OPTIMIZATION OF THE PROPERTIES OF ACTIVATED CARBONS FOR THE ADSORPTION OF VOC's AT LOW CONCENTRATIONS

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Introduction

The abatement of VOC's pollutants is of great interest because they are very harmful for both human health and environment, even at very low concentrations. They are cancerigen and teratogenic agents, they can affect the nervous system and they interfere in the stratospheric ozone, in the acid rain, etc. [1-2]. Among these, aromatics compounds must be underlined because they frequently appear in gaseous streams and also because they are very toxic.

The removal of VOCs present in gas streams at very low concentrations (i.e., at ppm levels) is very difficult and requires an extremely optimised process. Adsorption of these pollutants in activated carbons (AC) could be one of the best solutions for the treatment of these streams. Activated carbons are hydrophobic materials with a large surface area, which pore size distribution (PSD) can be tailored, and then optimised, for a given application [3]. This makes that the use of activated carbons for the removal of VOC has been reported in the literature [1-4]. However, the preparation of appropriate AC for the removal of VOC at ppm levels necessitates a very specific pore size distribution.

In this sense, this work analyses the adsorption behaviour of AC prepared in our laboratory and which PSD and surface chemistry have been tailored for the removal of VOCs at ppm levels. Additionally, their performance is compared with high quality commercially available AC. Important conclusions on the influence of the surface chemistry and porosity on the efficiency of activated carbons for the adsorption of aromatics at low concentrations have been derived from this study.

Experimental

The adsorption of VOC streams either of benzene or of toluene with 200 ppmv concentrations is followed in the AC. The temperature of the adsorption experiments was $25 \pm 1°C$. The experiments were carried out in a reactor, containing a fixed bed of AC, coupled to a mass spectrometer. The bed of AC contains between 0.05-0.1 grams of sample and the flow used during the experiments were 90 ml/min.

The performance of a commercial activated carbon (Westvaco WV A1100, sample A), an activated carbon prepared by activation with steam (sample B) and a series of chemically activated carbons prepared by either NaOH or KOH [5] (samples C to F) is compared.

Selected samples were heat treated to remove oxygen surface groups. This treatment consists of heating the samples in a furnace with a helium flow of 100 ml/min using a heating rate of 20°C/min up to 900°C, and then cooled in helium. The nomenclature of the samples prepared in this way include a "T" to denote this treatment.

The characterisation of the porous texture of the activated carbons was done using 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 (pore size smaller than 2 nm) whereas the adsorption of CO_2 at 273 K allows us to assess the narrowest micropores (pore size smaller than 0.7 nm) [6-8]

Results and Discussion

Table 1 contains the results of porosity characterisation of the samples used in this study. As it can be seen, there is a wide range of samples with different micropore volumes and BET surface area. The range of BET surface area covered goes from 650 to 2750 m^2/g. Regarding the micropore volumes, the values obtained from N_2 and CO_2 adsorption show the existence of very different pore size distributions in the selected samples. Thus, the commercial sample A (one of the best in the market for the removal of hydrocarbons) has the widest micropore size distribution (i.e., the largest difference between N_2 and CO_2 micropore volumes), whereas the activated carbon D has the narrowest micropore size distribution, as it is evident from the similarity between V-DR N_2 and V-DR CO_2. It is remarkable that both materials have the same micropore volume evaluated by N_2 adsorption.

Some of these samples, as detailed in the experimental section, were treated in helium to eliminate most of the oxygen surface groups. The thermal treatment has no influence on the porosity of the samples.

Table 1. Porosity characterisation of the samples studied

Sample	BET (m^2/g)	V-DR N$_2$ (cm^3/g)	V-DR CO$_2$ (cm^3/g)
A	1757	0.67	0.36
B	883	0.35	0.26
C	656	0.26	0.25
D	1594	0.67	0.67
E	1872	0.80	0.73
F	2746	0.97	0.77

Figure 1 shows, as an example, the breakthrough curves for benzene adsorption obtained for samples AT and DT. Table 2 includes the quantification of the adsorption experiments from either benzene or toluene at 200 ppmv concentration. This quantification has been done by integration of the breakthrough curves obtained in the adsorption experiments. The table also includes the results for the heat treated samples. The samples tested have benzene adsorption capacities from 15 g/100 g carbon to 32 g/100 g carbon and toluene capacities from 17 g/100 g carbon to 64 g/100 g carbon.
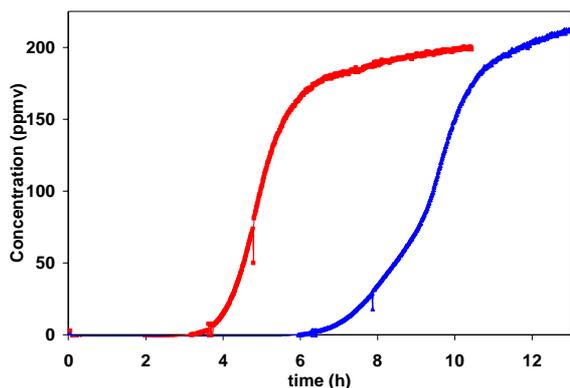

Figure 1. Breakthrough curves for benzene adsorption in samples A (red line) and D (blue line).

From this table it can be observed that, in all the samples tested, the adsorption capacity is higher for toluene than for benzene, in agreement with the higher boiling point of toluene. Moreover, Table 2 shows that we have been able to develop AC with very high adsorption capacities for benzene and toluene.

Additionally, Table 2 and, as a clear example Figure 1, demonstrate that the porosity has great influence on the VOC adsorption by the activated carbons. In this sense, Figure 1 contains the breakthrough curves for the commercial AC heat treated, sample AT, and a chemically activated carbon heat treated, sample DT, both with similar surface chemistry, which have comparable BET surface areas and the same micropore

volumes obtained by N$_2$ adsorption, but very different adsorption capacities for benzene and toluene.

Table 2. Quantification of benzene and toluene adsorption by AC at 200 ppmv concentration.

Sample	Benzene adsorption (g/100 g carbón)	Toluene adsorption (g/100 g carbón)
A	15	31
AT	20	-
B	12	-
C	11	17
DT	29	-
E	23	38
ET	29	56
F	27	50
FT	32	64

The above results demonstrate that the BET surface area cannot explain the results obtained and that other properties of the AC, such as the porosity and the type of microporosity, have to be the key factors. Therefore, it seems that at very low concentrations of VOC, only part of the micropores (i.e., the narrowest) intervene in the process. From Tables 1 and 2 we can deduce that a strong relationship exists between the adsorption capacity of benzene and toluene at very low concentrations and the V-DR CO$_2$.

Figure 2 contains a plot of the benzene and toluene adsorption capacities versus the micropore volume obtained by CO$_2$ adsorption (which accounts for the narrowest micropores with size lower than about 0.7 nm) for the non-treated AC. The figure shows this very good correlation between the micropore volume of the activated carbon, calculated by CO$_2$ adsorption, and the adsorption capacity, for both benzene and toluene. A similar relationship between the VOC adsorption and the micropore volume of the activated carbon calculated by CO$_2$ adsorption, is observed for the heat treated AC.

Thus, the larger the volume of micropores with a size close to 0.7 nm, the higher the adsorption capacity of VOCs at low concentration for the activated carbons tested.

Figure 3 analyses the effect of the oxygen surface groups on benzene adsorption. This figure shows that the VOC adsorption capacities are higher when the oxygen surface groups are removed of the activated carbons by thermal treatment in inert atmosphere. The adsorption capacity

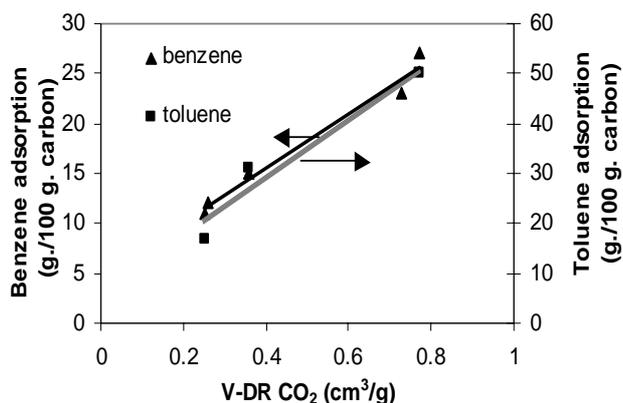increases from a 33% for the commercial sample (A) to a 19% for sample F.

Figure 2. Benzene and toluene adsorption capacity versus micropore volume calculated by CO_2 adsorption for non-treated AC.
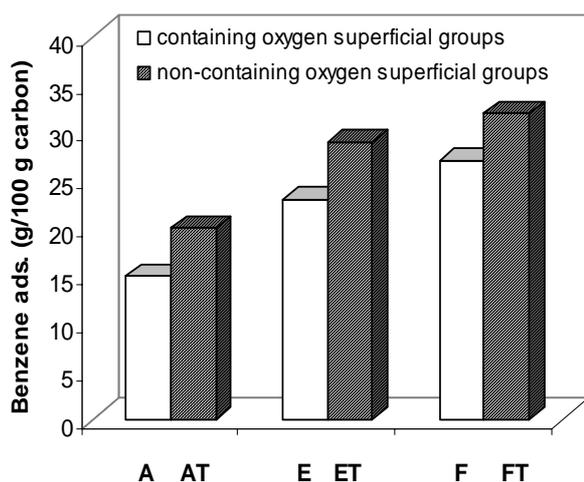

Figure 3. Effect of the oxygen surface groups on benzene adsorption.

Conclusions

Two important factors affecting the adsorption capacity of VOCs at low concentrations by AC have been studied: the pore size distribution and the surface chemistry.

The porosity has a great influence on the adsorption of VOC at low concentration on activated carbons. The micropore volume calculated by the adsorption of CO_2, that is the volume of the narrower micropores (size < 0.7 nm), explains the differences found between the samples analysed. However, N_2 adsorption at 77K, which evaluates the total micropore volume, fails in the prediction of the adsorption capacity.

The surface chemistry is the second factor affecting the performance of the AC. The removal of the surface oxygen groups increases the adsorption capacity of the AC.

In this sense, to improve the performance of the activated carbons for the adsorption of VOC at ppm levels, the optimised AC should contain few oxygen surface groups and the largest micropore volume calculated by CO_2 adsorption at 273 K, that is the largest amount of pores with a size near to 0.7 nm.

We have developed AC by chemical activation with very large adsorption capacities for the removal of hydrocarbons. Values of adsorption capacity as large as 32 g of benzene/100 g of AC and 64 g of toluene/ 100g of AC at 25 °C have been obtained. Therefore the chemical activation method, used for the preparation of the AC tested, is a very good method for this purpose. It permits the preparation of activated carbons with very homogeneous micropore size distribution.

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