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Usefulness of chemically activated anthracite for the abatement of VOC at low concentrations

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Abstract

A previous paper showed a very effective and simple chemical activation method for the preparation of activated carbons from an anthracite that allowed to obtain different ranges of porosity. In addition, these materials were suitable for the VOC adsorption because this activation method renders AC with high volumes of narrow micropores. In this paper, the method has been successfully extended to some other precursors, such as subbituminous and lignite coals and lignocellulosic materials. The developed method permits the easy preparation of AC with very well-developed porosities and with high narrow micropore volumes. These characteristics of the AC allow to reach high adsorption capacities to VOC (benzene and toluene) at low concentrations, which are much higher than previously reported in the literature. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Activated carbons are materials of great interest because they are needed in many applications, both in gas and liquid phase. Recently, they are subject of study in many fields related to the abatement of pollutants such as VOC because they are very harmful to both human health and environment [1,2]. The problem of their abatement increases because many of the streams where VOC are present are very diluted [1–3]. One of the most promising technologies for this application is the use of activated carbons [4,5].

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Previous works [6,7] have shown a method for the preparation of AC based on the chemical activation of Spanish anthracites by chemical activation with NaOH or KOH. From our studies [6,7], we propose a very simple method of activation, much simpler than the ones typically used in the literature. It consists of a direct physical mixing of the activating agent (NaOH or KOH) and the precursor. The samples prepared by this method can develop a very high porosity, depending on the experimental conditions used, with micropore volumes close to $1 \text{ cm}^3/\text{g}$.

In addition, the VOC adsorption at low concentration was tested with these samples [8] and the influence of some experimental variables was studied. This study revealed that both the surface chemistry and the volume of narrower micropores ($<0.7 \text{ nm}$) of the AC have a great influence in the adsorption capacity of these pollutants. The chemically activated carbons can be prepared with a high narrow micropore volume and they show very high adsorption capacities [8], much higher than previous studies at similar experimental conditions and, even higher, VOC uptake than the one which can be reached using high quality commercial AC.

Our purpose in this work is to determine if the activation method reported in previous works [6,7] can also be applied to other carbonaceous precursors, developing microporous materials suitable for the VOC adsorption at low concentration [8]. The new precursors tested include a non-Spanish anthracite, a subbituminous coal, a lignite and a carbonised coconut shell.

2. Experimental

The activated carbons for the VOC's adsorption have been prepared by chemical activation with NaOH and KOH [6]. We have to underline that some of the precursors used in this study have a high mineral matter content, as it is the case of the subbituminous coal, with 19 wt.% ash content (daf).

Different experimental variables have been tested to produce activated carbons with very different porosity. The conditions for the preparation appear on Table 1. The anthracite 1 is the one used in previous studies [6,7].

The characterisation of the porous texture of the activated carbons prepared from Spanish coals has been 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) [9,10].

Two different VOCs have been used in this study, benzene and toluene. The adsorption experiments have been carried out in a fixed bed of activated carbon (BTR-Jr.) coupled to a mass spectrometer (Thermocube, Balzers). The bed contains between 0.05 and 0.1 g of AC and the flows used during the experiments have been around 90 ml/min. The column diameter is 10 mm and the height of the bed is about 3 mm.

The VOC's streams of either benzene or toluene contain 200 ppmv concentration. The temperature of the adsorption experiments has been $25 \pm 1^\circ\text{C}$.

Table 1
Summary of the experimental conditions used in the preparation of the activated carbons

Sample	Precursor	Activating agent	Activating agent/coal ratio	Heating rate (°C/min)	N ₂ flow during carbonisation (ml/min)	Maximum temperature (°C)
A-1	anthracite 1	NaOH	2/1	5	500	730
A-2	anthracite 1	NaOH	3/1	5	500	730
A-3	anthracite 1	KOH	3/1	5	500	730
Ab-1	anthracite 2	NaOH	2/1	5	500	750
Ab-2	anthracite 2	NaOH	3/1	5	500	750
Ab-3	anthracite 2	KOH	3/1	5	500	850
S-1	subbituminous	NaOH	2/1	5	250	760
S-2	subbituminous	NaOH	3/1	5	250	760
S-3	subbituminous	NaOH	3/1	5	1000	730
S-4	subbituminous	KOH	2/1	5	250	730
L-1	lignite	NaOH	3/1	5	500	730
CS-1	cococut shell	NaOH	3/1	5	500	750
CS-2	cococut shell	NaOH	3/1	5	500	850

By this experimental set-up, adsorption breakthrough curves have been obtained. The adsorption capacity has been calculated by numerical integration from the breakthrough curves.

3. Results and discussion

As detailed in Section 2, activated carbons have been prepared by chemical activation using different experimental conditions and then characterised by physical adsorption of gases. Fig. 1 includes the nitrogen adsorption isotherms for some of the AC prepared. They

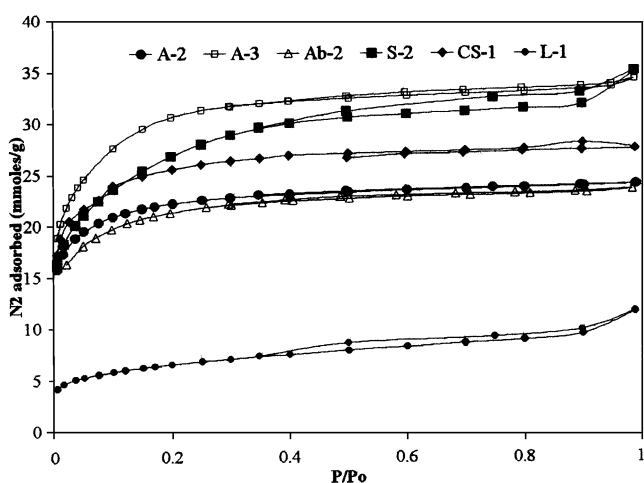


Fig. 1. Nitrogen adsorption isotherms over some of the chemically activated carbons.

correspond to samples prepared at similar experimental conditions to analyse the effect of the precursor in the activation. These isotherms are of type I corresponding to microporous AC, and they show that, in general, there is a high porosity development independently on the precursor used. However, the porosity distribution of the AC is very different depending on the precursor. The samples prepared with the anthracites are essentially microporous materials and also the ones from the coconut shell precursor. The lignite develops very low porosity, whereas the subbituminous coal produces AC with a high porosity development, with isotherms corresponding to materials that have both micro and mesoporosity (see the slope at relative pressures higher than 0.2).

Table 2 summarises the characterisation by N_2 and CO_2 adsorption (77 and 273 K) of some of the samples prepared. These results corroborate the comments obtained from the isotherms and permit the analysis of some experimental variables. For example, the nitrogen flow increases the porosity development, as it can be inferred from samples S-2 and S-3, and an increase in the activating agent to coal ratio also has the same effect, as it is shown by S-1 and S-2. These effects were already discussed elsewhere [6,7].

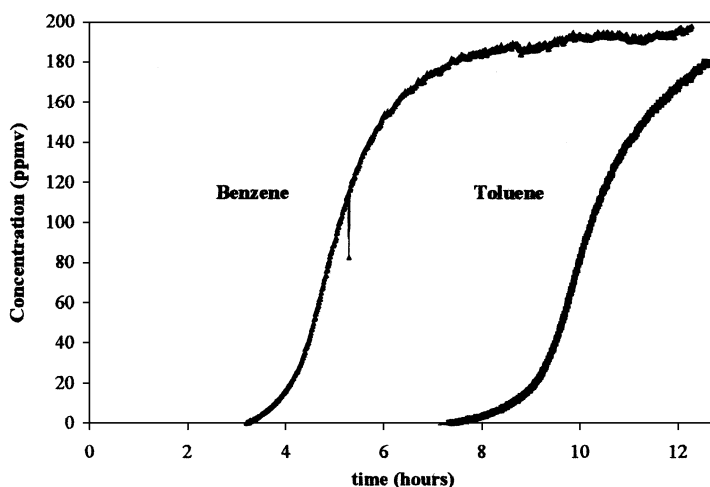
Thus, the method proposed, permits the preparation of samples with different porosities depending on the experimental conditions chosen. With the suitable experimental conditions, activated carbons with very high narrow micropore volumes can be prepared (example Ab-3).

Over some of the chemically activated carbons benzene and toluene adsorption experiments have been carried out, as described in Section 2. As an example, Fig. 2 includes the breakthrough curves for benzene and toluene adsorption over A-3. The numerical integration provides the adsorption capacities. The quantification of these data, for some samples, is included in Fig. 2.

We have observed that the adsorption capacity of the AC depends strongly on the porosity. The analysis of the results shows that the micropore distribution seems to be the key factor governing the adsorption capacity, especially the micropore volume calculated with the adsorption of CO_2 . The higher the narrow micropore volume the higher the adsorption capacity.

Table 2
Porosity characterisation of the samples

Sample	BET (m^2/g)	V-DR N_2 (cm^3/g)	V-DR CO_2 (cm^3/g)
A-1	1594	0.67	0.67
A-2	1872	0.80	0.73
A-3	2746	0.97	0.77
Ab-1	1439	0.62	0.50
Ab-2	1741	0.71	0.61
Ab-3	2343	0.95	0.83
S-1	1770	0.68	0.54
S-2	2331	0.86	0.61
S-3	2478	0.88	0.62
S-4	1811	0.73	0.62
L-1	56	0.02	0.19
CS-1	2196	0.82	0.65
CS-2	2191	0.91	0.63
Commercial	1757	0.67	0.36



Sample	Benzene ads. Capacity (g. benzene/100 g. carbon)	Toluene ads. Capacity (g. toluene/100 g. carbon)
A-1	26	-
A-2	23	38
A-3	27	50
S-1	19	-
S-3	29	56
commer.	15	31

Fig. 2. Example of benzene and toluene adsorption breakthrough curve and VOC uptake.

The AC prepared show very high adsorption capacities, in comparison with the data from literature, achieving benzene and toluene adsorption capacities as high as 29 or 56 g/100 g carbon, respectively, values much higher than those obtained with a high quality commercial carbon. The higher capacities are related to the high CO₂ micropore volumes that can be reached with this preparation method.

4. Conclusions

The simple chemical activation method used in this work, that implies the direct mixing of NaOH or KOH and the precursor, is very suitable for the preparation of AC from different carbonaceous precursors.

This paper extends the work done with an Spanish anthracite; thus, chemical activation permits the efficient development of porosity with many other precursors and, moreover, the porosity can be tailored by changing the experimental variables in the process of preparation, achieving micropore volumes close to 1 cm³/g. The porosity of the prepared activated carbons strongly varies depending on the coal precursor. For the purpose of this work, microporous activated carbons are preferred for the retention of VOC.

The adsorption tests carried out over the activated carbons show that the adsorption capacity of the samples vary depending on the porosity. The described method permits the preparation of activated carbons with very high adsorption capacities for the abatement of VOC at low concentration much higher than those previously shown in the literature.

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