^2/g have been prepared. These materials have exhibited large benzene and toluene adsorption capacities at 200 ppmv each, as large as 31 g benzene/100 g ACF or 53 g toluene/100 g ACF at 298 K. Our study has shown that a large volume of narrow microporosity and a low content in surface oxygen groups are the desired parameters to achieve large adsorption capacities. In this sense, the preparation method selected must be underlined since it leads to ACFs with a very low content in surface oxygen groups. Thus, the advantage of the ACFs for this application, in comparison to other carbonaceous materials, is only due to their low oxygen contents, and neither to their morphology, nor to a different type of narrow microporosity. Comparison between the adsorption capacities determined from dynamic and static (isotherm) experiments has shown very good agreement. The adsorption isotherms obtained let us explain, comparing their different shapes in a normalised plot, the fact that larger ratios of toluene are adsorbed at low concentration in comparison to benzene at the same relative pressure.

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