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REVALORIZATION OF MINERAL COAL, TO OBTAIN CARBONACEOUS MATERIALS WITH HIGH ADDED VALUE

This paper shows the possibility that the mineral coal existing in the mining basins of northern Spain have a high added value. This would facilitate its future use in different fields such as new materials, nanotechnology, energy use *in situ*, coal bed methane, enhanced coal bed methane and coalmine methane.

An analytical study of mineral coal samples is carried out. The samples come from two deposits located in coal basins of the Cantabrian Mountains. The duly prepared samples are subjected to an activation process. Within this transformation, different treatments are applied to different sub-samples. Some of the sub-samples suffer a previous demineralization by successive attacks with acids, followed by oxidation and pyrolysis. Finally, all of them are activated with CO₂ and H₂O_(steam).

The carbonaceous products resulting from each treatment are characterised. The results show that all the pre-treatments used were positive for the textural development of the materials. Likewise, proper management of the processes and of the different operating variables allows the procurement of carbonaceous materials with a “tailor-made” structural development of the coal type. This material receives the name “activated” and can be employed in specific processes.

Keywords: active carbon, activation, adsorption, pyrolysis, porosimetry

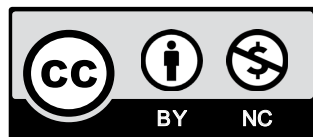
1. Introduction

The aim of this study is to analyse a new application for thermal coal. Among the analysed applications, its transformation into activated carbon was chosen. Several aspects defined this selection:

- Economic: Activated coal can reach a revalorization of almost 200 times the value of thermal coal.

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- Environmental: It can be used in the treatment and purification of fluids and in the adsorption of contaminants from industrial processes.
- Social: The progressive reduction of the use of mineral coal as an energy resource in Spain has produced in an industrial, socioeconomic and population decline of entire regions.

The study shows that the mineral coal from certain deposits is suitable as a raw material in the production of carbonaceous materials with high added value. This use could be compatible with traditional energy use. The extraction costs (38€/t) would be borne by the benefits resulting from the new obtained products. The sale price of thermal coal is currently quoted at 76€/t, while the activated carbon has a price that varies from 1000€/t to 1000000€/t, depending on its quality with a production cost around 100€/t (previous treatments 30€/t, activation process 60€/t, classification and packing 10€/t).

The generic active carbon presents disadvantages such as the irregular size of the pores and the unequal connection between them or the presence of imperfections. These problems come from the origin of the coal. In many occasions, it is derived from mixtures of “low-range mineral coals”, which do not stop being “wood old”, as is peat and, to a lesser degree, lignite. Biomass derived from agricultural by-products and materials derived from the processing of food are taken as a raw material (Benedetti et al., 2018).

However, due to the growing demand for active carbon it is experimented on raw materials from very different areas: waste oil industry (Chaparro et al., 1987), lignin from the paper industry (González-García, 2018), tanning (Rodríguez, 2014), and agricultural residues such as fruit peels, mainly coconut husk (Gratuito et al., 2008), etc.

The innovation of this proposal lies in the advantages of the starting materials: mineral coal with a medium-high range, specifically, “bituminous low in volatile”.

The raw material “is already pre-carbonized”. The material has a high starting porosity, which is a remarkable advantage as it saves on the activation process. This saving means a lower consumption of electricity and time. In addition, there is no need to manipulate and eliminate polluting substances used in the chemical activation of other raw materials.

Both the extraction of the material and its processing are done in the mining basins of northern Spain, which are currently in decline. Here, the know-how of mining still exists, and it would be a socioeconomic advantage to reopening and maintain the mine exploitations.

The implementation of the facilities for the processing of activated carbon would give rise to an industrial fabric which would require the contribution of skilled workers.

Consumption in Spain in 2016 amounted to 68805 tonnes. All the material was imported because of the nil domestic production. On the other hand, the universities and research institutes produce the activated carbon but only at an experimental level. So attempts at industrial production implies a total dependence on outside producers and a long delay in relation to other EU countries.

Although the necessity of producing active carbon for its common and classic applications is assured, the most promising and innovative future is aimed at obtaining “designer coals”. The investigations are directed, both to the search for new processes for its procurement, as for new applications such as: molecular sieves, storage of energy, capture and storage of CO₂, CH₄ and natural gas, super-capacitors and batteries of Li-S, biomaterials, etc.

2. Material

The raw material was collected in two deposits of upper Carboniferous-Pennsylvanian, located in the northern area of Spain: Dorada Layer and Aurora Layer.

The characterization of the two types of coal (Table 1) was carried out by means of an immediate analysis, elemental analysis, analysis of ashes, the determination of C, H₂ and N₂, the determination of S, the contents of Si, Al, Fe, Ca, Mg, Na, K and Ti, by X-ray fluorescence (AENOR, 1984; 1995a; 1995b, 1995c; 1995d; 1999; ASTM, 2013).

The results of the immediate analysis highlight the low ash content (Huggins, 2002). This is very important for manufacturing activated carbon, since in some of the stages there is a progressive increase in ash (Jankowska et al., 1991).

TABLE 1

Coal characterization from Dorada Layer and Aurora Layer

Analysis	Dorada Layer	Aurora Layer
Immediate (% weight)		
Moisture (sample)	1.12	1.10
Ash (db)	4.98	5.51
Volatile (db)	8.41	8.95
Volatile (pc)	8.85	9.47
Fixed Carbon (db)	86.17	85.02
Elemental (% weight, pc)		
Carbon	91.52	91.47
Hydrogen	2.57	3.05
Nitrogen	1.66	1.99
Total Sulphur	0.95	1.34
Oxygen (by difference)	3.30	2.15
Reflectance/maceral comp. (% volume, pc)		
Inertinite	3.60	1.80
Reflectance	1.77	1.72
Standard deviation	0.10	0.09

db: dry base; pc: pure coal

The range of the selected coals has been determined by the vitrinite reflectance value of $R_0 = 1.7\%$. This value, according to (ISO, 2005) implies that the two types of coal can be considered Bituminous A. This allows defining them as lbv (low bituminous in volatile), which corresponds to a medium-high-range coal, not very abundant in coalfields worldwide. This determination is in concordance with another study carried out with the same starting materials (Casado-Sulé, 2013).

In view of the preliminary results obtained, a physical activation process of the coal was applied, with CO₂ and H₂O_(steam) as activating agents. This choice was made for three reasons:

1. Quality of the obtained product. The physical activation allows obtaining activated carbons richer in micro-pores and with larger specific surfaces than those obtained by the chemical method (Kirk-Othmer, 2007).

2. **Ecology.** The elimination or reuse of these agents does not imply environmental problems, as occurs with the compounds: KOH, ZnCl₂, H₃PO₄ and NaOH, used for direct activation (Byamba-Ochira et al., 2016). The elimination of these last ones is expensive and involves environmental and handling risks (Benaddi et al., 1998).
3. **Economy.** H₂O_(steam) and CO₂ are the two most effective physical activating agents due to their low cost.

Although the most classic and economical process has been applied, this does not impede the subjugation of the original coal to more innovative processes, such as microwave and ultrasound treatments (Wenya et al., 2018; Yeng & Hameed, 2009).

3. Methodology

30 kg of coal was collected in the face of the exploitations. This coal was stored in hermetically sealed containers in the presence of Argon and in absence of light to avoid possible alterations. With this material, 30 samples were prepared, 23 from Dorada Layer and 7 from Aurora Layer. The selected material was divided in two different granulometric fractions: fine (0.125-0.425 mm) and granular (1-3 mm). These particle sizes are adapted to the two types of activated carbon used and commercialized, such as the Powdered Activated Carbon (PAC), with particle size less than 0.18 mm and the Granular Activated Carbon (GAC), whose size varies from 0.2 to 5 mm.

For the preparation of the samples, a reduction of the grain size of the coal was carried out and, subsequently, a division of the sample using partition dividers of different sizes, complying with (ASTM, 2017).

The general and standardized conditions (Serrano, 1994) of operation to which the samples were submitted are (Table 2):

- a. **Demineralization.** Attack with HCl (1:1), HF (49%) and HCl (37%), wash with distilled water, attack with acids, and finally, wash with drying at temperature 383.15 K.
- b. **Oxidation.** Exposure to the air in an oven, at a temperature of 543.15 K, for 5 days.
- c. **Pyrolysis.** Atmosphere of N₂, heating speed 60 K min⁻¹, final temperature 1123.15 K, "Annealing" of some sample (1 hour more at 1123.15 K), cooling.
- d. **Activation.** Taking into account the burn-off obtained (Dubinin et al., 1969), the two activating agents with different degrees of activation were applied:
 1. Activation with CO₂. Degrees of 50%, 60% and 70%. According to (Dubinin & Zaverina, 1949) and (Pis et al., 1998), when the degree of activation does not exceed 50%, a basically microporous activated carbon is obtained, and when it exceeds 75% a macro-porous activated carbon is achieved, while in the range between 50% and 75% the activated carbon contains all pore types (macro, meso and micro). A temperature of 1123.15 K was reached, with a flow of 50 cm³ min⁻¹. The final cooling was carried out in N₂ atmosphere.
 2. Activation with H₂O_(steam). A degree of 50%. The temperature reached is 343.15 K, with a flow of 28 cm³ min⁻¹. The final cooling is also in atmosphere N₂.

TABLE 2

Correspondence of references of samples and operating conditions

N	Reference	Sample type	Oxidation Temp. / time	Pyrolysis Temp. / time of annealed	Activation agent/grade
AURORA					
1	CA-G-N	Coal			
2	CA-G-S	Coal	543.15 K/5 days		
3	CA-G-S-R	Pyrolyzed	543.15 K/5 days	1123.15 K / +1 hour	
4	CA-G-S-R-AY5	Activated carbon	543.15 K/5 days	1123.15 K / +1 hour	CO ₂ / 50%
5	CA-G-S-R-AY6	Activated carbon	543.15 K/5 days	1123.15 K / +1 hour	CO ₂ / 63%
6	CA-G-S-R-AY7	Activated carbon	543.15 K/5 days	1123.15 K / +1 hour	CO ₂ / 74%
7	CA-G-S-R-AW5	Activated carbon	543.15 K/5 days	1123.15 K / +1 hour	H ₂ O / 50%
DORADA					
8	CD-G-N	Coal			
9	CD-G-S	Coal	543.15 K/5 days		
10	CD-G-N-R	Pyrolyzed	No	1123.15 K / +1 hour	
11	CD-G-S-P	Pyrolyzed	543.15 K/5 days	1123.15 K	
12	CD-G-S-R	Pyrolyzed	543.15 K/5 days	1123.15 K / +1 hour	
13	CD-G-N-R-AY5	Activated carbon	No	1123.15 K / +1 hour	CO ₂ / 50%
14	CD-G-S-P-AY5	Activated carbon	543.15 K/5 days	1123.15 K	CO ₂ / 50%
15	CD-G-S-R-AY5	Activated carbon	543.15 K/5 days	1123.15 K / +1 hour	CO ₂ / 50%
16	CD-G-S-R-AY6	Activated carbon	543.15 K/5 days	1123.15 K / +1 hour	CO ₂ / 60%
17	CD-G-S-R-AY7	Activated carbon	543.15 K/5 days	1123.15 K / +1 hour	CO ₂ / 70%
18	CD-G-S-R-AW5	Activated carbon	543.15 K/5 days	1123.15 K / +1 hour	H ₂ O / 50%
19	CD-F-N	Coal			
20	CD-F-S	Coal	543.15 K/5 days		
21	CD-F-S-R	Pyrolyzed	543.15 K/5 days	1123.15 K / +1 hour	
22	CD-F-S-R-AY5	Activated carbon	543.15 K/5 days	1123.15 K / +1 hour	CO ₂ / 50%
23	CD-F-S-R-AW5	Activated carbon	543.15 K/5 days	1123.15 K / +1 hour	H ₂ O / 50%
24	CD-X-N	Coal			
25	CD-X-S	Coal	543.15 K/5 days		
26	CD-X-N-R	Pyrolyzed	No	1123.15 K / +1 hour	
27	CD-X-S-R	Pyrolyzed	543.15 K/5 days	1123.15 K / +1 hour	
28	CD-X-N-R-AY5	Activated carbon	No	1123.15 K / +1 hour	CO ₂ / 50%
29	CD-X-S-R-AY5	Activated carbon	543.15 K/5 days	1123.15 K / +1 hour	CO ₂ / 50%
30	CD-X-S-R-AW5	Activated carbon	543.15 K/5 days	1123.15 K / +1 hour	H ₂ O / 50%

CD: coal from Dorada layer. CA: coal from Aurora layer. G: granular. F: fine. X: fine and demineralized. N: no oxidation. S: 5 days of oxidation. P: pyrolysis at final temperature. R: pyrolysis for more than 1 hour. A: Activated. Y: activation with CO₂. W: activation with H₂O. 5: degree of activation equal to 50%. 6: degree of activation equal to 60%. 7: degree of activation equal to 70%.

4. Results

After the treatment of the samples, an immediate analysis (Table 3) was conducted with the same equipment and standards that were used with the raw material and a textural characterization was calculated according to IUPAC (Rouquerol et al., 1994) (Table 4).

TABLE 3

Immediate analysis results of the samples

N	Moisture, (%)	Ash, (% bs)	Volatile, (% bs)
1	1.10	5.51	8.95
2	1.60	5.28	26.82
3	1.12	7.32	1.19
4	1.75	11.20	—
5	3.55	15.03	—
6	2.25	18.41	—
7	0.80	10.99	—
8	1.12	4.98	8.41
9	2.64	4.33	27.40
10	1.29	5.43	1.83
11	0.94	5.57	4.85
12	1.05	5.99	1.62
13	1.00	6.97	—
14	1.60	8.63	—
15	1.30	9.22	—
16	1.00	11.46	—
17	1.00	15.40	—
18	1.40	9.43	—
19	0.70	4.03	—
20	2.80	3.96	—
21	0.90	6.31	—
22	1.50	9.94	—
23	0.90	10.09	—
24	0.25	0.45	—
25	1.85	0.31	—
26	1.80	0.31	—
27	2.15	0.56	—
28	2.20	1.28	—
29	3.00	1.55	—
30	1.20	1.42	—

For the textural characterization, the parameters calculated were the real density (D_r), bulk density (D_b), total volume of pore (V_T), porosity (ϵ), size distribution of pore (V), specific surface area determined with CO_2 (Dubinin-Raduschkevich) ($S_{\text{CO}_2\text{-DR}}$), specific surface area determined with N_2 (BET) ($S_{\text{N}_2\text{-BET}}$) and pore size distribution ($V_{\text{micro}} \leq 2 \text{ nm}$, $2 \text{ nm} < V_{\text{meso}} > 50 \text{ nm}$, $V_{\text{macro}} \geq 50 \text{ nm}$).

TABLE 4

Textural characteristics of the final material

N	D_r (g/cm ³)	D_b (g/cm ³)	V_T (g/cm ³)	ϵ	S_{CO_2-DR} cp (m ² /g)	S_{CO_2-DR} (m ² /g)	S_{N_2-BET} cp (m ² /g)	S_{N_2-BET} (m ² /g)	V_{micro} (cm ³ /g)	V_{meso} (cm ³ /g)	V_{macro} (cm ³ /g)
1	1.142	—	—	—	—	—	—	—	—	—	—
2	1.581	—	—	—	—	—	—	—	—	—	—
3	1.875	1.50	0.13	0.20	—	—	—	—	—	—	—
4	2.127	1.04	0.49	0.51	697	619	777	690	0.276	0.010	0.158
5	2.198	0.96	0.59	0.56	747	635	962	817	0.329	0.014	0.197
6	2.254	0.86	0.72	0.62	848	692	1147	936	0.385	0.018	0.216
7	2.099	1.07	0.46	0.49	692	616	1008	897	0.364	0.022	0.105
8	1.423	—	—	—	—	—	—	—	—	—	—
9	1.601	—	—	—	—	—	—	—	—	—	—
10	1.851	—	—	—	—	—	—	—	—	—	—
11	1.686	—	—	—	—	—	—	—	—	—	—
12	1.889	1.49	0.14	0.21	—	—	—	—	—	—	—
13	2.083	1.22	0.34	0.41	570	530	587	546	0.221	0.008	0.091
14	2.145	1.06	0.48	0.51	719	657	804	735	0.296	0.009	0.046
15	2.156	1.03	0.51	0.52	750	681	920	835	0.333	0.015	0.160
16	2.233	0.95	0.60	0.57	785	695	1031	913	0.369	0.014	0.193
17	2.310	0.86	0.73	0.63	772	653	1286	1088	0.447	0.026	0.259
18	2.092	1.06	0.47	0.49	720	652	1052	953	0.378	0.034	0.089
19	1.443	—	—	—	—	—	—	—	—	—	—
20	1.627	—	—	—	—	—	—	—	—	—	—
21	1.931	—	—	—	—	—	—	—	—	—	—
22	2.164	1.11	0.44	0.49	786	708	919	828	0.330	0.012	0.093
23	2.115	1.04	0.49	0.51	723	650	1117	1004	0.398	0.040	0.097
24	1.440	—	—	—	—	—	—	—	—	—	—
25	1.582	—	—	—	—	—	—	—	—	—	—
26	1.832	—	—	—	—	—	—	—	—	—	—
27	1.885	—	—	—	—	—	—	—	—	—	—
28	2.155	0.99	0.55	0.54	856	845	1224	1208	0.485	0.017	0.069
29	2.171	0.91	0.64	0.58	887	873	1307	1287	0.512	0.025	0.072
30	2.056	1.01	0.50	0.51	756	745	1130	1114	0.438	0.046	0.075

cp: Results expressed on dry and ash-free sample

In general, the progressive increase in the real density, as well as a decrease in the bulk density, stand out. This effect becomes evident, both with the application of the different treatments and with the increase of each of them, according to the following sequence:

DEMINERALIZATION → OXIDATION → PIROLYSIS →
→ ANNEALED → ACTIVATION

The most significant increase occurs in the activation stage, as a consequence of the significant increase in the total volume of pores due to the gasification, also as CO₂ as H₂O_(steam) (Bansal & Goyal, 2005).

4. Discussion

Those samples from Dorada Layer and Aurora Layer subjected to the same treatments (samples 4, 5, 6, 7, 15, 16, 17 and 18) were compared.

From this analysis, it is possible to say that the material from Dorada Layer presents superior results in total pore volume, porosity, specific surface and pore size distribution.

When the experimental data are plotted, by isotherms of N_2 adsorption, the results are called Langmuir isotherms (ISO, 2016). This type of isotherm is characteristic of microporous materials and therefore of processes in which an important filling of the microporous takes place. Once the microporous are filled with the adsorbate, the amount adsorbed is constant. It is observed that the adsorption process takes place mainly with low values of the relative pressure P/P_0 (Fig. 1) (Sing, 1982).

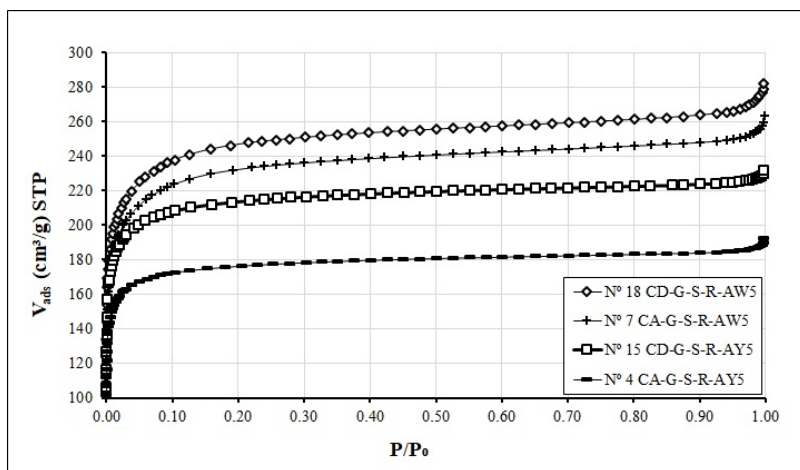


Fig. 1. N_2 adsorption isotherms (77 K) of Dorada and Aurora Layer. Activation CO_2 (50%) and $H_2O_{(steam)}$ (50%)

The adsorption isotherms show that the two types of precursor coal, Dorada Layer and Aurora Layer, are appropriate for the intended purpose. In both cases, greater adsorption was recorded in the samples subjected to activation with $H_2O_{(steam)}$ than in those subjected to activation with CO_2 . This effect is more noticeable in the samples from Dorada Layer.

For this reason the coal from Dorada Layer was considered more interesting and, thus, it was selected as the basis of the main study, in which the influence of different operating variables on this coal would be analysed.

4.1. Effect of previous demineralization

When comparing the Langmuir Isotherms of samples 22 and 29 (the latter demineralized) it is clear the considerable positive effect produced by the previous demineralization treatment

of the mineral starting coals, in their capacity of adsorption (Fig. 2). These exceed in quality all materials not subjected to this treatment, as shown in sample 29 that reaches a value of $V_{\text{ads}} = 350 \text{ cm}^3/\text{g}$, when P/P_0 tends to 1.

With respect the distribution of the pore size, there is a large increase in micro-porosity, less in meso-porosity and a moderate decrease in macro-porosity, due to the “fine” granulometry.

With the previous demineralization, very high specific surface values have been achieved, even with moderate degrees of activation (50%), both with CO_2 and with $\text{H}_2\text{O}_{(\text{steam})}$. The best result corresponds to sample 29, with a $S_{\text{N}_2\text{-BET}}$ of $1307 \text{ m}^2/\text{g}$ and a $S_{\text{CO}_2\text{-DR}}$ of $887 \text{ m}^2/\text{g}$, in addition to an ash content of 1.55%.

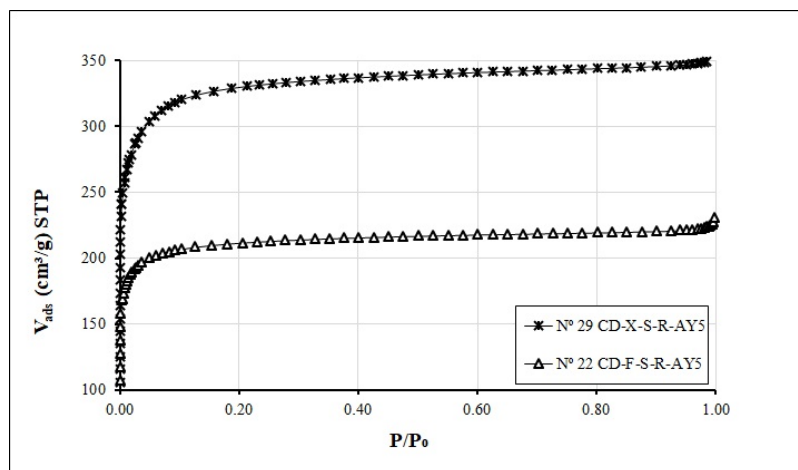


Fig. 2. N_2 adsorption isotherms (77 K) from Dorada Layer. Activation CO_2 (50%).
Effect of previous demineralization

4.2. Effect of previous oxidation

The pre-oxidation produces important changes in the chemical composition, plastic properties and pore structure of the precursor materials (Pis et al., 1998b). There is a very significant increase in the content of volatile materials, because of the increase in the content of chemisorbed oxygen in the shape of surface groups of carbonyl or carboxyl type. This effect is noticed in the carbonized, in which a high content of volatile materials is still observed in the pyrolyzed samples without annealing time. Likewise, the oxidation has produced a densification of the material, with a significant increase in its real density by more than 11% when comparing samples 13 and 15 (Fig. 3). From the figure, a significant increase in intruded volume is observed. In both samples, the increase occurs in the large-sized macro-pore area (2000-9000 nm).

The comparison of the N_2 (77 K) adsorption isotherms corresponding to the samples 13 and 15 shows a remarkable improvement of the textural properties because of the previous oxidative treatment. The most significant increase occurs in the $S_{\text{N}_2\text{-BET}}$ approaching 35% between the un-oxidized sample and previously oxidized sample (Fig. 4).

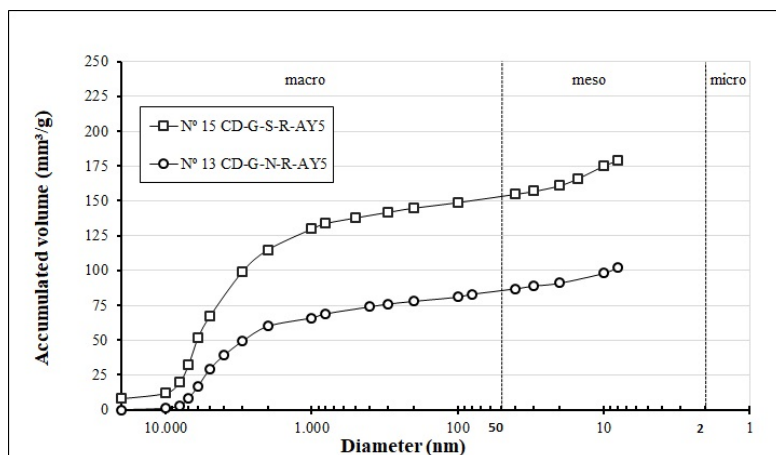


Fig. 3. Porosimetry of Hg of Dorada Layer. Effect of previous oxidation

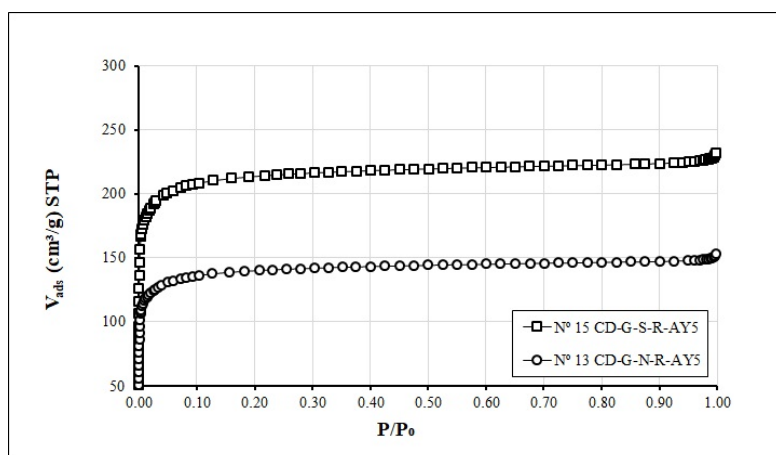


Fig. 4. Adsorption isotherms N₂ (77 K) of Dorada Layer. Effect of previous oxidation

4.3. Effect of pyrolysis stage

Pyrolysis is a transcendental step in obtaining activated carbon. In it, a deep structural reorganization in carbonaceous and a strong evolution of volatile materials are produced. This change is the basis of the creation of a porous structure developed in the subsequent gasification-activation stage.

Different studies (Acevedo et al., 2013) have demonstrated the importance of some operating variables such as heating speed, particle size, final temperature and annealing time.

The final temperature set in the present study was 1123.15 K, in order to coincide with the activation temperature. The heating rate was set at 333.15 K/min, because it is one of the most commonly used in this type of experiment.

The time of annealing is one of the variables that produces a significant influence on the properties of the obtained materials. This is because, during this period, at the maximum treatment temperature, an intense de-volatilization of the material takes place. Thus, a fine final structure is generated. This structure develops along the subsequent activation stage. Once the pyrolysis ends, the time of annealing begins, which is one hour at the final temperature of the pyrolysis (1123.15 K). To determine the effect of annealing, the sample 15 subjected to pyrolysis was compared to the sample 14 not subjected to this treatment. The analysis of the adsorption isotherms (Fig. 5) and the porosimetry of Hg (Fig. 6) show the beneficial effect of annealing for the textural development of the activated materials. The most notable effect was a significant increase in the volume of macro-pores. However, the effect is not as pronounced as that achieved with oxidation pre-treatment.

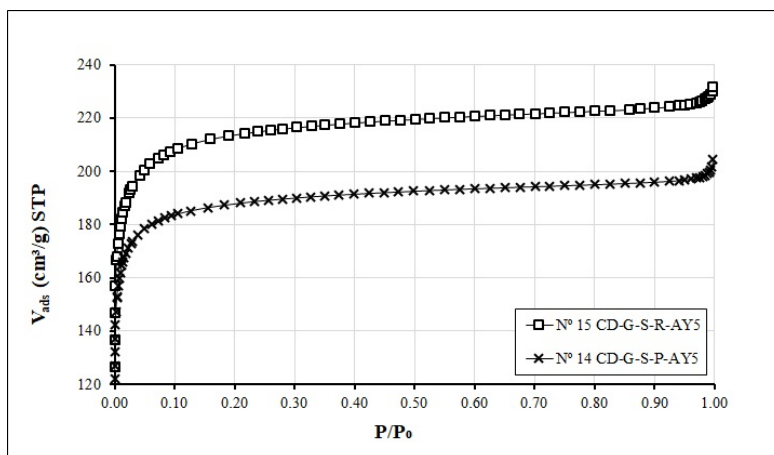


Fig. 5. Adsorption isotherms N₂ (77 K) of Dorada Layer. Effect of “annealing” post-pyrolysis

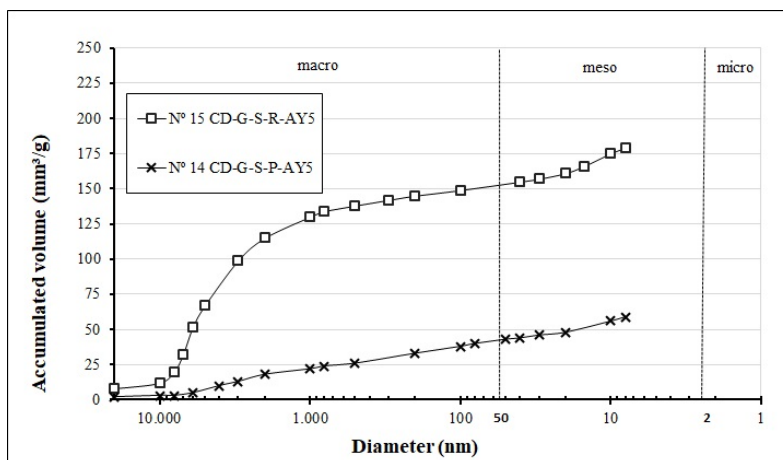


Fig. 6. Porosimetry of Hg of Dorada Layer. Effect of annealing post-pyrolysis

4.4. Effect of Activation

The most used gasifier or activating agents are CO_2 and $\text{H}_2\text{O}_{(\text{steam})}$. The first one is the most used in small-scale studies due to an easier control of gasification conditions. The second one presents a superior industrial interest due to its lower cost of production, non-polluting nature and easy disposal or reuse. The optimal activation conditions were determined by studying and analysing the effect of the different previous treatments.

4.4.1. Influence of the activation degree

Three degrees of activation were applied: 50%, 60% and 70%, with CO_2 as the activating agent because of its superior operation. As the activation degree was increased, there was a substantial improvement in the textural characteristics of the obtained materials and a significant increase in the adsorption capacity of the materials. Figure 7 shows the porograms of the granular coal samples from Dorada Layer (samples 15, 16 and 17) subjected to the three degrees of activation. Sample 12 corresponding to the pyrolyzed material without activating is also included for comparative purposes.

It is possible to say that activation (gasification) to higher degrees fundamentally originates a burning of the carbonaceous material of the pores, producing both an increase in their size, and an opening of some areas previously not accessible due to their small size.

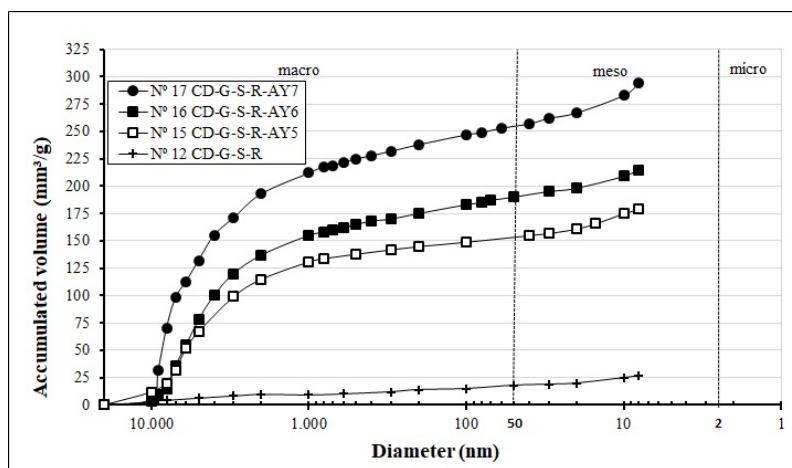


Fig. 7. Porosimetry of Hg of Dorada Layer. Effect of activation degree

From a practical point of view, it is necessary to take into account the following two considerations on the effect of the degree of activation:

1. The net field of the obtained material is significantly reduced by increasing the degree of activation, since the gasification stage causes a substantial disappearance of the carbonaceous matter because of its "burn-off".

2. Because of this process of progressive burning, the mineral substance enriches the material, producing a significant increase in ash content. This effect is clearly noticed in the variation from 11.20% in sample 4 activated at 50%, to the value of 18.41% in sample 6 activated at 70%.

4.4.2. Type of activating agent

Two types of activating agent have been used: CO_2 and $\text{H}_2\text{O}_{(\text{steam})}$. The N_2 adsorption isotherms (77 K) from different samples (Fig. 8) show that the use of $\text{H}_2\text{O}_{(\text{steam})}$ allows a superior textural development to be reached with the exception of those samples from fine demineralized coal (samples 29 and 30).

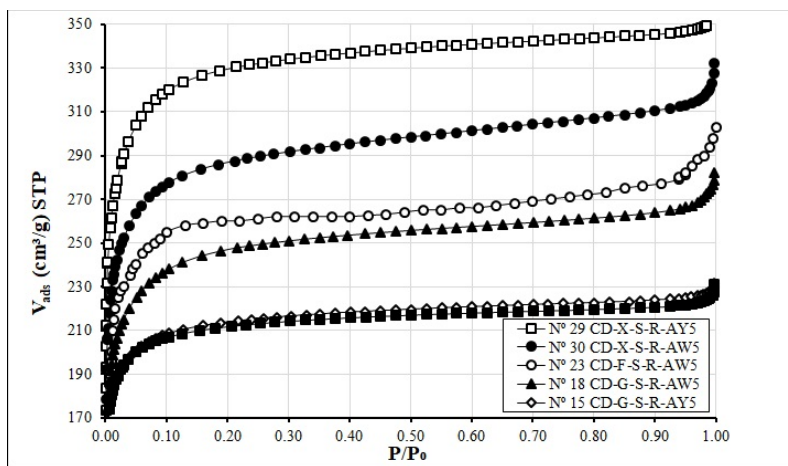


Fig. 8. Adsorption isotherms N_2 (77 K) of Dorada Layer: granular, fine and demineralized fine. Effect of activating agent

5. Conclusions

After studying, processing and analysing the obtained results in the present work, it is possible to say:

1. All the treatments, prior to activation, were positive for the subsequent textural development of the starting materials.
2. The decreasing quantitative order of influence of the application of the treatments is the following: demineralization, oxidation, post-pyrolysis annealing. The sequential and joint application of the treatments prior to the activation, allowed the materials with the best structural properties to be obtained. In this regard, the maximum surface development corresponded to the demineralized, oxidized and pyrolyzed sample with one hour of annealing.
3. The previous treatments of demineralization and oxidation, and the subsequent use of CO_2 as an activating agent allows the maximum textural development to be reached.

However, if there is no previous demineralization, the use of $\text{H}_2\text{O}_{(\text{steam})}$ as an activating agent allows materials with a better textural development to be obtained.

4. The most significant increase occurs in the case of the BET surface, approaching 35% between the un-oxidized sample and the previously oxidized.
5. Activation with $\text{H}_2\text{O}_{(\text{steam})}$ favours the development of meso-porosity, achieving maximum development in the demineralized sample. The activation of fine-sized samples, in general, develops a lower macro-porosity.
6. The study has achieved a precise knowledge of the obtained effects, both with previous treatments activation as the management of different variables of the process. Adapting the conclusions to the requirements of specific applications, it is possible to obtain carbonaceous materials with characteristics and custom structural development.
7. It is verified that the sub-bituminous mineral coal coming from Dorada Layer, can be used as raw material for obtaining activated carbons of high specifications and quality, provided that the treatments and operating variables tested in the present work are used properly. The use of the mineral coal proposed as raw material for the production of carbonaceous materials with high added value, in this case *activated carbon*, is justified. With the chosen mineral coals, it is possible to obtain products that face the main disadvantages of generic active carbon

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