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ACTIVATED CARBONS OBTAINED BY CHEMICAL ACTIVATION OF SPENT COFFEE BREW (BIOMASS)

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Abstract

The study reports on the preparation of *activated carbons based on biomass (spent coffee brew) and on the characterization of their porous texture.*

The developed laboratory technology appropriate for the purpose included (1) extraction of coffee grounds biomass to remove coffee oil residue; (2) carbonization of extracted biomass – individual or in mixture with 10, 20 and 30 mass % Bulgarian lignite coal and (3) chemical activation by potassium hydroxide.

The results obtained show the activated carbons prepared by the activation procedure used to have very high specific surface area (from 1600 to 2200 $m^2 g^{-1}$), with high microporous volume (0.600 – 0.800 $cm^3 g^{-1}$) and with homogeneous mesoporous size distibution (max. ~ 2 nm).

Key words: *spent coffee brew, activated carbon, extraction, chemical activation*

1. INTRODUCTION

Global energy use is approximately 140 000 TWh per year. Interestingly, biomass production amounts to approximately 270 000 TWh per year, or roughly twice as much, whereas the official figure of biomass use for energy applications is 10-13% of the global energy use. Hence, biomass is not a marginal energy resource but more than capable of meeting all our energy and food needs, provided it is used efficiently. The use of food in generating energy has been extensively debated, but there is actually no need for it given the comprehensive resources available from agriculture and forestry waste.

One way of using energy efficiently is to use waste biomass in biorefineries, where production of fibers and products from fibers is combined with production of most chemicals we need in our daily life. Such products include clothes, soap, perfume, medicines etc. Conventional pulp and paper applications, bio-fuel for vehicles and even fuel for aviation as well as heat and power production are covered (Dahlquist et al., 2013). Biomass can be converted into energy sources via pyrolysis or fermentation. Another way of organic/biomass wastes reuse is converting them into activated carbon (AC).

Due to their large specific surface area and high volume of AC micropores are widely used in separation processes where strong dispersive forces are responsible for the retention of species on their surface. It is well known that surface groups and their location in the pore network determine the application of certain carbons for specific separations. In most cases an AC surface is modified by

various techniques, such as impregnation, grafting, oxidation, or ammoxidation in order to enhance its reactivity. The processes mentioned increase significantly the cost of adsorbents (Kante et al., 2012).

Chemical activation is widely employed to prepare AC using mainly the activating reagents $ZnCl_2$ (Caturla et al., 1991)] or H_3PO_4 (Baquero et al., 2003). Oliveira and co-workers (2009) used ferric chloride as a new activating agent, to obtain AC from agro-industrial waste (coffee husks). Activated carbons were prepared from spent ground coffee. Zinc chloride was used as an activation agent. The obtained materials were used as a medium for separation of hydrogen sulfide from air at ambient conditions. It is used as an additive to prepare activated carbon cloths by physical activation, later on. The method was widely used to obtain porous carbons from coals/coal tar pitches. It has also been used in the chemical activation of precursors such as rayon and its pyrolysis effect onto lignocellulosic matter has been studied (Oliveira et al., 2009). However, there are no literature on using KOH as an activating agent to prepare AC from extracted biomass (spent coffee brew– neat or in a mixture with lignite coal).

An appropriate three stage laboratory technology was developed. It included (1) extraction of coffee grounds biomass to remove coffee oil residue; (2) carbonization of extracted biomass – individual or in mixture with 10, 20 and 30 mass % Bulgarian lignite coal and (3) chemical activation by potassium hydroxide.

2. EXPERIMENTAL

2.1. Materials

The carbon precursor was a spent coffee brew. The coffee ground was dried in an oven at 110 °C for 6 h. The quantitative analysis of oil or crude fat is based on separating the lipids from the sample matrix by extraction with hexane. About 60 g of the dried sample was weighed in a thimble in the Soxhlet extractor and fitted to a flask. Coffee oil was extracted with 250 ml solvent under reflux for time spans minimum of 8 h. Time was recorded when the first droplet of the extraction solvent recycled back into the thimble. The maximum extraction time for each solvent was the time when the reflux became clear. After the extraction had been accomplished, the solvent was distilled under moderate vacuum. The solvent was then recovered in order to be used in the next batch of extraction.

Extracted waste coffee brew, individual or in mixture with 10, 20 and 30 mass % Bulgarian lignite coal were carbonized at 793 ± 5 K.

Table 1. presents the physical properties of the spent coffee brew and lignite coal (Takahata et al, 2009; Tonchev, 1973).

Table 1. The physical properties of the spent coffee brew (SCB) and Bulgarian lignite coal

Sample	Wet, %	Ash,%	Volatile matter, %	Sulphur, %
SCB	6.41	0.10	76.80	-
Lignite coal	7.63	32.4	61.50	2.0

The elemental analysis of the initial samples (Takahata et al, 2009; Tonchev, 1973) is shown in Table 2.

Table 2. Elemental analysis of the spent coffee brew and Bulgarian lignite coal
(Takahata et al, 2009; Tonchev, 1973)

Sample	Content of carbon, C %	Content of oxygen O, mass. %	Content of hydrogen H, mass. %	Content of nitrogen N, mass. %
SCB	57.3	28.4	7.1	4.7
Lignite coal	67.4	25.8	5.0	1.8

The precursors were mixed with granular KOH at a 1:1.2 ratio. Before the activation the mixtures were ground to the particle size smaller than 600 mkm. The obtained materials were activated in a furnace under pressure of ~ 6.0 – 6.5 Torr at the temperatures 973 K and 1073 K, for 2 h.

The samples were washed with distilled water, after that with 10 % solution of hydrochloric acid (HCl) in order to remove inorganic mater. Then the products were washed with distilled water until reaching neutral pH. The patterns were activated for the second time in a furnace for 1 h under the same pressure at 873 K.

The carbons obtained are referred to as PACTRm, P - according to the condition: with prior activation; T – temperature, R - ratio of the activating agent to the precursor; m – mass % of the lignite coal.

2.2. Methods

The surface and porous texture of the samples was characterized by adsorption of nitrogen (77.4 K) using a conventional volumetric apparatus. The nitrogen adsorption-desorption isotherms were used to determine the following parameters: surface area, A_{BET} (Brunauer–Emmet–Teller method) $p/p_o = 0.05 \div 0.35$; micropore volume, V_{MI}; total pore volume, $p/p_o = 0.95$, V_t; mesopore volume V_{mes} (determined by subtracting the total micropore volume from the total pore volume). The mesopore size distributions were calculated implementing Pierse method (using the adsorption branch of the isotherms); the micropore volume V_{MI} and the micropore size distributions parameter x_0 (the half width of the curve maximum), according to the Simplified equation; the mean pore radius (as the ratio of the double total volume and A_{BET}, assuming a cylindrical pore model).

The chemical composition (C, N, and O) of carbonized ground coffee and KOH activated samples was determined by elemental analysis using an ESKALAB Mk II X-ray photoelectron spectrometer.

The specific surface area of the samples semicoke was determined using the “Gurvich method” (Klichko-Gurvich, 1961).

3. RESULTS AND DISCUSSION

In the first item are introduced the results of the synthesis condition and characterization of the resultant materials, with the inherent discussion.

To content of carbon, nitrogen and oxygen on the surface of the materials was estimated by elemental analysis. The data obtained are shown in Table 3.

Table 3. Elemental analysis for the carbonizated sample from coffee brew and lignite coal (results in % in mass; SCB and SCB+m, m = 10, 20 or 30 %)

Sample	Content of C, mass. %	Elemental analysis on the surface of the sample, %			
		C	N	O	$H^{calcul.}$
PSC 0-520	85.0	83.0	5.0	8.0	4.0
PSC 10-520	89.0	85.0	4.0	7.0	4.0
PSC 20-520	88.0	84.0	3.0	8.0	5.0
PSC 30-520	89.0	88.0	3.0	6.0	3.0

The prepared samples exibit closer levels of carbon content. The presence of lower contents of carbon on the surface could be a consequence of its containing higher hydrogen and nitrogen amounts.

The specific surface area values of the samples (carbonizated at 873 K) are presented in Table 4.

Table 4. Specific surface area of the samples determined by one point method apparatus.

Sample	Specific surface area, m^2/g
PSC 0-520	15.0
PSC 10-520	17.0
PSC 20-520	20.0
PSC 30-520	19.0

As seen, the presence of lignite coal does not affect the specific surface area. Specific surface areas values of the smples are close within the limits of method accuracy.

The AC prepared by the described procedure was subjected to elemental analysis. The results are shown in Table 5.

Table 5. Elemental analysis of the AC surface

Sample	Content of C, mass. %	Surface compozition, %			
		C	N	O	$H^{calcul.}$
PCAC700120	91.7	92.2	0.81	5.54	1.45
PCAC800120	91.9	92.1	0.76	5.75	1.39
PCAC8001220	92.5	92.2	0.73	5.37	1.40

The prepared samples (T=700 and 800 K) comprise the higher amounts of carbon (about 92 mass. %). The contents of oxygen and nitrogen on the external surface of the AC samples averages about 5 % for the oxygen and obout 0.77 % for the nitrogen. In this aspect our active carbons (incl. PCAC8001220) do differ from the conventionally used active carbon based on biomass waste.

Low temperature adsorption/desorption N_2 isotherms are used for the calculation of the specific surface area and the porosity of the samples (Fig. 1). The main textural parameters of AC prepared from coffee brew are given in Table 6.

Table 6. The main textural parameters of activated carbons under investigation

Sample	A_{BET} ($m^2.g^{-1}$)	V_t ($cm^3.g^{-1}$)	V_{MI} ($cm^3.g^{-1}$)	V_{MES} ($cm^3.g^{-1}$)	X_o (nm)	R_p (nm)
PCAC700120	1580	0.931	0.580	0.351	0.7	1.2
PCAC800120	2035	1.215	0.730	0.485	0.6	1.2
PCAC8001220	2180	1.264	0.810	0.454	0.7	1.2

The AC obtained via the activation of the extracted coffee brew possess high specific surface areas of 1580 $m^2.g^{-1}$ for PCAC8001220) and very high (> 2000 $m^2.g^{-1}$) specific surface areas for PCAC800120 and PCAC8001220. The surface area of AC prepared is greater compared to the convential materials with specific surface areas about 1200 $m^2.g^{-1}$. These values can be favourably compared with the ones of AC's produsedfrom coffee endocarp (245-892 $m^2.g^{-1}$) (Nabais et al., 2008).

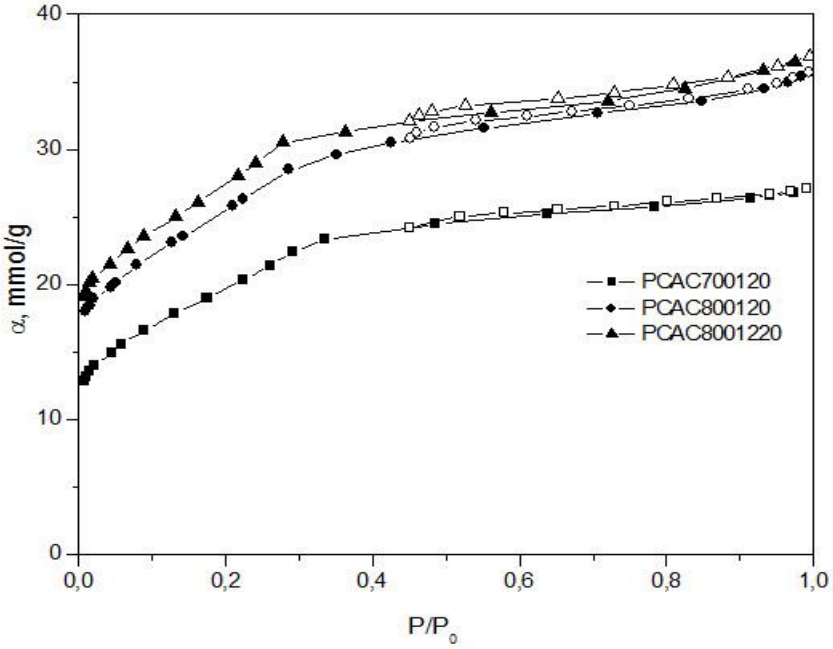

Fig. 1. Adsorption/desorption isotherms of the activated carbon samples

The high micropore volume values of the prepared AC samples reveal their appropriateness for usage in gas phase adsorption.

Fig. 1 shows that the isotherms refer to mixed type ? (1 and 4), with a relatively narrow hysteresis loop, type H3 (for PCAC800120 and PCAC8001220) and type H4 (for PCAC700120) according to the IUPAC classification (1985), characteristic of materials containing slit-shaped pores.

Fig. 2 presents the pore size distributions for PCAC700120, PCAC800120 and PCAC8001220 activated carbon. The same figure shows that the pore structure of these materials consists of micro- and mesopores. It is observed for the samples from Table 6 that the micropore volumes increase from PCAC700120 to PCAC8001220 (1.4 times). However, on the contrarythe value synchronism in the increasing of adsorption-texture parameters from PCAC800120 to PCAC8001220 is desynrchronized. Hence, mesopore volume (V_{MES}) of PCAC800120 increases with about 6 %: as compared to that of PCAC8001220.

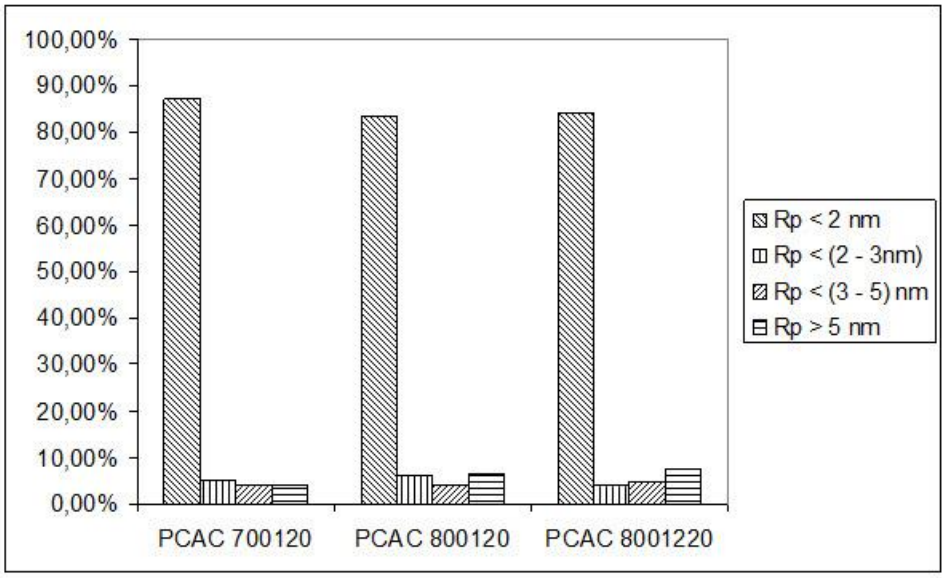

Fig. 2. Mesopore Size Distribution of the activated carbons.

Mesopores are grouped in four groups. Fig. 2 allows the conclusion that, AC's mesoporous texture is characterized by comparative uniformity and a strong predominance of the fine mesopores (R_p < 2 nm), respectively 87.3 % (for PCAC700120), 83.2 % (for PCAC800120), and 84.0 % (PCAC8001220). As seen, the content of fine mesopores is higher for PCAC700120, while for PCAC800120 and PCAC8001220 that content is lower, regardless of the initial substance of precursors.

On the other hand, the content of the larger mesopores (R_p > 5 nm) have closer value for PCAC800120 and PCAC8001220 which is higher as compare to the value of PCAC700120 sample.

The mean pore radius of all samples (Table 6) is the same (1.2 nm). The fact is in full accordance with the contents of the prevaled quantity of the pores with R_p < 2 nm.

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Micrpore Size Distribution of AC (Fig.3.) shows that the maximums of the curves are shifted to the region typical for micropores range (half width parameter ≤ 0.5 – 0.7 nm). The latter could be explained with the nature of the current technology for preparation of active carbon.

Obviously that volume of micropores of PCAC8001220 (Table 6) is higher as compared to the same of PCAC800120, but Micrpore Size Distribution in the latter is homogeneous.

Similarly, despite the significant difference in the values of microporous volume of PCAC700120 and PCAC8001220 (Table 6), x_0 values for the two samples are the same. Therefore, in this techpology for preparation of active carbon from SCB, both the activation temperature and precursor composition influence the development of microporosity.

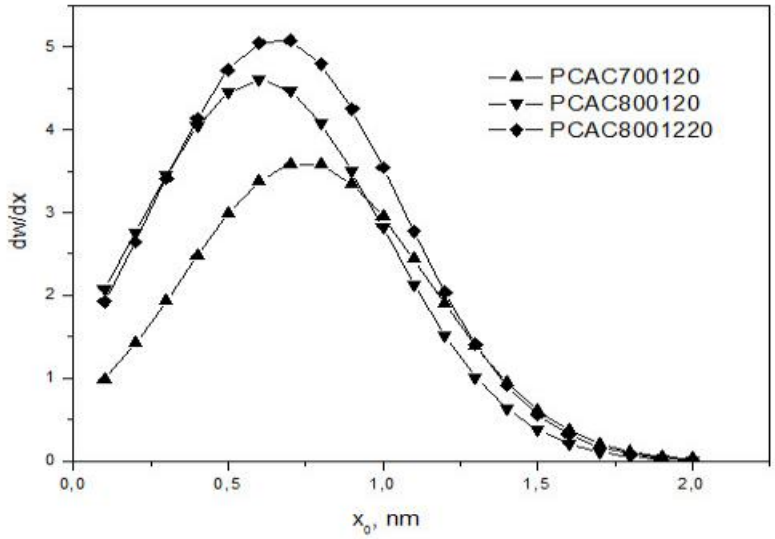

Fig. 3. Micrpore Size Distribution of the activated carbons.

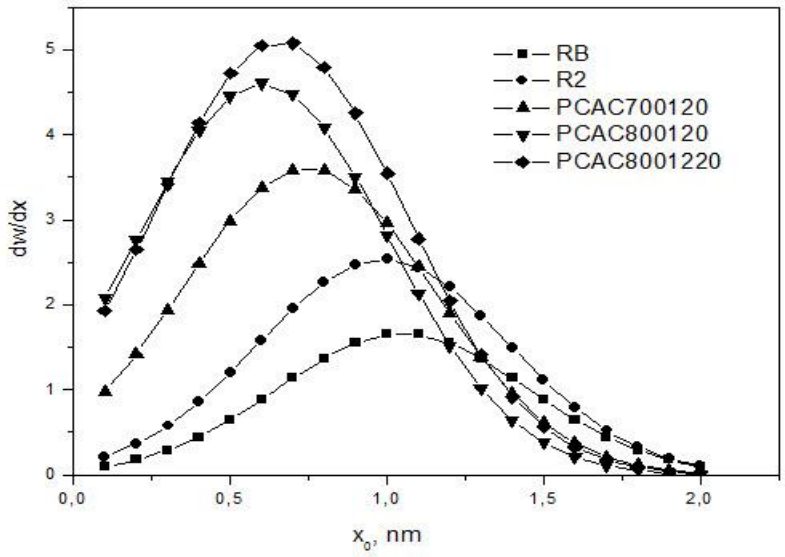

Fig. 4. Micrpore Size Distribution of the activated carbons from two and three stage technology

Fig. 4 shows Micropore Size Distribution of the activated carbon RB (A_{BET} = 706 m^2/g,V_{MI} = 0.270 cm^3/g) and R2 (A_{BET} = 1126 m^2/g,V_{MI} = 0.400 cm^3/g) prepared from SCB wthout previous extraction of the coffee brew, at the same precursor/activator ratio and activation temperature (Nikolov et al., 2011).

Micrpore Size Distribution of RB and R2 activated carbon (Fig. 4) shows that the half width of the curve maximums are shifted to the upper limit of the characteristic supermicropores values. The same Micrpore Size Distribution curves exibit the heterogeneous distribution of micropores, i.e. the microporous volumes of those samples include micropores of all size ranges from ultramicropores to wide size supermicropores. Hence, the preliminary extraction is significant for the development of AC porous texture.

4. CONCLUSION

The activated carbons produced via the described laboratory technology are characterized by a very high specific surface area (from 1600 to 2200 $m^2\ g^{-1}$), a high microporous volume (0.600 – 0.800 $cm^3\ g^{-1}$) and by a homogeneous mesoporous size distibution (max. ~ 2 nm).

The activation temperature, precursor/activator ratio and precursor composition (pure carbonizated biomass or mixture with 10, 20 and 30 mass % Bulgarian lignite coal) influence the parameters of AC texture. The best AC surface and porous texture was obtained at the activation temperature 1073 K and using preliminary extracted and carbonizated spend coffee brew mixed with 20 % lignite coal as a precursor.

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