SEM, WAXD AND EDP-XRFS CHARACTERIZATION OF A BIOMASS PRECURSOR ACTIVE CARBON

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In lucrare este prezentat un nou mod de evaluare a performanţelor unui material carbonic activ utilizând investigaţii SEM, WAXD si EDP-XRFS. De aemenea, lucrarea prezintă un proces de recuperare dublă, respectiv transformarea biomasei reziduale în material de purificare a factorilor de mediu poluaţi cum sunt apele şi aerul poluat din sectoarele energetice.

Autorii prezintă sintetic datele morfologice, structurale si de analiză elementală obţinute pe un sort de material carbonic activ care are ca precursor sâmburi de prune. Pe baza datelor prezentate se pot estima performanţele de purificare a sortului respectiv şi se poate lua o decizie fundamentată privind utilizarea acestuia.

The papes addresses a new way of active carbon performances assessing using SEM, WAXD and EDP-XRFS investigations. The paper also addresses the possibility of production of cheaper active carbon from waste biomas which is a challange project because it represents a double waste recuperation i.e. to use a waste to recuperate other wasted environmental factors as water or gas. The authors present the morphological, structural and chemical results obtained on active carbon having plum stone precursor. On these data one could estimate the purifying perfomances of an active carbon sort and could make a fundamentated decision on its usage.

Key words: SEM, WAXD, EDP-XRD, active carbon, regenerative biomass

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1. Introduction

There are a lot of industrial sectors as metallurgical, electrical power plants, heat plants, chemical plants etc. that should purify a huge volume of technological waste water. The clasical water cleaning technology could not remove the heavy metal from waste waters [1, 2].

On the other hand, the huge volume of waste waters need large quantities of purifying agents which cost a lot. In this direction, a lot of research work has been done to find the cheapest solution for electrical power and heat plant waste waters purification and to recuperate the valuable substance contained in such waters [3, 4]. In this sense, SC OVM-ICCPET SA and its parters UPB, SC ICPE-CA SA and SC ICEMENERG SA initiated researches to find a way of advanced waste water purification using active carbon (AC) with cheapper indigene precursors. The main arrgument of this research project is an important amount of annual regenerated waste biomasses that could be used as active carbon precursor. On the other hand, the biomass the project addresses can be considered as waste of the agricultural industries.

The puriffing performance of AC depend on many morphological and physico-chemical parameters as: particle morphologies, particle size distribution, porosity, specific surface, the nature and density distribution of functional groups and the way of AC product usage as powder filter, powder beds, pellet. Thus, the preliminary evaluation of the active carbon performances can be done based on particle size, pore morphology and other aspects estimated from scanning electron microscopy (SEM) images.

In this paper the authors propose an indirect assesing of the apparent inner pore size by apparent size of turbostratic crystals calculated on the X-ray diffraction (WAXD) data. The elemental composition of the crude AC is of a crucial importance for water and gas purifying because the effluent leaching through the AC is effective only if the pollutant substances in AC are at lower concentrations in the filtrant AC product [3-6].

The authors consider that the most effective elemental analysis of AC could be done with X-ray fluorescence spectrometrical technique (XRFS). The modern wavelength dispersive XRFS (WD-XRFS) could determine the elemental composition in the range Be-U while energy dispersive XRFS (ED-XRFS) in the range Na-U. The newest ED-XRFS use the polarized X-ray to improve the accuracy of light element analysis and are denoted EDP-XRFS [7].

2. Theoreticaly considerations

The major problems in developing a efficient sorbent is to produce active carbon with higher specific surface and with adequte surface chemical reactivity that favorize the adsobtion of heavy metals and the other pollutant molecules or

clusters. The higher specific surface could be achieved by powdering the AC and by producing active carbon with higher porosity.

Any solid material that contains cavities, channels or interstices may be regarded as porous. Porous and finely divided active carbons exhibit enhanced chemical reactivity, higher adsorption capacity [8]. Consequently, among the most commonly determined characteristics are the particle size, the specific surface area (area per unit mass), the specific pore volume (pore volume per unit mass), and the pore size distribution [9].

The active carbon porous structure is quite complex depending on their precursor and producing technology. Thus, the pores are classified according to how accessible they are to an external fluid, in two categories:

1. closed porosity consisting of pores that are inaccessible to an external fluid (a);

2.open porosity consisting of pores that are accessible to an external fluid as is shown in Fig. 1.(b, c, d, e).

The pores that have a navigable channel of communication with the external surface of the body (like b, c, d, e, and f in Fig.1.) are further classified into "through pores" and "blind pores". Through pores have an open channel that begins at one location on the surface, extends into the particle, and re-emerges on the surface at a different location (like the pore channels c-e-c and c-e-d). Blind pores (also called dead-end or saccate pores) are open to the surface only at one end (like b and f).

According to the above classification, small surface irregularities are technically blind pores. On the other side, it is often more useful and convenient to consider them separately as part of a distinct attribute, called surface roughness.

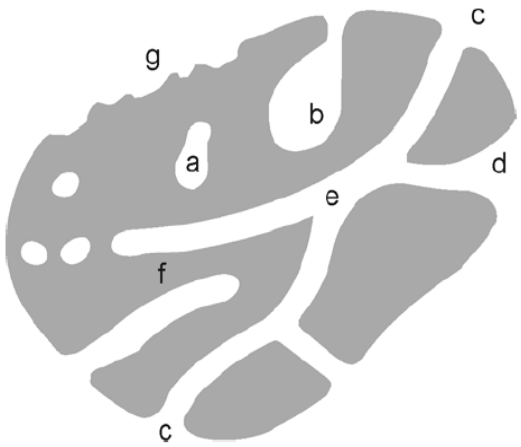

Fig. 1. Schematic cross section of a porous AC grain [10].

IUPACT has recommended [11] the following conventional classification of porosity based on pore size:

a). Micropores: widths < 2 nm;

b) Mesopores: 2 nm < widths < 50 nm;

c) Macropores: widths > 50 nm.

The porosity of solid materials could be investigated using different tehniques depending on their size distrbution and the available equipment (Fig. 2)

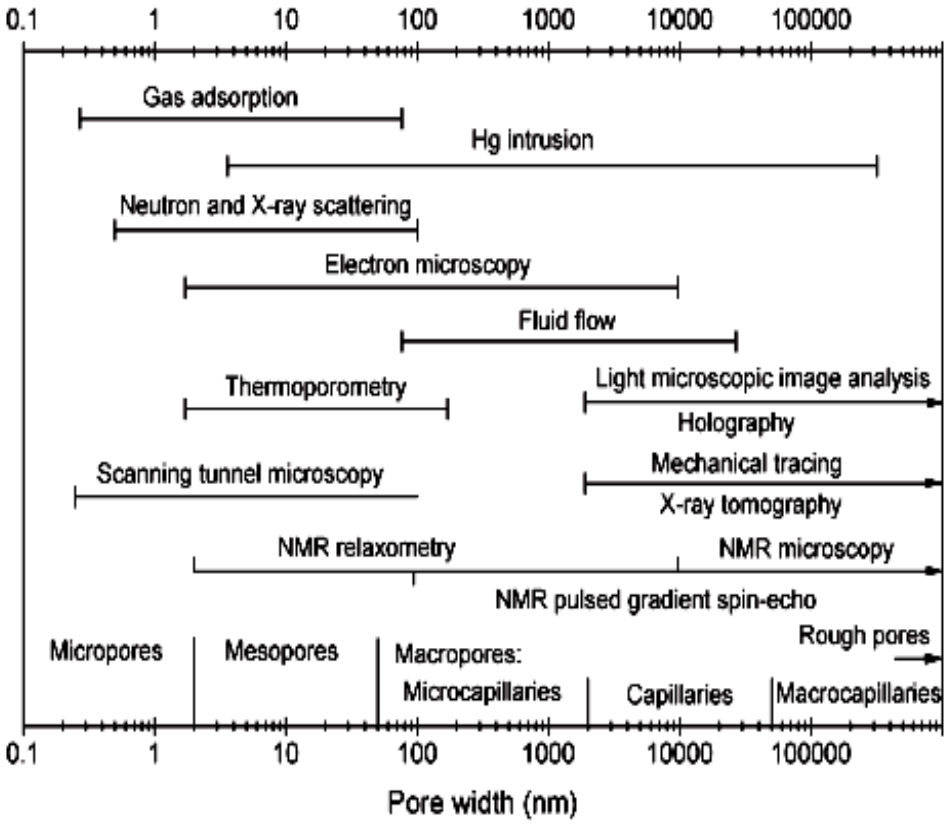

Fig. 2. Measuring ranges of methods for pore size determination [12]

Based on the fact that AC belongs to the non-graphitizing carbons [13, 14] and that the apparent size of turbolayered crystals in AC is of the order of the average micropore apparent diameter (see Fig. 3) the authors propose an easy and effective way of simultaneous characterisation of the AC crystalinity and of its microporosity based on WAXD data.

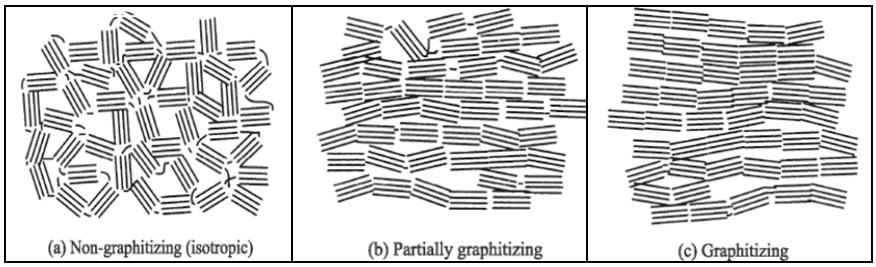

Fig. 3. Schematic representation of carbon graphitical structures [15]

The graphitical structure is characterized by the average distances between graphenes, the average heigth of graphene stack, the average number of graphenes in the turbostratic stack and by the apparent diameter of the graphene [14]. These parameters could be calculated on the base of X-ray diffractogram shown in Fig. 4. The diffractogram in Fig. 4 is one of the best that could be obtained on carbonised caustobiolite. This is because the diffractogram shows all the specific graphite peaks, having (hk) Miller indices different from zero while isotropic and partially graphitizing carbons give only (00l) peaks and)hk(bands, as it is shown in Fig. 4.

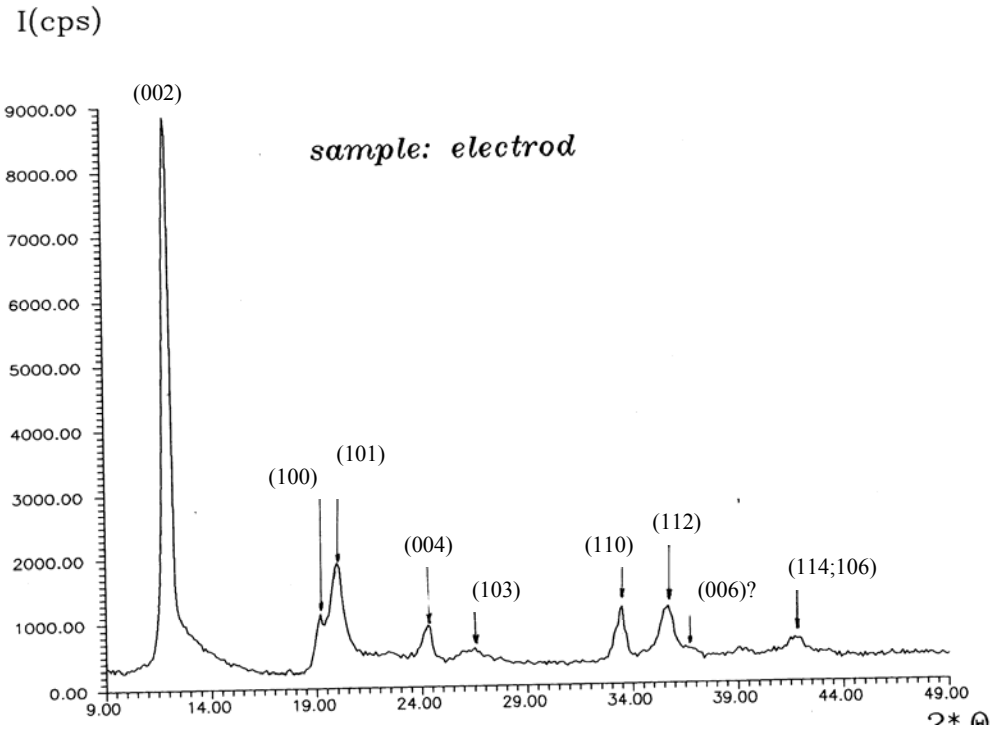

Fig. 4. Diffractogram on a graphitizing carbon

The diffractogram in Fig 4. is appropriate to calculate the main structural parameters of carbon as folows:

- average distances between graphenes(d_c) [16, 17]:

$$d_c = \lambda/(2*\sin(\theta_{(002)})) \quad (1)$$

where: λ- X-ray wavelength, $\theta_{(002)}$ – the angular (002) peak position (see Fig. 4)

- the average heigth of graphene stack (L_c):

$$L_c=\lambda/(\beta*\cos(\theta_{002})) \quad (2)$$

where: λ and $\theta_{(002)}$ have the same significances as above, β-the integral intensity of (002) peak [16]

- the average diameter of graphene layer (L_a) [16, 17, 18]:

$$L_a=1.22\lambda/(\beta*\cos(\theta_{110})) \quad (3)$$

where: λ- X-ray wavelength, $\theta_{(110)}$ – the angular (110) peak position; β-the integral intensity of (110) peak [16] (see Fig. 4)

- the average number of graphenes in the turbostratic stack (N_c) [16, 17]:

$$N_c=L_c/d_c \quad (4)$$

where: are the above defined parameters

The graphitical stacking order is better as the distance between graphenes decreases toward 0.335 nm which is the (002) distance in graphite[14].

Based on this previous experimental proved feature it became a practice to characterize the graphene stacking order by the so called „degree of graphitization" (D_G) defined by the expresion [14]:

$$D_G= (2-d_c/d_{(002)})*100\ \% \quad (5)$$

where: d_c- average distances between graphenes ; $d_{(002)}$ – the (002) distance in graphite (0.335nm)

3. Experimental

The waste biomasses considered in this paper are plume stones (PS). These biomasses were carbonised at about 480 ^oC in an experimental model of fluidised bed oven and in controlled neutral atmospheres. The carbonised products were steam activated and subsequently dried. The plum stone active carbon (PS-AC) laboratory sample was subdivided in three subsamples and were analysed.

The contents of AC-PS are shown in Table 1.

Table 1

The main contents of the pyrogenated products

Contents/subsample	W (wt %)	A (wt %)	V (wt %)	S (wt %)
AC-PS-1	5.95	0.57	32,9	0,068
AC-PS-2	5.86	0.53	34,1	0,066
AC-PS-3	5.91	0.55	33,8	0,071

where: W-water, A-Ash, V-Volatile substances, S-Sulfur

The SEM images were take on Tesla BS 300 and BS 350 instruments under secondary electron mode at accelerating voltage in the range 15 - 20 kV.

The WAXD investigation have been done with an upgraded DRON 3 diffractometer equipped with a Mo Kα X-ray tube operated at 35 mA and 45 kV. The WAXD specimens were prepared as pellets and were anlysed using the two-theta Bragg-Brentano method.

The EDP-XRFS elemental analyses were done using a SPECTRO XEPOS spectrometer. The XEPOS spectrometer is equiped with 3 secondary X-ray targets that divide the available XRF spectrum in three ranges for a better excitation of the light element fluorescence and to make use of the advantage of X-ray pollarized excitation and detection.[19, 20]. The EDP-XRFS specimens were prepared as pellets and were analysed using the Turboquant pellet method.

4. Results and Discussion

The SEM investigation addresses the PS-AC morphology, sizes and porosity. The image on PS-AC in Fig. 5 shows the bulk morphology of PS-AC and justifies why active carbon has a higher specific surface among the sorbents. The open pores (voids) are of polygonal shape and have apparent diameters in the range 1-8 μm i.e. the image reveals the macroporosity.

The surface add-on particles shows composite rough (Fig.5) and plate-like (Fig.6) morphologies.

Among the particulate roughness there are a lot of micrometric pores that belong to macroporosity.

The plate-like surface (Fig. 6) reveal a network of slit-like porosity and a lot of surface adhered particles. The characteristic morphology of surface add-on particles is shown in Fig. 7 and suggest that they are of caustobiolitic nature.
Fig. 8 gives a significant picture of the complex morphology of the open pores.

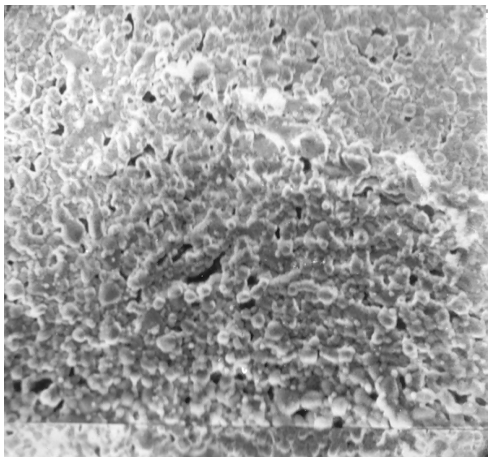

Fig. 5. SEM image of PS-AC bulk morphology of (100x)

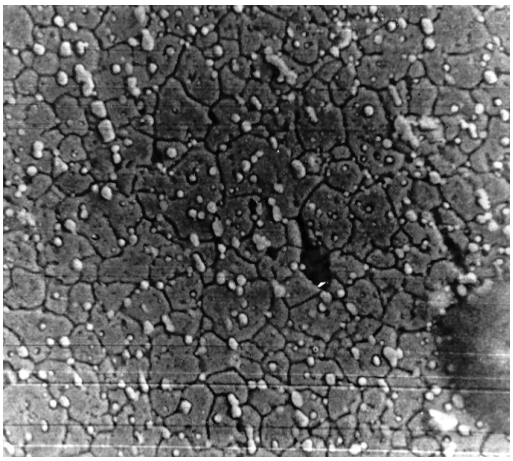

Fig. 6. SEM image of PS-AC plate-like morphology (1000x)

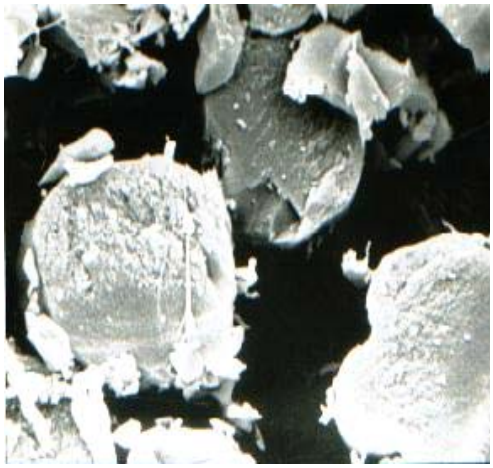

Fig. 7. SEM image of PS-AC macroporosity (aggregate voids) (5000x)

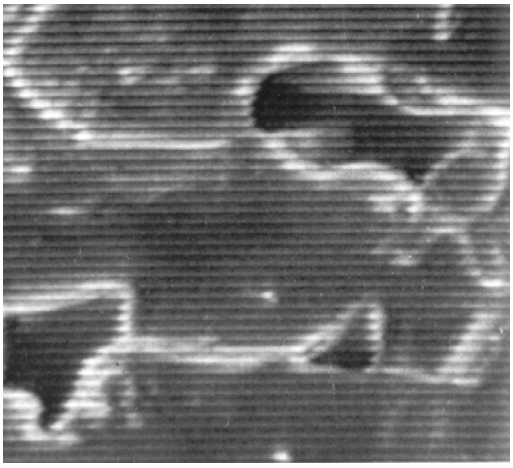

Fig. 8. SEM image of PS-AC mesoporosity (10^5x)

The shapes of the open end of the pores are very complex and their apparent diameters are hardly to be assessed. Thus, the average apparent diameter of the macropores shown in Fig. 8 is about 100nm. A roughly estimation of the macroporosity is 10^6 m^{-2}. The SEM investigations shows that PS-AC has micronic and submicronic rugous surfaces that are proper for adsorption of polluant gas molecules The same PS-AC show a well developed macroporosity that increase the specific surface but the macroporosity is advantageous when AC is used for water filtration because it contributes to the microparticle retention and even of

microorganisms. On the base of SEM data one could infer that the AC-PS are appropiate for both water and air purification but it could be used for gases.

The carbonised AC-PS diffractogram (Fig. 9) shows the known pattern of turbostratic carbon specific to about all natural solide caustobiolite[4]. The graphene stacking order is lower because only (002) peak is well shaped while the characteristic peaks (004) and)10(and)11(bands are very large. The characteristic parameters of graphitelike structure of AC-PS are given in Table 2.

Table 2

Structural coke data.

Samples	$d_{(002)}$ [nm]	Lc [nm]	La [nm]	Nc*	DG
PS-AC - 1	0.350	1.9	1.3	3.9	90-92
PS-AC -2	0.395	1.9	1.3	4.9	91
PS-AC -3	0.392	2.0	1.4	5.1	91

** Nc -the average lattice number in a crystal, G - graphitization degree[1].*

The apparent graphene diameter of AC-PS were hardly estimated from diffractogram in Fig 9, with lower confidence levels.

Considering the hypothesis that the Lc estimate the average width of the pore then the AC could be considered as mesoporous ones. Since the range of mesopore width is 0.5 to 2.0 nm then all PS-AC sort wich has apparent diameters of about 16-29 nm could be considered some how at the boundary between meso- and macroporous classes.

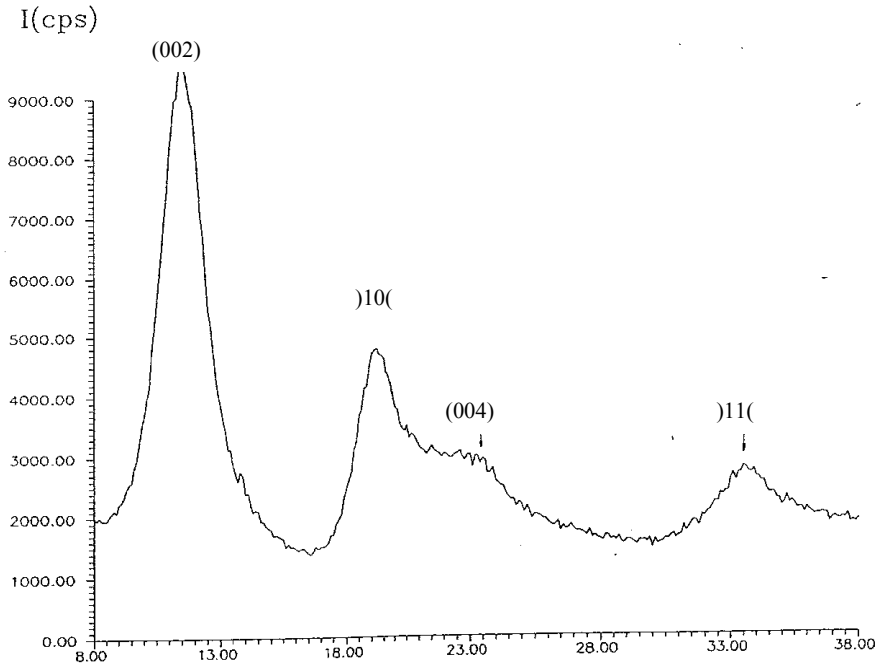

Fig. 9. Diffractograms undertaken on the AC-PS test sample

The G parameter is a low sensitivity one (Table 2) and it can be disregarded when analysing AC of the main structure parameters.

The SEM and WAXD investigations show that the AC-PS has bemodal porous structure i.e. an inner mesoporous structure and an inner and other macroporous complex structure. Thus these PS-AC sorts are appropiated for water and for gas purification. From the WAXD point of view it is hard to differentiate their effectiveness in water or gas purification.

The elemental compositions is another keystone for AC. Thus the AC-PS were analysed by XEPOS to estimate the elemental composition of the test samples in the range Na-U. The results in Table 3 show that all samples contain significant quantities of Na, Mg, Al, Si, S, K, Ca, Ti, Fe that is quite normal for AC with biomass precursors.

Fortunately, the heavy metal concentrations in all AC samples are lower. Thus, the AC test samples could be considered as free of heavy metals as Cd, Hg, Pb, U even Cu and Zn, while Cr and Ni are at least two times greater in concentration than the others.

Table 3

Chemical composition of AC-PS (c in ppm) and their satandard errors

		PS-AC 1		PS-AC 2		PS-AC 3	
Z	Symbol	c (ppm)	Abs.Error (ppm)	c (ppm)	Abs.Error (ppm)	c (ppm)	Abs.Error (ppm)
11	**Na**	1763.0	85.0	1768.0	84.0	1886.0	88.0
12	**Mg**	508.0	13.0	488.0	13.0	540.0	13.0
13	**Al**	1600.0	20.0	1574.0	20.0	1630.0	30.0
14	**Si**	3325.0	30.0	3269.0	30.0	3366.0	30.0
15	**P**	72.3	1.3	70.5	1.2	74.7	1.3
16	**S**	8176.0	6.0	8091.0	6.0	8270.0	6.0
17	**Cl**	104.8	0.4	101.6	0.4	102.4	0.4
19	**K**	1357.0	8.0	1309.0	8.0	1361.0	8.0
20	**Ca**	1698.0	6.0	1715.0	6.0	1721.0	7.0
22	**Ti**	878.2	8.4	928.7	8.3	909.9	8.1
23	**V**	28.4	3.9	32.0	3.8	38.7	3.7
24	**Cr**	11.2	0.7	10.9	0.7	14.6	0.8
25	**Mn**	28.2	1.0	28.5	1.0	28.6	1.0
26	**Fe**	2241.0	4.0	2265.0	4.0	2199.0	4.0
27	**Co**	< 4	1.0	< 4	2.0	< 4	2.5
28	**Ni**	12.7	0.3	13.1	0.3	13.1	0.3
29	**Cu**	5.2	0.2	5.5	0.2	5.0	0.2
30	**Zn**	5.2	0.2	5.5	0.2	6.0	0.2
31	**Ga**	8.6	0.2	9.0	0.2	8.8	0.2
32	**Ge**	7.2	0.2	7.2	0.2	7.4	0.2
33	**As**	1.0	0.1	0.5	0.1	0.9	0.1
34	**Se**	< 0.5	0.0	< 0.5	0.0	< 0.5	0.0
35	**Br**	2.9	0.1	2.9	0.1	3.0	0.1
37	**Rb**	7.9	0.1	7.9	0.1	7.9	0.1
38	**Sr**	41.5	0.1	41.7	0.1	41.5	0.1

(continued)

39	**Y**	11.9	0.1	11.9	0.1	11.8	0.1
40	**Zr**	67.5	0.6	66.8	0.6	66.6	0.6
41	**Nb**	4.4	0.2	4.6	0.2	3.8	0.2
42	**Mo**	1.1	0.2	0.5	0.2	1.1	0.2
47	**Ag**	< 2	0.0	< 2.0	0.0	< 2	0.0
48	**Cd**	< 2	0.0	< 2.0	0.0	< 2	0.0
50	**Sn**	10.4	0.8	9.2	0.8	11.1	0.8
51	**Sb**	< 3	0.0	< 3	0.0	< 3	0.0
52	**Te**	< 3	0.0	3.0	0.5	3.0	0.4
53	**I**	< 3	0.0	< 3	1.4	< 3	0.0
55	**Cs**	< 4	0.0	< 4	0.0	< 4	0.0
56	**Ba**	84.1	7.4	93.7	7.5	94.0	7.4
57	**La**	<2	0.0	<2	0.0	<2	0.0
58	**Ce**	<2	0.0	<2	0.0	<2	0.0
72	**Hf**	3.7	0.4	3.2	0.3	3.2	0.3
73	**Ta**	5.3	0.4	4.2	0.4	5.2	0.4
74	**W**	7.6	0.3	7.2	0.3	7.1	0.3
80	**Hg**	<1	0.0	<1	0.0	<1	0.0
81	**Tl**	<1	0.0	<1	0.0	<1	0.0
82	**Pb**	3.4	0.2	3.8	0.2	3.4	0.2
83	**Bi**	<1	0.0	<1	0.0	<1	0.0
90	**Th**	4.0	0.2	3.5	0.2	3.8	0.2
92	**U**	2.4	0.1	2.3	0.1	2.2	0.1

5. Conclusions

There is a challenge possibility to use the cheaper biomass precursors as plum-stone and other stones to produce active carbons for environmental applications.

The PS-AC morphologies revealed by SEM is very complex, but it is possible to asses the dominant morphological aspect which can be correlated with their performances as purifiers, as it was shown in the paper. From the morphology point of view the PS-AC is more apropriate for water purification.

The WAXD investigations proved the non-graphityzing nature of the biomass precursor AC and the randomly graphene packing.

The equivalence between Lc and average apparent diameter of pore in AC is a consistent hypothesis. Thus, the clasification of AC sample as mesoporouse on the base of Lc parameter fits with data reveals by high magnification SEM images undertaken on all PS-AC subsamples. To a better consistency of this hypothesis one should perform SAXS investigations to assess the average apparent diameter size distribution of these AC samples.

The XRFS is an efficient technique for elemental analysis of AC in the range Na-U and proved that the PS-AC is quite free of heavy metals

The paper proved that SEM, WAXD and EDP-XRFS provide valuable data on AC that could not be obtained by other technics. Thus, the above

mentioned techniques should be integrated with adsorbtion/sorbtion wet chemistry and other AC specific techniques to get a complete system for AC characterisation.

Aknowledgements

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