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Wastewater treatment by the use of some new carbon based adsorbents

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The paper presents a solution of water depolluting by the use of new carbon based adsorbents (CA) made of different renewable wastes from industrial and agricultural processing. The new biomaterials have proven high efficiencies towards solutions which contain phenol in comparison with some commercial activated carbons (AC). The solution represents a cost benefit opportunity, beside the environmental friendly aspect of the proposed manufacturing technology of pyrogenation-activation.

1. Introduction

The problem of renewable materials and wastewater purification represents today one of the key elements dictated by the need of natural resources preservation.
There is an increased interest on international and national market to identify new raw materials for the sorbents manufacturing used for environmental purposes. This is largely the result of demand for implementation of environmental regulations related to the air and water pollution, gas purification, gas separation, gas storage and regeneration.
AC manufacturing based on raw materials of vegetal origin such as peat and wood are rather expensive. Moreover, they represent diminishing resources relevant to forest protection, land rehabilitation etc. affecting, in general, the global warming. Thus there is a necessity to search for other comparative raw materials appropriate for AC manufacturing. In the last decades complex researches have been carried out regarding the obtaining, characterization and use of the AC (Marsh et al., 1997, 2000, 2006).
Some of the national research programs have been undertaken concerning the superior valorization of xylites (fossil wood) of the Romanian's lignite deposits in the process of AC manufacturing (Ţicleanu et al., 1994; Predeanu et al., 1997, 1998). Additional information has been brought by the petrographic studies (Panaitescu, 1991; Panaitescu and Predeanu, 1999; Predeanu and Panaitescu, 2004, 2007). The research was going on (Predeanu et al., 2003, 2005) focusing on the elaboration of improved thermal treatment processes especially by application of non-polluting technologies. Integrated in the world's present context of finding new resources for producing new biomaterials for

wastewaters depollution, the research is progressing on (Călinescu et al., 2007a, 2007b; Predeanu, 2007a, 2007b, 2007c, 2008) widening the CA utilization area.
The paper describes: (1) the selection of raw material, (2) the effect of pyrogenation - activation conditions on the structural properties which give the adsorptive capacity of the final product, and (3) the adsorption efficiencies of the new bioproducts towards phenol pollutant.

2. Materials and methods

Some types of wastes of vegetal origin as xylite, particleboard PAL, fruit kernels and agricultural wastes, were chosen after a special preparation, to provide the high quality and grain sizes demanded for the pyrogenation-activation processes. The wastes have been selected taking into account the low inorganic content of the raw materials and the availability of the wastes amount in case of the developing the technology on the industrial level. The results of the wastes characteristics are shown in Table 1.

Table 1. Wastes characteristics (db*, %)

Wastes type	Moisture	Ash	Volatile
Xylite	20.5	2.30	68.50
PAL	5.63	1.82	79.36
Corn cob	9.80	0.90	81.20
Plume kernels	4.96	1.37	79.31
Peach kernels	6.36	1.21	79.93

*db = dry basis

The following operations were required by the laboratory-pilot scale experiments: low-temperature pyrogenation (I) and charcoal physical activation (II).
First operation (I) consists of charcoal manufacturing in a pilot scale rotary kiln. Here, the drying, preheating and conversion of wastes into charcoal through low-temperature carbonization at 500-600°C, at a heating rate of 8-9^{0}C/min, reaction time of maximum 60 min and an overpressure of almost 30-100 mm H_2O took place. The maximum oxygen content in the burned gases is 0.2-0.3%. The main advantage was the development of an important porous network in the resulted charcoal, which represents the intermediary porous structure of the CA. The necessary heat amount was produced in a combustion chamber. During the low-temperature carbonization, the only variable used was the type of the raw material supplied.
The basic principle of the second operation (II), which took place in a laboratory vertical reactor, was the development of a porous network in wastes' charcoal by physical activation. The main activation parameters were: wastes' charcoal size between 5-10 mm and 10-20 mm, temperature 1000°C; activation agent: CO_2.
Sampling, preparation and wastes analyzing followed the national standard laboratory methodology, according to ISO. The degassing development and the structural transformations in the stage of activation were also evaluated in terms of adsorption as iodine value, surface area BET and micropore volume, Table 2.

In terms of quantitative petrographic composition of CA, polished sections of 20 average samples were investigated having five different origins: xylite, particleboard PAL, corn cob, fruit kernels, and a commercial sample.

The method of preparing CA samples and determining microstructure characteristics and composition by microscopy followed ISO 7404-2 (1994). The polished blocks were studied using polarizing light, the measurements recording a minimum of 500 points.

Table 2. Chemico-technical and adsorption characteristics of CA

Waste type	Chemico-technical characteristics,%			Adsorption characteristics			
	A^{db}	V^{db}	Fixed Carbon	Iodine value, mg/g	S_{BET} m^2/g	S_L [1)] m^2/g	Micropores volume[2)] cm^3/g
Xylite	7.54	1.01	91.45	758.02	547.70	562.2	0.136
PAL	5.27	1.67	93.06	964.56	889.76	840.92	0.230
Corn cob	2.50	7.63	89.87	300.59	127.59	110.54	0.039
Plume kernels	2.76	1.87	95.37	723.61	578.22	538.73	0.156
Peach kernels	2.23	1.55	96.22	912.89	880.40	781.2	0.267
Commercial	3.00	1.00	96.00	920.00	871.0	771.0	0.270

[1)] Surface area determined by Langmuir equation

[2)] Micropores average radius: 0.31 – 0.43 nm

To evaluate the microscopically porosity regarding degassing extent of CA, the structural types specific to the native wastes were registered on seven pore sizes (µm): <2.5; 2.5-5.0; 5.0-7.0; 7.0-10.0; 10.0-12.0; 12.0-15.0; >15.0, Table 3. The structure repartition within the seven porosity categories was made using the ocular micrometer. Only particles greater than 0.2 mm, on which the inter-grain porosity could be determined, were counted as the smaller particles having usually an opened porosity, typical for the walls of very fine and fractured pores.

Table 3. CA inter-grain porosity repartition (%) by grain sizes

CA origin	Pore size, µm						
	<2.5	2.5-5	5-7	7-10	10-12	12-15	>15
Xylite	37.5	40.3	9.2	6.5	3.2	1.5	1.8
PAL	32.5	40.5	12.3	7.6	1.6	4.0	1.5
Corn cob	28.2	31.3	10.5	10.0	9.2	6.1	4.7
Plum kernel	40.8	38.5	11.7	6.5	1.5	0.2	0.8
Peach kernel	41.3	39.5	11.9	5.6	1.3	0.4	-
Commercial	36.2	42.5	14.3	3.4	2.3	1.3	-

In order to determine the CA adsorption efficiency, the work has been done in dynamic conditions using as liquid effluent an aqueous solution which contains phenol. The flow of the polluted water was varied with a peristaltic pump, the concentration of the solution that have been passed through the column being continuously monitored, by taking water samples on the column outlet point for the chromatographic analyses made by a HPLC Jasco Borwin equipment.

3. Results and discussion

For the industrial wastes, especially provided by mining and wood sectors, we noticed the high purity of the raw material, of maximum 2.3% ash content (db). For the agricultural wastes the inorganic content represents max. 1.37% in hard lignocellulosic wastes (fruit kernels) and max. 1% in case of the soft ones (corn cob). The analytical results from Table 1 reveal that both industrial and agricultural wastes chosen are suitable for CA manufacturing because of the low inorganic content. In case of soft agricultural by-products the disadvantage of low CA yields is balanced by the supply low cost. Depending on the raw material origin and laboratory processing conditions, CA highlights interesting adsorptive characteristics, such as: iodine value (300 mg/g for soft materials, 700-912 mg/g for hard materials, 750-964 mg/g in case of industrial wastes); S_{BET} (≈130 m^2/g for soft and 578-880 m^2/g in case of fruit kernels and between 548-890 m^2/g in case of industrial wastes) and an enhanced development of microporosity comparatively to that of the commercial AC.

A CA having an extended surface area and high adsorbent properties could be obtained following a special process of charcoal gasification. The main problem for physical-textural structure of CA is represented by its porosity, being the key for the adsorption capacity. The porosity depends on the initial structure of the raw material, the temperature and the activation time. The higher the specific surface area, the higher the adsorption capacity. In the wastes charcoal of different kind of wooden origin materials, the activation causes typical changes such as the extension of pores depending on the weight loss extent. The weight loss (ΔM) and the pores system formed during the activation (Pf) were calculated in accordance to the Yuntgen mathematical model, as:

$$\Delta M = 100 \quad x \quad \frac{Mc\,(100\text{-}Ac) - [Ma\,(100\text{-}Aa)]}{Mc\,(100\text{-}Ac)} \tag{1}$$

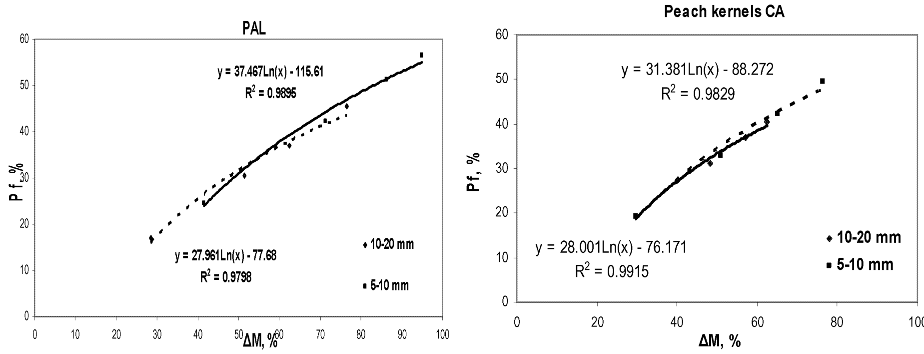
and

$$Pf = (1- \frac{Ac}{100}) \quad x \quad \frac{\Delta M}{\rho} \tag{2}$$

in which:

Mc – mass of carbonized material;
Ma – mass of activated material;
Ac – ash of pyrolized material;
Aa – ash of activated material
ρ - real density of pyrolized material

The strong relationship between these parameters is not influenced by the grain size of the parent materials, Figure 1 (a, b).



a b

Figure 1. Porosity developed during activation vs. weight loss and grain size for (a) industrial (PAL) and (b) agricultural (peach kernels) carbon based adsorbents.

Surface area BET is influenced by the activation time, weight loss and grain size, Figure 2 (a, b). It was observed that on activation times higher than 2 ½ hr., the weight loss increases as the surface area BET decreases. The size of 10-20 mm is favorable for the obtaining of higher adsorption surfaces in case of hard essences which decrease in the direction: fruit kernels > PAL > xylite > corn cob. The highest value of 1257 m2/g that have been obtained in case of peach kernels carbon adsorbents, placing our results in the very promising range towards the intended applications.

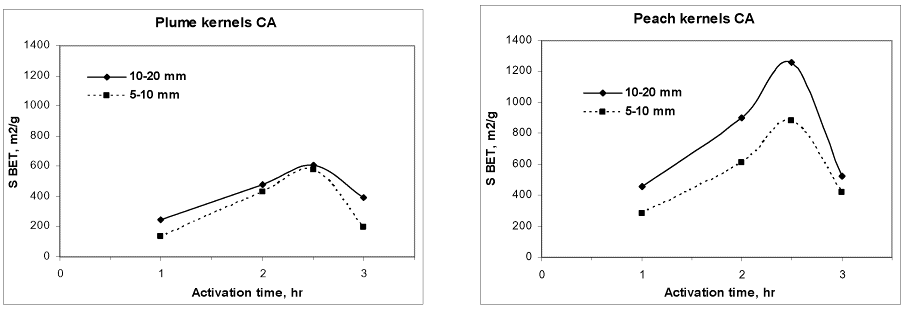


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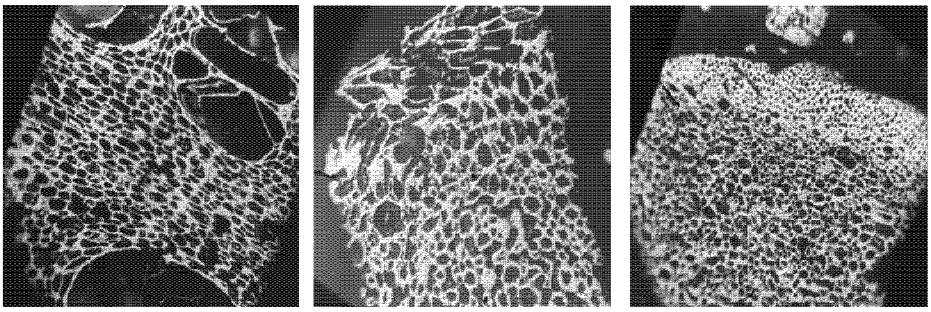
Figure 2. Surface area BET developed during activation vs. activation time and grain size in case of (a) plume kernels and (b) peach kernels carbon based adsorbents.

During the processes of pyrogenation and activation the CA microstructure displays the relation between the wastes lignocellulosic type (hard or soft) and the developed structures and textures. The microscopically porosity distribution shows that soft materials have around 28% of the pores under 2.5 µm, between 32-38% for industrial wastes (including commercial) and 40-42% for fruit kernels, Table 3.

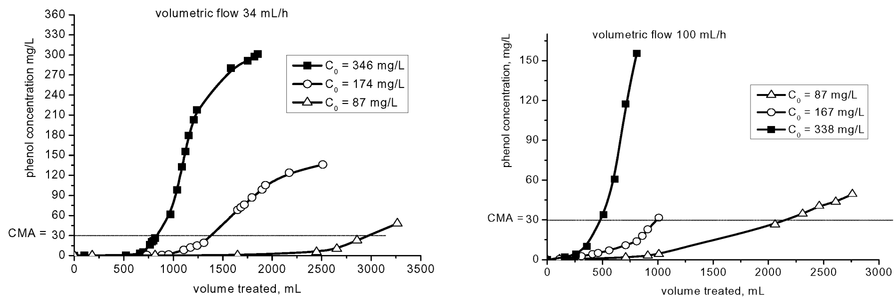
The microstructural studies on the CA reveal the different behavior of textures in CO_2 gasification processes. Fruit kernels show the finest of the majority of the pores. The photomicrographs taken on the optical microscope reveal the influence of the vegetal structure of the parent waste on the CA pores, Figures 3 (a-c).



a b c

Figure 3. Photomicrographs of CA of different vegetal origin: (a) Wooden structure in activated PAL carbon, under polarized light, oil immersion, 375x. (b) Pores in activated corn cob carbon, under polarized light, oil immersion, 375x. (c) Thin textural aspect of some activated fruit kernels carbon fragments, 375x.

For the running experiments have been established the optimal range between the height of the adsorbent, concentration, supply flow and CA grain size. The water flow varied between 34 and 100 mL/h and the phenol concentration between 87 – 338 mg/L, Figure 4 (a, b).



a b

Figure 4. Evolution of the effluent concentration after passing through the peach kernels adsorbent column of constant heigth, at different initial phenol concentrations in case of the supply flow of (a) 34 and (b) 100 mL/hr.

The effluent samples have been collected on appropriate time. The pollutant remained into the water sample was represented as a function of the water which passed through the adsorption column. The point in which the pollutant concentration reaches the proposed level is called „the breakthrough point". The concentration that have been taken into account of CMA=30 mg/L represents for Romania the maximal admissible concentration for the waters containing phenol, discharged into municipal collecting drain. For a constant height of the adsorbent bed and a constant supply flow it was observed that the volume of the depolluted water increases as the concentration of the initial solution decreases. At the same time, some more information have been obtained: on small flows the volumes of the treated water at the breakthrough point are higher; at the breakthrough point, for a fixed CA bed of peach kernels with a grain size of 1-3 mm the treated water volume increases as the CA bed height increases and as the initial solution concentration and water supply flow decreases, Figures 5 and 6.

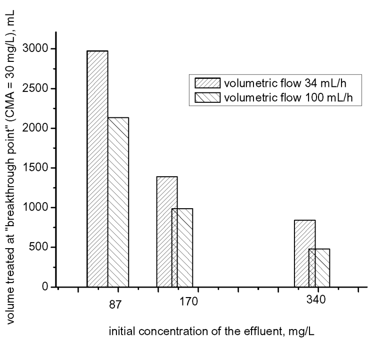


Figure 5. Evolution of the treated water volume by adsorption on CA at CMA of 30 mg/L at initial concentration of phenol at supply flows of 34 and 100 mL/h at a constant bed heigth.

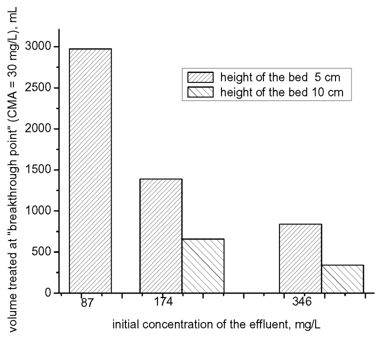


Figure 6. Evolution of the treated water volume by adsorption on CA at CMA of 30 mg/L at initial concentration of phenol at supply flows of 34 and 100 mL/h at a variable bed heigth.

4. Conclusions

The structured wooden material of vegetal origin provided by some industrial and agricultural wastes is adequate for CA manufacturing and promising for wastewaters purification. The use of industrial and agricultural wastes allows the transforming of the costless and pollutant wastes, in high grade biomaterials for the environment protection.
The structures of the CA are characterized by an enhanced development of porosity – investigated by physically and microscopically methods - depending on the amount of structured wooden material and the degree of degassing. The adsorption characteristics e.g. surface area BET emphasizes high adsorption capabilities comparable to commercial samples as well as the pore size distribution which reveals a satisfactory micropore volume. The peach kernels CA shows an increased of the total porosity based on the submicron pores development

It has been demonstrated the possibility of phenols removal by adsorption on peach kernels CA. The laboratory results permit the scale-up of the phenols depolluting scheme by adsorption on CA.

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