FACTORS CONTROLLING THE ADSORPTION OF PAHs CONTAINING 2, 3 AND 4 AROMATIC RINGS FROM HOT GAS EMISSIONS

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Abstract

The removal of polycyclic aromatic hydrocarbons (PAH) containing different aromatic rings number, Napthalene (Np), Phenanthrene (Phe) and Pyrene (Py) from combustion hot gas by sorbents has been studied. The aim was to relate the sorbents textural characteristics with the adsorption capacity of these 2-, 3- and 4-ring polyaromatic hydrocarbons at the conditions they are emitted at energy generation. The sorbents textural parameters, total micropore volume, V_{N2}, narrow micropore volume, $V_{CO2,}$ mesopore volume, V_{BJH}, and the free active sites, were analyzed trying to correlate them with their Np, Phe and Py adsorption capacities. To get this aim, single and multiple linear regressions (MLR) were applied to the three Polycyclic Aromatic Hydrocarbons (PAH). A principal component analysis was performed to generate new and uncorrelated variables. It enabled that the relations between the textural parameters were analyzed using a principal components regression (PCR). The PCR analysis had a good statistical quality, but neither did it allow differentiating free active site types nor V_{N2} and V_{CO2}. The correlations were thus set up applying a multiple linear regression (MLR) to the original variables The regression statistical quality was similar to the PCR analysis and it could give an easier explanation of the parameters that affected the adsorption.

Keywords: PAH (Napthalene, Phenanthrene, Pyrene), Adsorption, Active Carbons, Hot Gas Cleaning

Introduction

It is known that the main advantage of energy production in FBC is associated to inorganic emissions abatement due to the combustion conditions allow controlling and decreasing SO_x, NO_x and CO_x emissions. However, organic emissions also constitute an important source of pollution. Although the organic compounds show a wide variety, a special group constituted by the Polycyclic Aromatic Hydrocarbons (PAHs) is notable because they are able to modify the normal metabolic functions of cells, originating mutagenic and carcinogenic effects. PAHs are mainly generated in combustion processes of fossil fuels (1) through mechanisms that can be classified in two processes: pyrolysis and pyrosynthesis (2).

Due to the PAH high volatility and reactivity they can be released not only supported onto the particulate matter (PM) but also in gas phase (1). While the more volatile compounds, compounds of 2 and 3 aromatic rings, are mainly released in gas phase, the compounds containing 3 and more aromatic rings in their molecule, could be the majority associated with the PM. Therefore, the PAH gas/solid partitioning is associated to the liquid vapor pressure, the size and surface area of the suspended particulate matter, the PM chemical composition and ambient temperature. These characteristics joined to the PAH volatile character will determine the way in which they are emitted from a combustion process.

The main advantage of the PAH supported onto the particulate matter is that they can be trapped using proper systems to collect the PM as

cyclones, electrostatic precipitators, scrubbers, etc. On the contrary, the most volatile compounds can be released to the atmosphere by chimney and their control is more difficult making the use of sorbents necessary to capture them (3).

Experimental

The active carbons used in this work were deeply characterized through their textural parameters and the obtained data are compiled in Table 1.

The sixteen porous carbons were characterized by N_2 and CO_2 adsorption at 77 and 273 K, respectively, using an ASAP 2000 (Micromeritics). Their micropore volumes were obtained applying the Dubinin-Radushkevich equation (DR) and mesopore volume, V_{BJH}, by applying the BJH method *(18)* to the N_2 isotherm data. Their corresponding micropore distribution and diameter mean size, were calculated applying the Dubinin- Astakhov (DA) equation to the CO_2 isotherm data.

The surface oxygen groups characterization was carried out on a Pulse Chemisorb 2700 (Micromeritics) by temperature-programmed desorption (TPD). The carrier flow rate was adjusted with an electronic mass flow controller. The gases evolved by thermal decomposition from the surface groups were measured by gas chromatography with Porapak N-120 and Molecular Sieve columns. The temperature program was as follows:

35ºC isothermal for 4 min
from 35 to 180ºC at 35ºC/min.

Experiments were carried out using the laboratory scale and the protocol published elswhere(1).

Table 1. Active Carbons Textural Parameters.

Sample	Origin	DR equation		DA equation		TPD		BJH method
		V_{N2} (cm³/g)	V_{CO2} (cm³/g)	n	L (nm)	CO (? mol/g)	CO_2 (? mol/g)	V_{BJH} (cm³/g)
CA-1	**Tire**	0.06	0.03	2.39	0.9	864	373	0.130
CA-2	Tire	0.04	0.01	2.23	1.1	277	121	0.390
CA-3	Coal	0.11	0.12	2.06	1.3	499	542	0.110
CA-4	Tire	0.15	0.08	1.61	1.4	944	295	0.390
CA-5	Cherry	0.13	0.18	2.40	0.7	1860	874	0.004
CA-6	Grape	0.19	0.21	2.32	0.8	1476	1009	0.070
CA-7	Coal	0.21	0.19	1.98	1.1	1405	578	0.060
CA-8	Apricot	0.46	0.25	2.00	1.6	839	592	0.220
CA-9	Coal	0.30	0.28	2.04	1.0	669	353	0.110
CA-10	Coal	0.36	0.28	1.93	1.1	678	392	0.260
CA-11	Apricot	0.57	0.42	2.32	1.1	681	465	0.100
CA-12	Coal	0.41	0.22	1.54	1.5	1134	344	0.250
CA-13	Coal	0.52	0.27	1.63	1.4	661	357	0.430
CA-14	Apricot	0.52	0.32	1.64	1.4	705	161	0.570
CA-15	Coal	0.48	0.36	1.72	1.3	612	321	0.140
CA-16	Apricot	0.62	0.29	1.52	1.6	884	482	0.510

Results and Discussion

The aim of this work was to look for any correlation between the sorbents textural parameters and their adsorption capacity at the conditions that Np, Phe and Py are emitted at the chimney from power stations. Therefore, a deep textural characterization of the sixteen used carbon materials was performed. Sorbent characteristics are shown in Table 1, where V_{N2} is the total micropore volume (pore size < 2 nm), calculated from the DR equation for the N_2 isotherm data; V_{CO2} (pore size < 0.7 nm) is the narrow micropore volume, calculated from the DR equation for the CO_2 isotherm data and the mesopore volume; V_{BJH} is the pore size 2-50 nm, which was calculated from the BJH method for the N_2 isotherm data; and the n exponent was obtained from applying the Dubinin Astakhov equation to the CO_2 isotherm data. For most of the carbon adsorbents, n ranged from 1 to 4. An n value higher than 2 means a highly homogeneous, small micropore carbon adsorbent and an n value lower than 2 means a strongly activated and heterogeneous carbons. The L value was obtained at the maximum value of the distribution curve using the Stoeckli equation when the characteristic adsorption energy, from de DA equation to the CO_2 isotherm data, ranges from 42 to 20 KJ/mol and using the Dubinin Equation when the E_0 values were lower. Table 1 also shows the decomposition products from the surface oxygen-containing groups (CO and CO_2) which were determined by TPD. The CO_2 was released at low temperatures, as a result of the decomposition of acid surface groups. CO has their origin from weakly acidic, neutral and basic groups, which are thermally more stable and therefore was released at higher temperatures.

Np, Phe and Py molecular parameters, molecular volume and mean diameter, were calculated according to Bondi (4), see Table 2. The PAH adsorption capacity was obtained from the breakthrough curves. Figure 2 shows that CA-16 was the most efficient sample.

Table 2. Molecular Parameters for the Three PAH Studied.

Compound	Vw (cm³/mole)	?? ?nm)
Np	73.97	0.62
Phe	107.80	0.70
Py	132.33	0.75

The high slope for each PAH indicated that the three polyaromatic hydrocarbons adsorption happened very quickly, with minimum mass transfer effect, and very fast kinetics. However, the different adsorption capacities for each studied hydrocarbon were depending on their molecular size and volatility.

The adsorption capacity of the sixteen carbon materials for the three studied PAH are showed in Table 3, where the w^*/C_0 ratio is given. Due to the experimental design, it was not possible to keep constant the three PAH inlet concentration in all experiences run, so the w^* could not be compared. Later on, these values will be compared with the textural characteristics of the carbon materials.

Table 3. Polycyclic Aromatic Hydrocarbons Adsorption Capacities

Sample	Np	Phe	Py
CA-1	1.5	12.9	21.0
CA-2	1.5	8.0	41.7
CA-3	25.2	61.7	71.8
CA-4	21.4	64.2	90.5
CA-5	1.9	11.8	13.3
CA-6	35.5	73.8	61.1
CA-7	45.6	101.8	122.8
CA-8	64.7	199.0	198.7
CA-9	71.2	161.4	157.6
CA-10	67.2	188.8	260.0
CA-11	106.6	271.5	288.3
CA-12	54.4	233.8	230.7
CA-13	57.7	260.4	332.3
CA-14	63.2	285.2	330.3
CA-15	113.6	274.4	253.8
CA-16	109.4	332.2	384.3

Table 4: Relationship Between Pore Volume and PAH Adsorption Capacities for the Carbonous Materials

Pore Volume	Regression Coefficient Parameter, r (% explained variance)		
	Np	**Phe**	**Py**
V_{N2}	0.892 (79%)	0.984 (97%)	0.959 (92%)
V_{CO2}	0.893 (80%)	0.848 (71%)	0.785 (61%)
V_{BJH}	0.173 (3%)	0.460 (21%)	0.573 (33%)

A single variable analysis was carried out to evaluate the influence of each textural parameter, in the three PAH adsorption capacities. In Table 4 the influence of V_{N2}, V_{CO2} and V_{BJH} on the adsorption capacity of each compound, the regression coefficient parameters, r, and, in parenthesis, the explained variance percentages are shown. It was observed that the statistical quality of this regression was only acceptable in the cases of Phe and Py in relation to V_{N2}, but these values were not

Table 5: Relation Between PAH Adsorbed and Surface Groups Evolved During Heat Treatment (O*=Total Oxygen Evolved Calculated as CO + CO$_2$)

Sample	Np/CO	Np/CO$_2$	Np/O*	Phe/CO	Phe/CO$_2$	Phe/O*	Pyr/CO	Pyr/CO$_2$	Pyr/O*
CA-1	0.0	0.1	0.0	0.1	0.2	0.0	0.1	0.3	0.1
CA-2	0.1	0.2	0.0	0.3	0.7	0.2	1.0	2.3	0.5
CA-3	0.8	0.7	0.2	1.0	0.9	0.3	1.3	1.2	0.4
CA-4	0.6	1.8	0.4	0.8	2.5	0.5	1.0	3.1	0.6
CA-5	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.1	0.0
CA-6	0.6	0.8	0.2	0.4	0.6	0.2	0.4	0.5	0.1
CA-7	0.6	1.6	0.4	0.7	1.6	0.4	0.8	2.0	0.5
CA-8	1.7	2.5	0.7	2.4	3.4	1.0	3.1	4.4	1.3
CA-9	2.3	4.3	1.1	2.2	4.1	1.0	2.3	4.3	1.1
CA-10	2.3	3.9	1.1	2.7	4.6	1.2	3.7	6.4	1.7
CA-11	3.8	5.6	1.6	4.7	6.9	2.0	4.5	6.6	1.9
CA-12	1.2	3.9	0.7	1.4	4.6	0.9	2.1	6.9	1.3
CA-13	3.1	5.7	1.5	3.4	6.3	1.6	5.3	9.9	2.6
CA-14	2.4	10.5	1.6	3.1	13.5	2.1	5.5	23.9	3.7
CA-15	4.2	8.0	2.1	4.1	7.8	2.0	4.2	8.1	2.1
CA-16	2.5	4.7	1.2	4.0	7.4	1.9	5.1	9.4	2.5

high enough and a multivariable analysis was recommended to increase the model statistical quality. Previous to this analysis, the effect of surface chemistry upon the Np, Phe and Py retention was studied. The sixteen samples

studied in this work cover a wide range of surface chemistry allowing knowing the influence of surface groups. However, hydrocarbons show low polarity and the active

sites in the sorbents should not have relevant influence in the PAH adsorption.

Results in Table 5 show that the ratios PAH/CO, PAH/CO_2 and PAH/O* differed from 1, corroborating that there was poor correlation between the three PAHs adsorbed and the site formed after CO or CO_2 desorption. There was also poor correlation to the total number of free sites (CO + 2CO_2). Therefore, although the samples showed great differences in their surface chemistry, Table 1, their behavior regarding the three studied PAH adsorption showed to be mainly porous texture dependent.

To improve the quality of the model, a multivariate analysis to the data obtained was performed. A principal component analysis was carried out to try to reduce the number of independent variables by generating new and uncorrelated variables, the principal components (PCs). The analysis was developed using SPSS software and the eight normalized variables were V_{N2}, V_{CO2}, n, L, CO, CO_2, V_{BJH} and O*. The correlation coefficients, see Table 6, between the normalized variables and the PCs were calculated as the product of the square root eigenvalues and scores. The chosen PCs number was a total of four, which explained more than 95% of the data variance. In Table 7 (supporting information) the eigenvalues and the proportion variance explained for each one of them are compiled.

To know the PCs chemical meanings, an equamax rotation to the generated autovector space was carried out. In this new space, PC1 was positively correlated to the total active sites, CO and CO_2 desorbed groups and the total number of free sites (CO + 2CO_2).

PC2 was strongly correlated to V_{O2} and V_{CO2}, indicating that the total volume microporosity and PC3 was positively correlated to L and negatively correlated to n. Therefore, PC3 showed the micropore distribution and, finally, PC4 was negatively correlated to the mesopore volume. From this analysis, it was possible to differentiate between the micropore distribution, PC3, and the micropores volume influence, PC2. However, the model did not allow differentiating between the influence of the different superficial oxygenated groups, acid and basic, and the V_{CO2} and V_{N2} for the three studied polyaromatic hydrocarbons.

Once the PCs were known, a multiple linear regression (PCR) was carried out using a stepwise procedure with SPSS software.

The t Student parameters associated with each variable coefficient were all higher than 2, indicating a significant relation between PCs and PAH adsorption capacities. It could be observed that the %explained variance was higher than the one obtained through the single variable analysis.

The next step consisted of the chemical interpretation related to the adsorption process.

The Np adsorption was independent of the free active sites according to its hydrophobic nature and to the V_{BJH} value, because at 150ºC the volatility of the molecule avoided the capillary condensation in the mesopores. On the other hand, the Np adsorption was positively correlated to the micropore volume and to the wide micropore distribution.

The Phe adsorption was dependent on the four PCs. As could be expected, Phe was positively correlated to the micropore volume, to the mesopore volume and to the wide micropore distribution with a high mean diameter. However, a negative correlation to the free active sites was observed. It means that the lower the free active sites number, the higher the micropore volume and therefore, the higher the amount of Phe adsorbed.

The Py adsorption showed the same dependence than Phe, but for Py the relative importance of each variable was different.

Results where the relative importance of each variable was calculated from the change produced in the r^2 value, % variance explained, when a new variable was introduced to the regression, are shown in Table 8. From this table, it appears that the micropore volume was the most important variable for the three PAH adsorptions. The micropore distribution also contributed to the Np, Phe and Py adsorption capacities. A wide distribution with a high mean

Table 6. Correlation Coefficients Between the Normalized Textural Parameters and the PCs.

Variable	Component			
	PC1	**PC2**	**PC3**	**PC4**
CO	0.951			
O	0.925			
CO_2	0.796			
V_{CO2}		0.989		
V_{N2}		0.890		
L			0.895	
n			-0.764	
V_{BJH}				-0.845

Table 7. Eigenvalues and Associated Variances of the PCs.

	PC1	**PC2**	**PC3**	**PC4**
Eigenvalue	2.532	1.885	1.762	1.443
% Variance	31.65	23.56	22.02	18.04
% Accumulated	31.65	51.21	77.24	95.27

Table 8: Relative Importance of Each Variable in PCR Analysis

	Relativa Importance %		
variable	**Np**	**Phe**	**Py**
PC1	0.0	1.8	2.9
PC2	90.0	74.3	66.8
PC3	10.0	17.2	15.7
PC4	0.0	6.5	14.7

micropore diameter favored these three PAHs adsorption avoiding diffusional problems. Moreover it was observed that the mesopore volume influenced the Phe and Py adsorption. The relative importance of this variable was higher for Py, according to its lower volatility. The Phe and Py adsorption was also correlated to free active sites but their relative importance was very low. The sign of the coefficient was negative and according to the hydrophobic nature of these molecules, the adsorption was not being produced on the free active sites. The lower the free active sites, the higher the micropore volume in the studied adsorbents.

As the influence of some variables, like V_{CO2} and V_{N2} or different free active sites, could not be evaluated separately from the PCR analysis, a multiple linear regression (MLR) of normalized variables was carried out in order to study the influence of each one.

The statistical quality of regressions, variance percentages explained from standard deviations and Student t parameters were similar to those introduced in the PCR analysis, but the chemical information obtained from the correlation was more direct.

The Np adsorption was positively correlated to the V_{CO2} and L although the explained variance percentage was still low. This could be due to the Np high volatility at 150ºC and its adsorption would be produced in pores of molecular dimensions in the range d_p=???? . Therefore the adsorption was carried out partially at the V_{N2} and partially at the V_{CO2} micropores. About the L value, the Np adsorption was favored by high values, which did not imply diffusional problems.

The Phe adsorption was positively correlated to the V_{N2} and negatively to the n value. The regression quality was good because the V_{N2} includes all micropore range where the adsorption was produced. This agreed with the Phe molecular diameter and its volatility, which allowed the cooperative process in the wider micropores $(d_p$=?????) and involved the adsorbate-adsorbate interactions. With respect to the n value, the appropriate carbon materials for the Phe adsorption were those with a wide micropore distribution and strongly activated carbons.

The Py adsorption was positively correlated to the V_{N2} and to the V_{BJH} and it was a consequence of the Py diameter and its low volatility. In addition to the micropore filling and the cooperative process in the wider micropores, the capillary condensation into the mesopores was also produced.

Table 9 shows the experimental results compared to the predictable values by the model. In most cases, there was a good concordance between them, except for CA-1, CA-2 (only for Np) and CA-5 samples. In the case of low microporosity samples, CA-1 and CA-2, the values obtained with the model were

Table 9: Comparison of the Predictive Ability of PCR and MLR for Three PAH

Sample	Observed values			Predicted values by PCR			Predicted values by MLR		
	Np	Phe	Py	**Np**	Phe	Py	**Np**	Phe	Py
CA-1	2	13	21	-4	-18	-4	-9	4	21
CA-2	2	8	42	-11	9	46	-7	1	49
CA-3	25	62	72	28	64	56	29	46	45
CA-4	21	64	91	17	95	128	22	88	109
CA-5	2	12	13	26	28	29	24	39	40
CA-6	36	74	61	40	68	66	35	74	83
CA-7	46	102	123	41	98	103	41	101	92
CA-8	65	199	199	77	215	217	75	227	252
CA-9	71	161	158	59	164	181	61	144	149
CA-10	67	189	260	63	194	223	65	180	204
CA-11	107	272	288	103	273	286	102	268	294
CA-12	54	234	231	65	210	232	63	224	230
CA-13	58	260	332	77	263	304	73	276	317
CA-14	63	285	330	78	293	356	86	276	337
CA-15	114	274	254	92	268	285	94	251	251
CA-16	109	332	384	91	307	350	86	333	383

lower than the expected ones. For the narrow microporosity sample, CA-5, the values were overestimated with the model. Anyway, CA-1, CA-2 and CA-5 samples did not show to be proper for these three PAH abatement from hot gas due to that their adsorption was close to the blank. The elimination of these samples from the model was assessed but the results obtained implied a decrease in the regression quality and, for this reason, the model obtained is not showed in this paper.
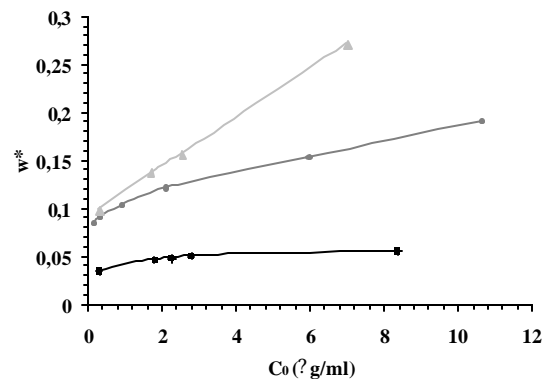

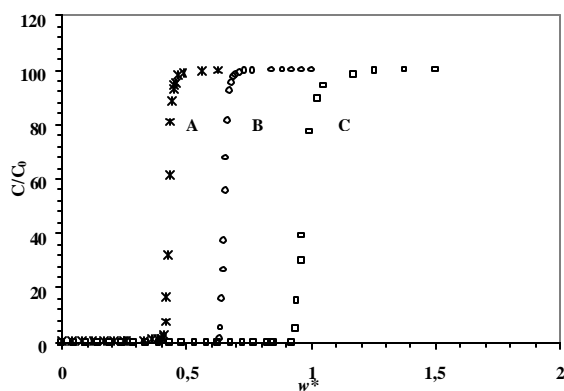**Figure 1.** Np, Phe and Py Adsorption Isotherms at 150 ºC

Figure 2. Breakthrough Curves for the Three Polyaromatic Compounds for the CA-3 Sample A) Np, B) Phe and C) Py.

Conclusions

In Np adsorption the 87% data variance was explained and the adsorption was positively correlated to V_{CO2} and the micropore mean diameter (L). In the Phe regression there was 98% variance explained and its adsorption was positively correlated to the V_{N2} and the micropore distribution, n. Finally, in the Py adsorption, the 96% data variance was explained and this adsorption was positively correlated to the V_{N2} and V_{BJH}.

These dependencies were according to the molecular parameters of these compounds, molecular diameter and volatility, because the higher the number of aromatic rings of the PAH, the more favored the adsorbate-adsorbate interactions. Besides, the higher the mean diameter micropores, the lower the diffusional problems showed by Np, Phe and Py.

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