Non-porous reference carbon for N_2 (77.4 K) and Ar (87.3 K) adsorption

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Abstract

A new non-porous carbon material from granular olive stones has been prepared to be used as a reference material for the characterization of the pore structure analysis of activated carbons. The high precision adsorption isotherms of nitrogen at 77.4 K and argon at 87.3 K on the newly developed sample have been measured, providing the standard data for a more accurate comparative analysis to characterize disordered porous carbons using comparative methods such as t- and α_S-methods.

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1. Introduction

Activated carbon constitutes one of the most important types of industrial carbon. The structure is associated with a disordered arrangement of defective graphitic layers in the form of twisted lamellae, thus leaving a distorted slit-shaped void network of pores and/or cavities in the range of micropores (lesss than 2.0 nm), mesopores (between 2 and 50 nm) and macropores (higher than 50 nm). The advanced sustainable technology has requested for a better porous carbon of which pore structure is well controlled and known. Therefore, we need an efficient and convenient pore characterization analysis for porous carbons. One of the most important methods for the characterization of the porous structure on porous carbons is vapour adsorption at cryogenic temperatures and, among the different probe molecules, N_2 is the most widely used. Once the adsorption isotherm has been obtained, N_2 adsorption data can be used to evaluate the surface area, pore volume and pore size distribution, after application of the corresponding analysis [1-3]. One of the most widely used analysis for determination of the micropore volume is the one proposed by Dubinin-Radushkevich [4]. Unfortunately, the application of the Dubinin-Radushkevich plot analysis to the nitrogen adsorption data gives rise to several types of deviations from the linearity, which makes sometimes the determination of the micropore volume difficult [5]. Other popular empirical methods for micropore volume determination are the *t*-plot and the α_s-plot. These two methods are based on the comparison of the adsorption isotherm for a given porous carbon with that of a standard non-porous solid (reference sample). These comparative methods allow evaluating, not only of the micropore volume, but also the surface area, the external surface area and information about mesoporosity [6-10]. In the micropore analysis, the α_s-plot method originally introduced by Sing et al. has been recommended for nanoporous carbons due to absence of the layering adsorption on the defective pore walls [7,8]. When using the

t-plot and α-plot for the textural analysis, it is mandatory to select a non-porous reference material with a similar structure and properties (chemical nature and BET´s C constant) to the test material. Another critical point concerns the availability of high-resolution adsorption values for the reference and the test material. In this sense, the presence of high-resolution values allows to extend the comparative analysis to the low α_s region where a markedly enhanced adsorption due to the overlapped molecule-wall interactions can be clearly observed. The α_s plot below $\alpha_s = 1$ gives essential information on adsorption process in micropores. Setoyama et al. described the presence of two different types of deviations below $\alpha_s = 1$, a first one called “filling swing” attributed to the enhanced surface-molecule interactions in narrow micropores ($w < 1.0$ nm) and a second upward deviation called “condensation swing” attributed to presence of larger micropores ($w > 1.0$ nm) [9].

A few standard isotherms can be found in the literature for graphitized and non-graphitized carbon black as a reference non-microporous carbon [9-13]. However, the structure and the chemical nature of carbon black differ considerably from that of the activated carbons under analysis. For instance, graphitized carbon black has a polycrystalline three-dimensional graphite structure in which the basal planes are oriented parallel to the surface of the carbon black particles, so that N_2 and Ar adsorption often gives stepped isotherms at around the second adsorbed monolayer [13,14].

On the contrary, activated carbon consists of nanoscale defective graphitic layers and the three-dimensional structure of activated carbon is highly disordered. For this reason, our group has suggested since 1987 the use of a reference carbon obtained from olive stones as a better choice for the comparative analysis of activated carbon [14]. The reference carbon was obtained from an activated carbon originated from olive stones

after the application of a high temperature treatment under an Ar atmosphere, thus avoiding the uncertainties associated with the nature of the reference in respect to the test carbon.

Unfortunately, the standard N_2 adsorption isotherm reported in 1987 is not enough for a high resolution comparative plot analysis due to the instrumental limitation at that time. In addition, there is a renovated demand for the use of Ar adsorption at 87.3 K for a more accurate characterization of activated carbon [3]. This is because the absence of a quadrupole moment in the Ar molecule together with the higher boiling temperature in respect to N_2 (87.3 K vs. 77.4 K); thus, characterization with Ar adsorption would be superior to that of N_2 adsorption on nanoporous carbons having small micropores and surface functional groups. Furthermore, measurements of Ar adsorption at 87.3 K has become more popular due to considerable progress in the measuring instruments. Although some reference data for Ar are available, they also correspond to non-porous carbon blacks [13].

Consequently, the aim of this article is to synthesize a new non-porous reference carbon following the old recipe described by our group in 1987, extending the analysis of the reference carbon to the low α_s-region by using high resolution adsorption isotherms. This article describes the detailed standard adsorption data of the non-porous carbon for N_2 at 77.4 K and Ar at 87.3 K.

2. Experimental Section

The char was prepared by carbonization of granular olive stones at 1123 K in an N_2 atmosphere for 2h. In a second step, the so obtained char was submitted to a CO_2 treatment at 1098 K in order to develop the microporosity. Afterwards, the CO_2-treated sample was heated to 2273 K in an Ar atmosphere for 2.5h in order to obtain a non-

porous carbon. The final reference material, LMA10, is obtained after crushing the carbon heat-treated at 2273 K to a particle size lower than 300 μm. High-resolution N_2 (77.4 K) and Ar (87.3 K) adsorption data where obtained in a home-made fully automated manometric equipment designed and constructed by the Advanced Materials Group (LMA), now commercialized as N_2Gsorb-6 [15]. Samples were outgassed at 523 K for 4h before the adsorption measurement.

3. Results and discussion

N_2 at 77.4 K and Ar at 87.3 K reduced isotherms (i.e., n/n_m –where n_m is the monolayer capacity from which the BET surface area is determined- against P/P_0) for the new reference carbon LMA10 are shown in Figures 1 and 2, respectively. The isotherms were carefully repeated three times, the differences in the amount adsorbed being below 1-2%. The amount adsorbed at the relative pressure of 0.4 ($v_{0.4}$) is equal to 3.26 cm^3 STP/g and 2.68 cm^3 STP/g, for N_2 and Ar, respectively. The monolayer capacity (n_m) is 9.15 x 10^{-5} mol/g and 7.37 x 10^{-5} mol/g, for N_2 and Ar, respectively. In both cases the absence of any step in the reduced isotherm at P/P_0 = 0.3 indicates that LMA10 does not have any graphitized domain.

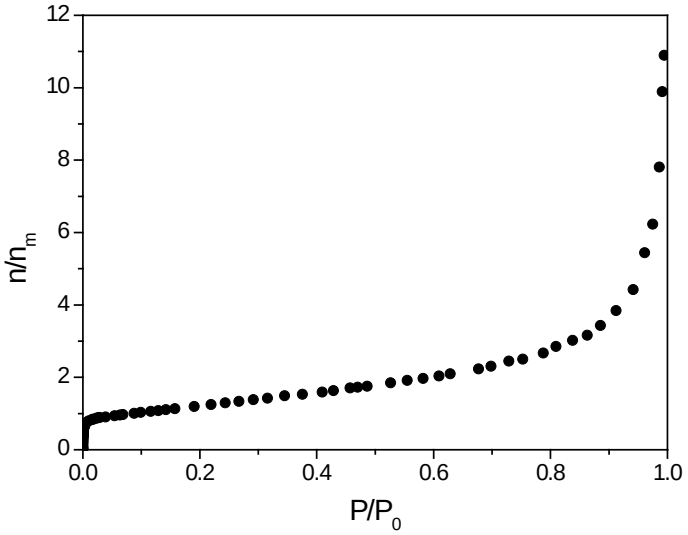


Figure 1. Reduced N_2 adsorption isotherm of the new non-porous reference carbon LMA10 at 77.4 K.

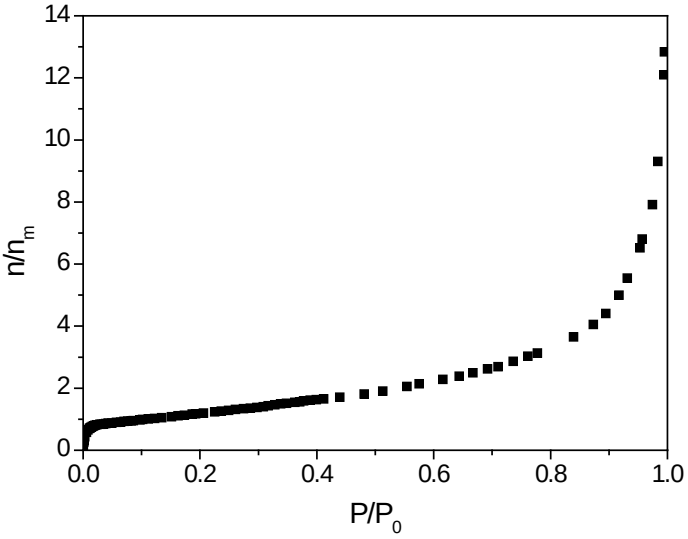


Figure 2. Reduced Ar adsorption isotherm of the new non-porous reference carbon LMA10 at 87.3 K.

Tables 1 and 2 list the standard high-resolution adsorption data in the reduced form to facilitate their application to the *t*-plot and α-plot construction.

Table 1: Standard data for the adsorption of N_2 at 77.4 K on reference carbon LMA10.

P/P_0	alpha	n/n_m	P/P_0	alpha	n/n_m
1.3033E-06	0.00918461	0.01462327	0.19042084	0.75121635	1.19604777
4.0205E-06	0.02096128	0.03337347	0.21945012	0.78642485	1.25210493
8.7354E-06	0.03088959	0.04918080	0.24375619	0.81627130	1.29962489
1.3376E-05	0.04315592	0.06871062	0.26720447	0.84201869	1.34061856
3.8161E-05	0.08388118	0.13355127	0.29165289	0.87356135	1.39083914
5.8282E-05	0.10761464	0.17133846	0.31593567	0.89679786	1.42783512
7.6355E-05	0.12360381	0.19679559	0.34534534	0.94018109	1.49690764
0.00010165	0.14096752	0.22444119	0.37557528	0.96720960	1.53994105
0.00013011	0.16046991	0.25549187	0.40940939	1.00539659	1.60074039
0.00016088	0.17405969	0.27712882	0.42880197	1.02873765	1.63790282
0.0002093	0.19835809	0.31581548	0.45698458	1.07454085	1.71082830
0.00025827	0.21267939	0.33861711	0.47001294	1.09123742	1.73741171
0.00032757	0.23636811	0.37633307	0.48621387	1.10684324	1.76225848
0.00038983	0.24710750	0.39343177	0.52639009	1.16558016	1.85577638
0.00041969	0.25706835	0.40929092	0.55476456	1.21061587	1.92747989
0.00047441	0.26538854	0.42253789	0.58205734	1.24369899	1.98015312
0.00058810	0.28489884	0.45360118	0.60923085	1.28549489	2.04669839
0.00089208	0.32133557	0.51161386	0.62834546	1.32128938	2.10368853
0.00127859	0.35011482	0.55743469	0.67717434	1.41015186	2.24517076
0.00245529	0.40139044	0.63907307	0.69837985	1.45541343	2.31723389
0.00379197	0.43514441	0.69281439	0.72877059	1.54353942	2.45754353
0.00677127	0.47635069	0.75842091	0.75276355	1.57786659	2.51219749
0.01014755	0.50179739	0.79893583	0.78791612	1.68520743	2.68309999
0.01809089	0.53403191	0.85025794	0.80927862	1.78755492	2.84605237
0.02638693	0.55652363	0.88606810	0.83778226	1.87792526	2.98993535
0.03883066	0.57188202	0.91052094	0.86283748	1.99696892	3.17947050
0.05441194	0.59140370	0.94160235	0.88532528	2.16804193	3.45184408
0.06865321	0.61128034	0.97324889	0.91238193	2.42490047	3.86080095
0.08783181	0.63560151	1.01197181	0.94129789	2.79074283	4.44327621
0.09916800	0.65145719	1.03721639	0.96123182	3.43282524	5.46556658
0.11622943	0.66601101	1.06038824	0.97483608	3.93157703	6.25965335
0.12911819	0.68113881	1.08447394	0.98625159	4.92716958	7.84478425
0.14211007	0.69575784	1.10774960	0.99112392	6.24052467	9.93584021
0.15766155	0.71354445	1.13606852	0.99458543	6.87846453	10.95153501

Table 2: Standard data for the adsorption of Ar at 87.3 K on reference carbon LMA10.

P/P_0	alpha	n/n_m	P/P_0	alpha	n/n_m
9.8238E-06	0.00165929	0.00269599	0.20616791	0.73646024	1.19658683
2.0399E-05	0.00712006	0.01156855	0.22537268	0.75983982	1.23457353
5.0985E-05	0.00859628	0.01396708	0.23665109	0.77239097	1.25496641
7.0384E-05	0.00884297	0.01436789	0.24916867	0.78865905	1.28139847
8.3197E-05	0.01350688	0.02194573	0.26102109	0.80839247	1.31346097
9.6036E-05	0.02008158	0.03262818	0.27456160	0.82230965	1.33607334
0.00016047	0.02387656	0.03879419	0.28643247	0.83126902	1.35063036
0.00026554	0.03687081	0.05990700	0.29748604	0.84834985	1.37838298
0.00034209	0.04637553	0.07535009	0.30835129	0.86344045	1.40290189
0.00058726	0.07750901	0.12593518	0.31706619	0.88269192	1.43418134
0.00123357	0.15798301	0.25668784	0.32832121	0.90067883	1.46340612
0.00160473	0.18868211	0.30656716	0.33833297	0.92131980	1.49694319
0.00308055	0.26731424	0.43432719	0.34821173	0.92793096	1.50768487
0.00574851	0.35417388	0.57545511	0.36266393	0.95113968	1.54539397
0.00831957	0.40258989	0.65412052	0.37061517	0.96034463	1.56034999
0.01070805	0.43049757	0.69946440	0.37755694	0.97839267	1.58967411
0.01214353	0.44284506	0.71952638	0.38869415	0.99172458	1.61133555
0.01370239	0.45677476	0.74215909	0.39921733	0.99997436	1.62473964
0.01570822	0.47133213	0.76581163	0.41173251	1.01878820	1.65530802
0.01802586	0.48080493	0.78120286	0.43943355	1.04866065	1.70384422
0.02064989	0.49224519	0.79979079	0.48122554	1.11289982	1.80821882
0.02359458	0.50155521	0.81491753	0.51310920	1.17033416	1.90153707
0.02891659	0.51070567	0.82978502	0.55437490	1.26271155	2.05163012
0.03122830	0.51251042	0.83271735	0.57507143	1.31611545	2.13839977
0.03493375	0.51740951	0.84067729	0.61567714	1.40280661	2.27925395
0.03908301	0.52791617	0.85774832	0.64390616	1.46718844	2.38386035
0.04290497	0.53529863	0.86974321	0.66739655	1.53651334	2.49649815
0.04941448	0.53931781	0.87627349	0.69219149	1.61324947	2.62117759
0.05720449	0.55387531	0.89992624	0.71022704	1.65720354	2.69259333
0.06438413	0.55908199	0.90838596	0.73636616	1.76173560	2.86243507
0.07039935	0.56963936	0.92553938	0.76148265	1.86209260	3.02549325
0.07635671	0.57633344	0.93641579	0.77778212	1.92495401	3.12762929
0.08245729	0.58277765	0.94688624	0.83945789	2.24411955	3.64620350
0.08618729	0.58616681	0.95239288	0.87334823	2.49297747	4.05054318
0.09723496	0.60166984	0.97758191	0.89448289	2.70842827	4.40060361
0.10213188	0.60760223	0.98722074	0.91735845	3.07514184	4.99643297
0.11182984	0.61840768	1.00477724	0.93146746	3.41458014	5.54794598
0.12266302	0.62952702	1.02284374	0.95317438	4.01491088	6.52335215
0.13452307	0.64437231	1.04696408	0.95706526	4.18627404	6.80177980

0.15120782	0.66257387	1.07653765	0.97466155	4.87102309	7.91434727
0.16266403	0.68129328	1.10695258	0.98350435	5.72501979	9.30190514
0.17332344	0.69274564	1.12556016	0.99393854	7.44402132	12.09490667
0.18687477	0.71535844	1.16230101	0.99493686	7.89925866	12.83456780
0.19276984	0.72234253	1.17364864			

As described above, our group synthesized in 1987 a reference material (carbon A) starting from an activated carbon and using a recipe very similar to the one described in this article. To validate the new synthesis, Figure 3 shows the comparison between the old adsorption isotherm on carbon A, obtained using conventional low-precision manometric equipments, and the new adsorption isotherm on carbon LMA10 using a newly developed high-resolution automated equipment. As it can be observed, both isotherms are coincident in the P/P_0 range of $5 \cdot 10^{-3}$ to 0.8, thus confirming the validity of the old reference carbon [14]. Deviations at high relative pressures must be attributed to the different precision of employed instruments. Additionally, Figure 3 shows the comparison between the reference carbon LMA10 and the reference carbon black 32B proposed by Setoyama et al. [9]. Once again, both samples are coincident over the low-medium relative pressure range up to high relative pressures where an upward deviation, due to the different nature and texture of the carbon black, can be observed. Additionally, a smooth step at $P/P_0 \sim 0.3$ can be envisaged on the reference carbon black 32B due to the formation of the second adsorbed monolayer on small graphite micro-domains, this deviation being absent in the reference LMA10 carbon. Interestingly, these deviations dissapear when comparing the N_2 adsorption isotherms for reference carbon LMA10 and the non-graphitized carbon black BP280, reported by Kruk et al. [12]. As it can be observed in Figure 4, both isotherms perfectly overlap over the whole relative pressure range, despite the different nature of the reference carbons.

Despite these similarities and in order to avoid uncertainty usage of LMA10 is highly recommended for the comparison plot when dealing with ordinary activated carbon.

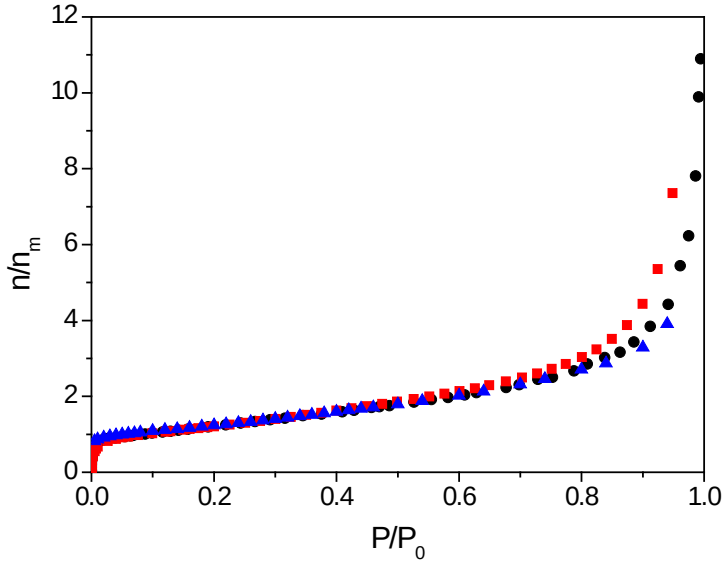
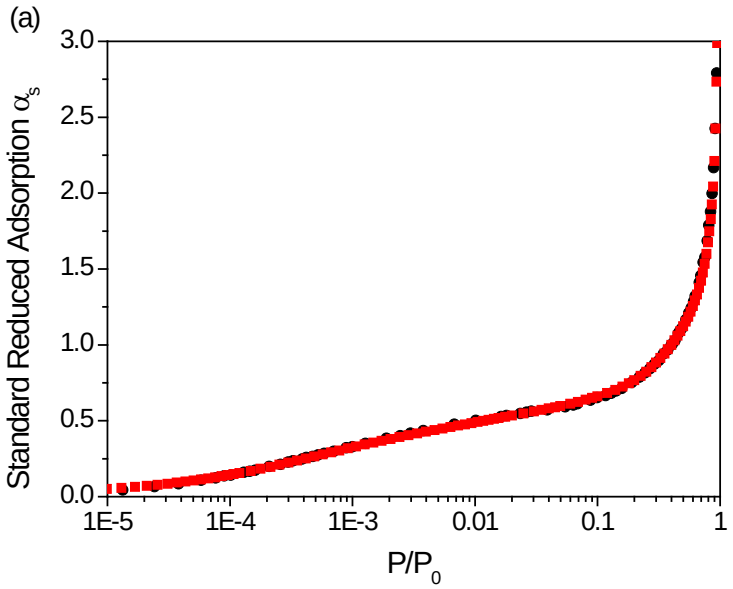


Figure 3: N_2 adsoption isotherm at 77.4 K for reference carbons: carbon A (▲), LMA10 (●) and 32B (■).



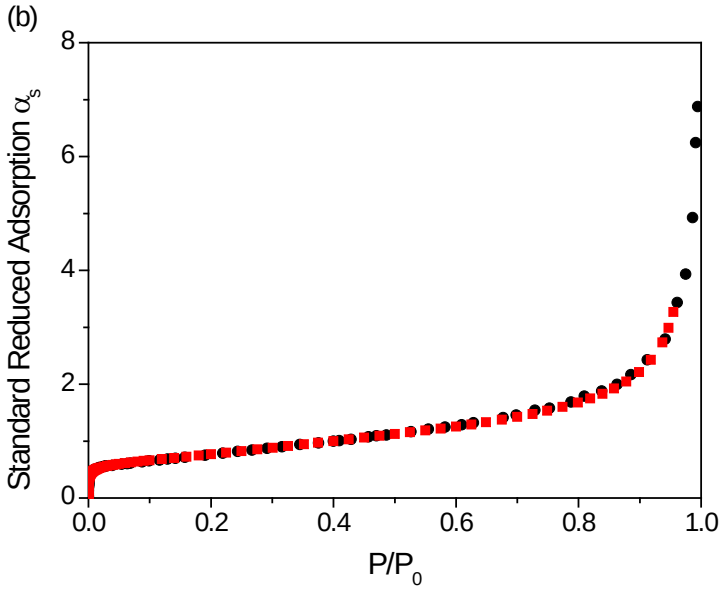


Figure 4: N_2 adsoption isotherm at 77.4 K for reference carbons: LMA10 (●) and BP280 (■) in (a) logarithmic and (b) linear scale.

A similar conclusion can be achieved after the comparison of the Ar adsorption data in the new reference carbon LMA10 and the reference carbon black 32B. As it can be observed in Figure 5, both reference samples are coincident over the whole relative pressure range from $P/P_0 \sim 10^{-6}$ to $P/P_0 \sim$ 0.8-0.9, deviations taking place at high relative pressures. The upward deviation together with the presence of a knee at relative pressure ~ 1 for carbon black 32B suggests the presence of some mesoporosity due to a partial aggregation, which are absent in the new reference carbon LMA10.

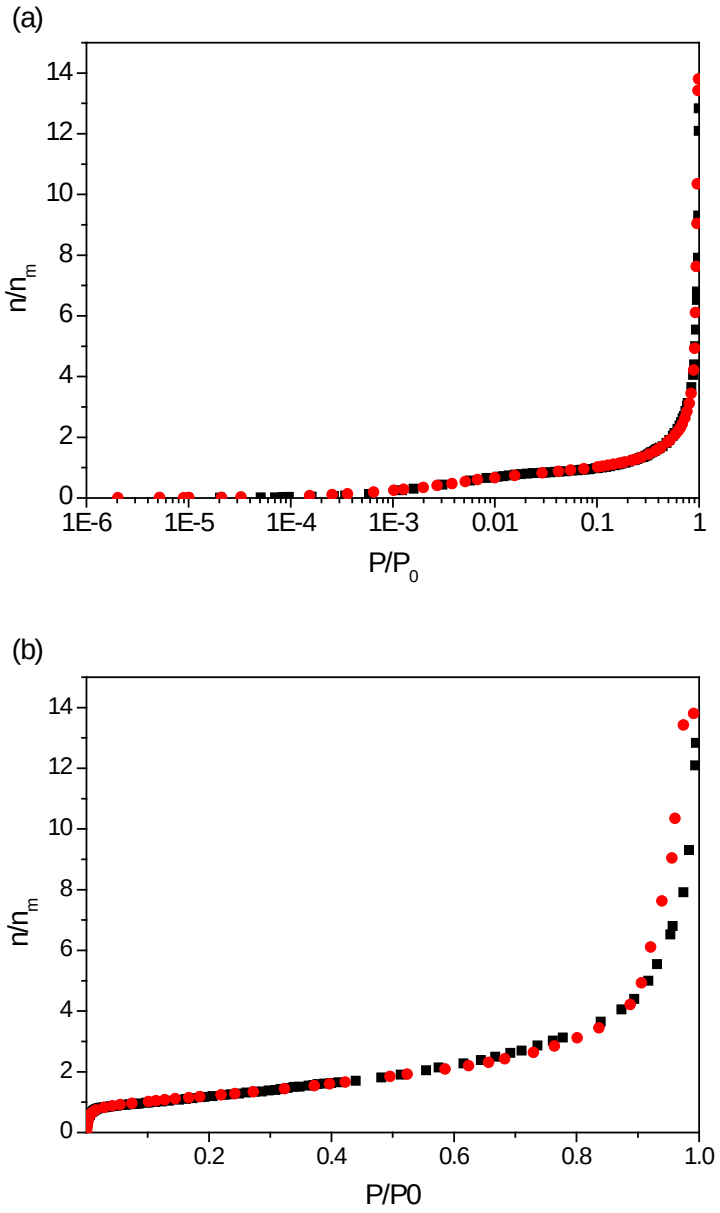
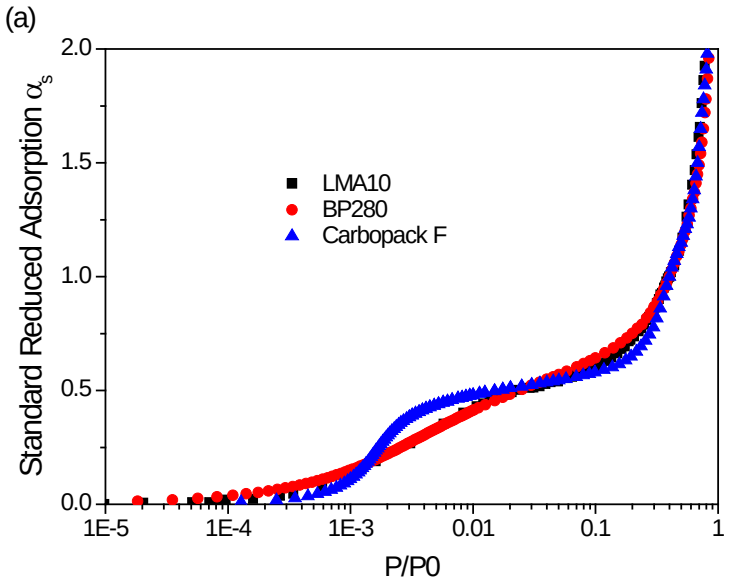


Figure 5: Ar adsorption isotherms at 87.3 K for the reference samples LMA10 (■) and 32B (●) in (a) logarithmic and (b) linear scale.

A more complex scenario takes place when comparing the Ar adsorption data in reference carbon LMA10 with the values reported by Gardner et al. in 2001 for graphitized and non-graphitized carbon blacks (see Figure 6) [13]. As expected, the Ar adsorption isotherm in graphitized carbon black exhibits important deviations already at low relative pressures (*ca.* 5 x 10^{-3}) attributed to the formation of the first adsorbed layer

due to the relatively high degree of graphite cristallinity in sample Carbopack F. On the contrary, the isotherms for samples LMA10 and non-graphitized carbon black BP280 are rather smooth due to the strong surface heterogeneity. However, a closer look to these two isotherms reveal that contrary to nitrogen, argon exhibits some small deviations both at low and high relative pressures, which must be attributed to the different nature of the carbon samples. Since the similarity in structure of the test sample with the non-porous reference sample is essential when using comparative plots, the fact that olive stones yield non-graphitizable carbon is very important for the use of LMA10 as reference carbon for the analysis of activated carbons.



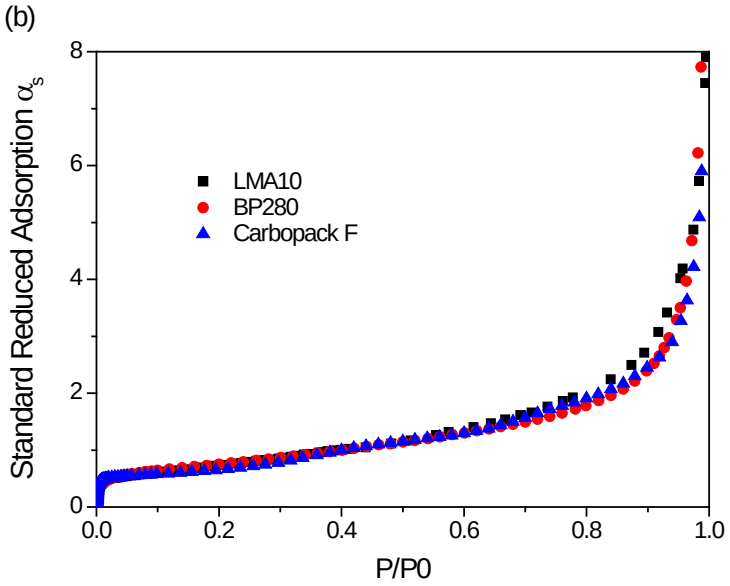


Figure 6: Ar adsorption isotherms at 87.3 K for the reference samples LMA10 (■), non-graphitized carbon black BP280 (●) and graphitized carbon black Carbopack F (▲), in (a) logarithmic and (b) linear scale.

4. Conclusiones

In summary, a new reference non-porous carbon has been synthesized from olive stones using the old recipe reported by Rodríguez-Reinoso et al. in 1987 [14]. The newly synthesized non-porous carbon LMA10 does not show any step coming from graphite micro-domain in both adsorption isotherms of N_2 and Ar. Then, LMA10 is an ideal reference carbon for porosity evaluation of highly disordered porous carbons with comparison plot analysis. LMA10 exhibits no anomaly even near $P/P_0 = 1$, guaranteeing the absence of the aggregation of carbon particles. Consequently, it is proposed as the new reference non-porous carbon for the analysis of disordered carbons, with special emphasis in activated carbon, using the comparative *t*-plot and α_s-plot analyses.

Acknowlegment

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