

THREE-RINGS PAHs EMISSIONS ABATEMENT BY CARBON MATERIALS

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Abstract

The adsorption of toxic organic emissions for hot gas cleaning from energy generation has been studied. For this goal, the adsorption capacity of different carbon materials with a wide range of textural characteristics has been assessed for PAHs removal from combustion hot gas. The study was carried out at laboratory scale and the main aim has been to test the PAHs adsorption capacities by the porous materials at the ranges that they could be emitted from new energy systems generation, fluidized beds.

The results obtained show that there is a good correlation between the PAH adsorption capacity and the total micropore volume calculated with the Dubinin-Radushkevich equation for the N₂ isotherm data. No relationship was found between PAH adsorption capacity and mesopore volume calculated by BJH method. Besides, no relationship was found between chemical surface, CO and CO₂ groups desorbed on Thermal Program Desorption (TPD), and adsorption capacity.

Keywords: Adsorption, VOC, PAH, Hot Gas Cleaning

Introduction

Polycyclic Aromatic Hydrocarbons (PAH) have started to be widely studied and a special concern is being paid to environmental subject due to their potential carcinogenic, mutagenic, or both. Furthermore, the interactions between volatile organic compounds, VOC, and adsorbing materials are acquiring a remarkable

concern, both from a kinetic and from a thermodynamic point of view.

PAH are mainly emitted from combustion processes, having their origin associated to anthropogenic sources, as engine exhaust, industrial processes, domestic heating systems or incinerators, and to natural sources as volcanic eruptions and forest fire. Whereas the natural sources can not be controlled, PAH emissions from anthropogenic sources could be reduced by controlling the combustion processes through combustion variables(1-3). Once these emissions are minimized by combustion optimization, a possible way of PAH abatement could be the use of solid adsorbents in the post-combustion stage. In the group of adsorbents, active and porous carbons are materials with a high surface/weight ratio and so very useful to trap emissions for environmental purposes.

One of the main organic pollutant groups in the exhaust gases from organic material combustion are the polycyclic aromatic hydrocarbons (PAH), and some of these polyaromatic hydrocarbons have been listed by USEPA as priority pollutants. It does not matter the nature of the fuel, neither whether these PAH are within the fuel structure, because PAHs can be generated during combustion as consequence of the pyrosynthetic process joined to organic material combustion. PAHs are not only associated to small particulate matter (the micro and nanoparticulate matter), but also PAHs are majority distributed in the gas phase (2,3), especially 3-rings size PAH. Due to their high volatility, these PAHs can not be totally retained

only using filters systems. This is the main reason why the adsorbents utilization has been applied in this work using Phenanthrene (Ph) as model aromatic hydrocarbon representing the PAH listed as priority pollutants.

The choice of adsorbents for PAHs pollution monitoring is determined by several factors such as collection efficiency, capacity of adsorbent, the adsorbent chemical stability during sampling, storage and extraction, low blank levels, low affinity for water vapor and high facile recovery of adsorbed vapors. This last factor makes that PAH sampling (6) has been performed with adsorbents as XAD-2, XAD-4, Tenax, Polyurethane foam, PUF, Fluorisil, Alumina, Bondapak C18 on Porasil, Chromosorb 102, SepPak-C18, Graphpac GC and Graphtrap GC instead of carbon compounds. The carbon compounds are characterized by a high PAH retention capacity, due to their high specific surface, but they have a low efficiency in PAHs desorption (7). Therefore, the carbon compounds are useful from an environmental point of view for decreasing emissions (8) but not for sampling systems.

The use of carbon materials as adsorbents has been studied in different applications, like solvent recovery in different industrial processes, protective filters for harmful vapor retention and purification of gaseous stream. For some of these applications carbon materials are directly used due to the retention is produced on the activated points of their surface, like for Volatile Organic Compounds, VOCs, SO_x and SH₂. In other cases the active carbon only acts as support of another active material which is impregnated or dispersed.

In this work, the retention capacity of different active carbons has been studied when a constant concentration flow of a three-rings PAH passes through an adsorbent fixed bed at constant temperature. It is not focused on the optimization of the characteristics shown by the carbon materials but on the influence of these characteristics on their corresponding PAH adsorption capacity.

Experimental

Ten non-commercial carbon materials of different origin were provided to study their performance in relation to their PAH adsorption capacity. CA-1, CA-2 and CA-4 were carbon blacks from tire pyrolysis. CA-3 was a coke from German lignite. The remaining carbon materials are active carbons from biomass. The ten samples (see Table 1) of porous carbons were characterized by N₂ and CO₂ adsorption at 77 and 273 K, respectively, using an ASAP 2000 (Micromeritics). Before the experiments, the samples were heated at 200°C and then outgassed at this temperature under a vacuum of 10⁻³ Torr to constant pressure. Micropore volumes were obtained applying the Dubinin-Radushkevich equation (DR) and mesopore volume, V_{BJH}, applying the BJH method (Barret E P. et al.) to the data of the N₂ isotherm.

The characterization of the surface oxygen groups was carried out on a Pulse Chemisorb 2700 (Micromeritics) by temperature-programmed desorption (TPD) of the decomposition products (CO₂ and CO) by flowing helium over the carbon support in a U-shaped quartz reactor while elevating the temperature at a rate of 10° C/min. The carrier flow rate was adjusted with an electronic mass flow controller. A temperature regulator was used to program the temperature between 150° and 1050° C with linear heating rates. The gases evolved on thermal decomposition of the surface groups were measured by a gas chromatograph equipped with Porapak N-120 and Molecular Sieve columns. The temperature program was 35° C for 4 min and then raising the temperature up to 180 °C at 35° C/min. Before its utilization, the gas was purified passing it through a zeolite moisture trap.

Experiments were carried out using a laboratory scale rig and following the procedure published elsewhere(9).

Adsorption capacities, w^* (mg Phe/mg AC), were calculated as $t_b * C_0 * Q/W$, see Table 2, where t_b is the breakthrough time for a 2% of penetration time (min); C_0 the Phe inlet stream

concentration (mg/ml), Q the flow (ml/min) and W the adsorbent weight (mg). The Phe concentration (C) in the outlet gas stream was directly measured by a FID, which had been previously calibrated.

Results and Discussion

The aim of this work is not focussed on the activation process of the carbon materials used but in their behavior in the PAH adsorption process. Each sample adsorption capacity was studied from their breakthrough curves (see fig 1a and 1b). These were carried out at 150 °C, common temperature of hot gas emissions at power stations; between 15 or 50 mg of mass adsorbent; a PAH concentration ≈ 1.5 ppm and a constant flow of 10 ml/min. The results allowed calculating the w^*/C_0 ratio, which correspond to the Henry's law constant in the low concentration range characterized by linear isotherm.

The loading curves obtained for the ten carbonaceous materials are reported in Figure 1a and 1b in which the results are the average of three runs with a %RSD=10%. Figure 1 also includes the blank experiment performed when the gas flows through a reactor containing sand and glass particles. The influence of the adsorbent amount on Phe adsorption capacities is null because a direct relationship, $r^2=0.98$, between the breakthrough time, t_b , and the bed weight has been found. That means that the adsorption wavefront is formed quickly in the sorbing bed and moves at constant shape and rate through it. It can be said that the "constant pattern assumption" (9) is confirmed. This can also be observed in the loading curves of the Figures 1a-1b, where the high slope for all samples shows a fast PAH adsorption with minimum mass transfer effect. From these results, a very fast kinetic, but with different adsorption capacities for each sample can be deduced.

Phe was selected to study the PAH adsorption capacity of different carbons due to both, to be one of the most abundant PAH emitted from

energy generation and one of the most volatile PAH listed by USEPA, it was necessary to characterize Phe through its molecular parameters. These parameters (Van der Waals volume and kinetic diameter) have been calculated from the contribution of the different $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ ($V_w=30.44$) to Naphthalene ($V_w=73.97$) molecule. The obtained values were $V_w=107.80$ cm³/mole as Van der Waals volume, and 0.7 nm as Phe kinetic diameter.

The comparison between the textural characteristics of the samples and their adsorption capacities shows that there is a very good correlation ($r^2=0.97$) between V_{N_2} and the w^*/C_0 ratio, as it is shown in Figure 2a. This is in good agreement with the pore size range studied with the N₂ isotherm and with the Phe molecular diameter. Concerning to the correlation between V_{CO_2} and the w^*/C_0 ratio, see Figure 2b, it can be observed a lower value ($r^2=0.72$). This result could be expected taking into account that the CO₂ isotherm gives the measuring of the narrow microporosity (size<0.7nm), it is to say, of the pores close to the Phe molecular diameter. In this way, only the entrance of Phe molecules in the upper limit of the narrow microporosity will be allowed. A deeper study of Figure 2b shows that CA-5, CA-6 and CA-16 are the samples which produce the linear deviation and their posterior elimination would lead to a good correlation, $r^2=0.98$. In the CA-5 and CA-6 samples, their narrow microporosity will avoid the Phe entrance, almost totally in the CA-5 micropore sample while in the CA-6 sample it will be partially allowed because of its more adequate narrow micropore distribution, which is close to the upper limit. In the CA-16 sample, where $V_{N_2}>V_{CO_2}$, most of the microporosity is not been taking into account and so the Phe entrance is favored. For the rest of the samples, the good correlation can be explained due to their narrow micropore distribution, which will be close to the upper limit allowing the Phe entrance.

Once the influence of the micropore distribution in the Phe adsorption capacity was studied, it was checked a possible correlation between the

TABLE 1. Characterization of the Textural Parameters of the Adsorbent used

Sample	Origin	DR		BJH		TPD	
		V_{N_2} , $cm^3 g^{-1}$	V_{CO_2} , $cm^3 g^{-1}$	V_{BJH} , $cm^3 g^{-1}$	$?_{BJH}$ $nm?$	$?mol CO g^{-1}$	$?mol CO_2 g^{-1}$
CA-1	Tire	0.06	0.03	0.23	16.2	864	373
CA-2	Tire	0.04	0.02	0.57	21.6	277	121
CA-3	Lignite	0.11	0.12	0.11	4.0	499	542
CA-4	Tire	0.15	0.08	0.62	13.0	944	295
CA-5	Cherry	0.13	0.18	0.01	2.0	1860	874
CA-6	Grape	0.19	0.21	0.07	3.3	1476	1009
CA-8	Apricot	0.46	0.25	0.22	3.5	839	592
CA-11	Coconut	0.57	0.42	0.11	2.6	1134	465
CA-14	Apricot	0.52	0.32	0.57	3.7	705	161
CA-16	Apricot	0.62	0.29	0.52	4.1	884	482

TABLE 2. Adsorption Capacities at 150 °C for the Adsorbent Samples.

Samples	C_0 (? g/ml)	w^* (mg/mg)	w^*/C_0 (ml/mg)
CA-1	0.85	0.011	12.9
CA-2	1.74	0.014	8.0
CA-3	1.43	0.088	61.7
CA-4	2.07	0.133	64.2
CA-5	1.19	0.014	11.8
CA-6	1.49	0.110	73.8
CA-8	1.29	0.257	199.0
CA-11	1.05	0.284	271.5
CA-14	1.65	0.387	235.2
CA-16	1.92	0.638	332.2

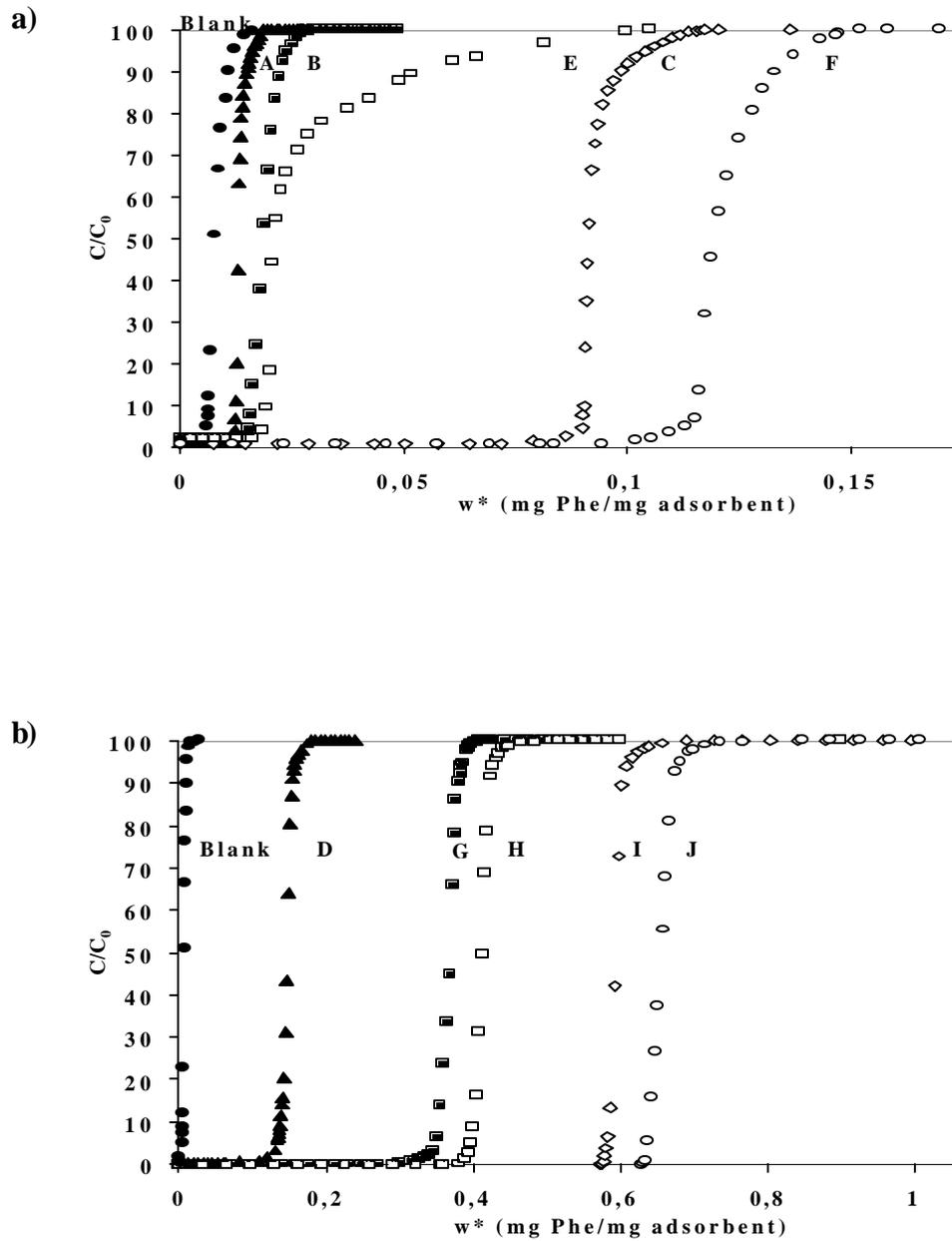


FIGURE. 1. Loading curves for the ten carbonaceous materials ($C_0 = 1.5\text{ppm}$, $Q = 10\text{ml/min}$)
 1a) for blank and the less efficacy carbonaceous materials, where $m=50\text{mg}$; A= CA-1, B= CA-2, C= CA-3, E= CA-5 and F= CA-6 and
 1b) for blank and the most efficacy carbonaceous materials, where $m=15\text{mg}$; D= CA-4, G= CA-8, H= CA-11, I= CA-14 and J= CA-16.

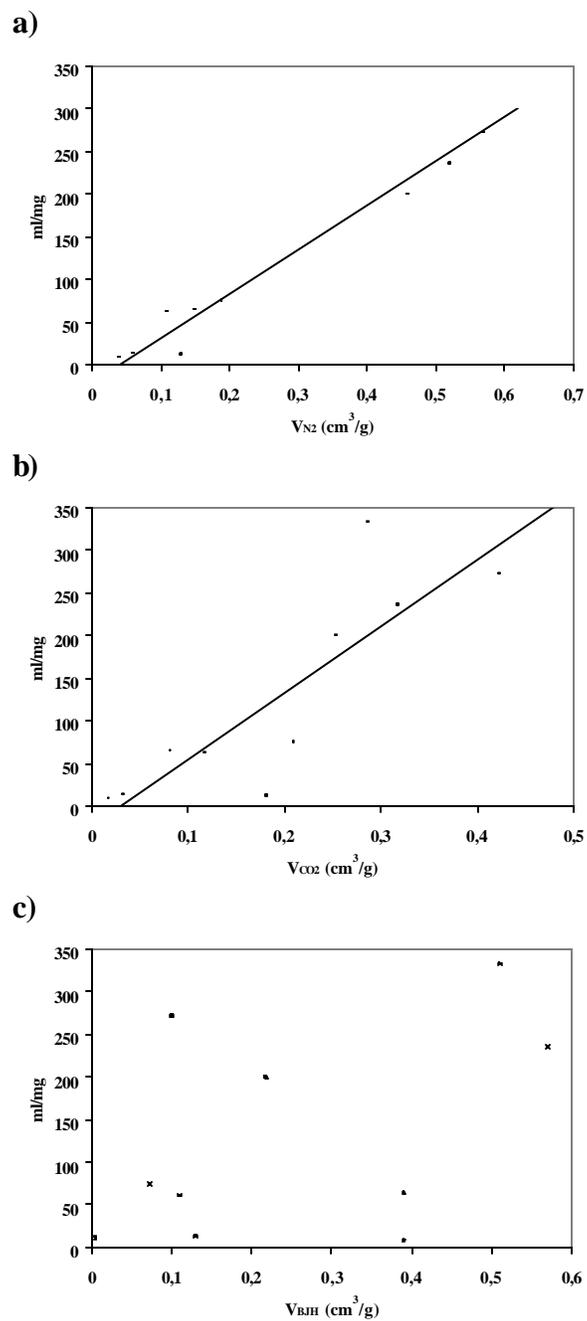


FIGURE 2- Relationship between Phe adsorption capacity and a) the micropore volume calculated from the N_2 adsorption, b) the micropore volume calculated from the CO_2 adsorption and c) the mesopore volume for the N_2 isotherm data.

mesopore volume of the different adsorbents with their PAH adsorption capacity (Fig 2c) and no correlation was found. It is according to the molecular size of Phe and to the Phe low concentration used in which the adsorbent-adsorbate interactions are predominant facing the adsorbate-adsorbate interactions, as it can be observed in Figure 2a. In fact at high concentrations the adsorbate-adsorbate interactions are more favored and therefore the capillary condensation in mesoporous is produced.

Afterwards, the effect of surface chemistry upon PAH retention was studied. The carbon samples used in this work cover a wide range of surface chemistry what that could allow getting knowledge on the surface groups influence. In principle, and because PAHs show a low polarity molecule, the active sites present in the samples should not have influence in the PAHs adsorption. If an active side is considered that generated in the carbon after the desorption of oxygen surface groups, such as CO and CO₂, the results should show that there is not correlation between the amount of PAH adsorbed and the amount of CO or CO₂ groups desorbed. Results obtained showed that the ratios Phe/CO, Phe/CO₂ and Phe/O* mostly differ from one, which confirms that there is not correlation between the Phe adsorbed and the sites formed after CO and CO₂ desorption. In addition, there is also no correlation with the total number of free sites, CO + 2CO₂.

Therefore, although the samples show great differences in their chemical surface, see Table 1, their behavior regarding Phe adsorption only showed to be depending on their porous texture.

Conclusions

Summarizing and according to the results obtained, it can be deduced that the three-rings PAHs adsorption capacity on carbon materials is not dependent on the chemical surface of the

adsorbents but it is a function of the sorbents texture.

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