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A study of the process of pyrolysis in a water-vapor stream of activated carbons, prepared from agricultural by-products by some physico-chemical methods

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Abstract

The changes in the radical concentration and the development of the porous structure of the activated carbon obtained by pyrolysis in the presence of water vapor of various agricultural by-products are investigated by EPR spectroscopy and argon thermal desorption. It was found that they depend on the nature of the raw material and the final temperature of the process. A similarity was established between the dynamics of the change in radical concentration and the development of new surfaces of some of the activated carbons.

Keywords: Activated carbon; Argon; Carbon; Desorption; EPRS; Pyrolysis

1. Introduction

The growing need for efficient adsorbents has led to the use of new raw materials for their manufacture. With regards to a particular activity, the use of carbon-containing wastes such as plum, apricot, peach, and olive stones, and coconut and nut shells has increased [1–5].

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It is known that the chemical composition and texture of the initial raw material have considerable influence on the formation of the porous structure and the physico-chemical properties of the carbon adsorbents [6].

Highly effective adsorbents, with a broad adsorptive capacity and also having a molecular sieve effect, are obtained by direct activation of plum stones and peach stones with CO_2. It has also been demonstrated that it is possible to obtain highly effective adsorbents by activation with water vapor of the following waste materials: apricot stones, nut shells, coconut shells, almond shells and grape seeds [3–6]. It was established that the adsorbents possess not only a microcrystalline structure (for efficient adsorption) but also a considerable proportion of small pores, as the adsorption is carried out according to the mechanism of capillary condensation. The investigations into the pyrolysis of solid fuels in the presence of water vapor have shown differences in the mechanism of this process [6]. It has been shown that during intensive pyrolysis of lignite coal, water vapor plays a part in the radical process of destruction of the organic mass [7,8].

A careful study of the pyrolysis mechanism of agricultural by-products in the presence of various reagents has not been carried out before. An expansion of our knowledge on the mechanism of the interaction of this type of carbon material with water vapor during the process of pyrolysis is also of practical and theoretical significance. The aim of our present investigation is to study the nature of the pyrolysis of agricultural waste products in a stream of water vapor, using EPR spectroscopy and by determining the specific surface area by desorption of argon. The results obtained will provide information on the nature of the surface of these carbon adsorbents.

2. Experimental

2.1. Samples

The samples of almond shells, apricot stones, nut shells, coconut shells and grape seeds, obtained from the fruit-scanning industry, were subjected to thermal treatment in a stream of water vapor by a method described earlier [9]. Analytical data for the raw materials and adsorbents are presented in Table 1. In our previous investigations [10], the temperature range 600–700°C and a treatment time of 2 hours were selected, to optimize the formation of a highly developed porous structure.

2.2. Surface measurements

The experimental data of the adsorption parameters of the samples studied are comprised of the specific area, based on the desorption of argon at $p/p_0 = 0.15$ [11,12].

2.3. EPR measurements

The samples were ground to a grain size of 0.07 nm, dried at 110°C for 25 h and then blended with SiO_2 (1 : 5).

Table 1
Proximate and ultimate analyses of the samples used before and after processing in the presence of water vapor

Sample	Proximate analysis			Ultimate analysis in wt%				
	Moisture wt% as received	Ash wt% dry	Volatiles wt% daf	C	H	S	N	O (by diff.)
Coal	8.06	2.68	68.14	72.20	6.69	0.83	1.55	18.73
Semi-coke	6.77	8.93	8.31	86.59	1.23	0.97	1.14	10.07
Coconut	5.63	0.52	76.45	49.39	6.21	0.75	0.40	43.25
Char	1.28	2.36	4.87	90.70	1.02	0.88	0.89	6.52
Walnut	9.20	0.99	76.80	48.24	5.78	0.54	0.61	44.83
Char	3.98	3.05	7.02	86.94	1.69	1.35	0.95	9.07
Almond	9.27	0.59	80.98	45.96	5.67	0.14	0.51	47.72
Char	2.32	2.71	3.30	89.49	1.03	0.23	0.63	8.62
Apricot	6.41	0.21	80.58	51.45	6.34	0.20	0.09	41.92
Char	2.83	1.63	5.77	85.45	2.48	0.75	0.65	10.67
Grapes	7.55	2.59	75.26	55.43	6.95	1.45	0.21	35.46
Char	1.83	3.12	4.36	84.72	1.29	1.60	0.25	12.14

The EPR analysis was performed using an X-band EPR spectrometer type SEX (19.3 GHz, modulation 100 kHz) made by Radiopan, Poznan, Poland. In order to avoid microwave saturation, the measurements were taken with a very low attenuation of 20 dB on this spectrometer.

Ultramarine was used as a reference for the concentration of paramagnetic centers and a ruby crystal, permanently placed in the resonance cavity and measured under the same conditions as the sample, was a secondary reference. The ruby concentration was rescaled by comparison with an ultramarine standard and diphenyl picrylhdrazyl (DPPH) radical, which served as a primary standard. To determine the total concentration, the spectrum was recorded with 0.02 mT steps and analyzed using a SARA software package (System of Automatic Recording and Analysis of EPR spectrum). The g-factor was determined by measuring the magnetic field at the maximum microwave absorption (zero value of the derivative). The linewidth (ΔH_{pp}) was measured from the spectrum.

3. Results and discussion

The basic EPR spectral parameters are the g-parameter and the concentration of paramagnetic centers (PMC). The measured g-values give information about the environment of the unpaired electron in the system; the radical concentration indicates the number of unpaired electrons in a sample unit and the spectral width is mostly determined by the proximity of unpaired electrons to the nuclei with magnetic moments.

Table 2
EPR and adsorption parameter measurements of activated carbons prepared from apricot stones

Temperature in °C	$N \times 10^{-17}$ in spin g^{-1}	g (± 0.0001)	ΔH_{pp} (± 0.01 mT)	$S_{sp}25$ in $m^2 g^{-1}$	$S_{sp}100$ in $m^2 g^{-1}$
Initial	0.90	2.0037	0.62	–	
600	164	2.0025	0.47	39.5	70
650	28	2.0025	0.47	313	91
700	2.9	2.0025	0.45	182	78

For calculation of the specific surface area of the samples, the volume of argon desorbed at 25°C was assumed to be equivalent to the surface area of the sample and is denoted as $S_{sp}25$ ($\theta = 25°C$). The volume of argon desorbed at 100°C, however, can only be conditionally related to the specific surface area, because micropores of a size comparable to the diameter of an argon molecule can take part in the adsorption process. This volume is denoted $S_{sp}100$ ($\theta = 100°C$). It is reasonable to assume that the volume of the adsorbed argon is equal to the specific surface area of the sample, so that the total specific surface area can be accepted as being proportional to the sum $S_{sp}25 + S_{sp}100$.

The characteristics of the samples are presented in Table 1. It is evident from the technical analysis that the amount of ash is very low; this is very important for the production of high-quality adsorbents.

Table 2 and Fig. 1 present the EPR results of initial and thermo-treated samples from apricot stones and the specific surface area, after treatment at 600-700°C for

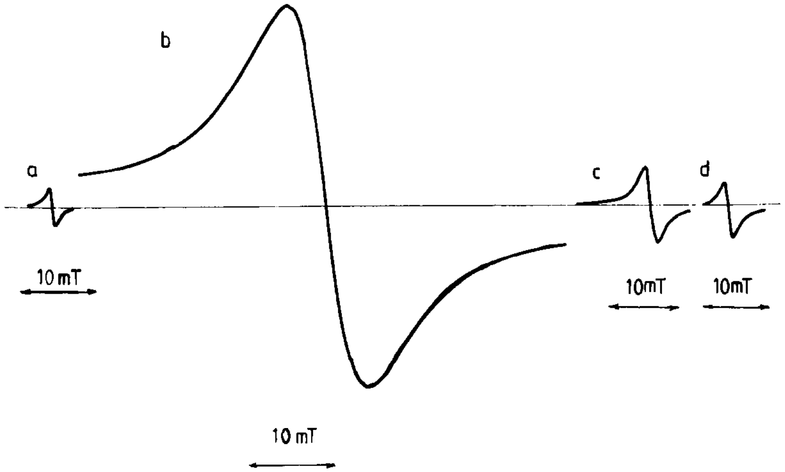

Fig. 1. EPR spectra of activated carbon prepared from apricot stones: a, initial sample; b, at 600°C; c, at 650°C; d, at 700°C, under the following conditions: CF (center field), 340 mT; G (gain), the same for all apricot samples; modulation (M), 0.125 mT; SW (sweep), 10 mT. Calculations for N, H_{pp} and g are made at various G values for the samples.

2 h. The data show that the increase in temperature leads to a considerable accumulation of PMCs in the thermo-treated samples. The concentration of PMCs increases considerably (approximately 164 times) at 600°C, which is the result of the accumulated high thermal energy, leading to the destruction of unstable bonds. Up to 600°C the temperature is the main factor in the destructive processes, while the water vapor exerts a stabilizing effect on the radicals obtained during the long treatment (2 h).

The measured values of S_{25} and S_{100} are low. A further rise in temperature to 650°C leads to a sharp increase in the specific surface area and a considerable decrease in the PMCs. Thus, both the temperature increase to 600°C and the interaction of water vapor with the treated material lead to the occurrence of chemical processes, as a result of which the stabilization of more radicals occurs, contributing to the production of a more highly developed active porous structure. The participation of water vapor in the radical mechanism of the process is confirmed by the high content of oxygen-containing components in the liquid products as well as by the high number of hydroxyl groups in the carbonizate [13]. The absence of water vapor leads to a sharp decrease of these values [13]. The reduction of PMC concentration beyond 650°C indicates the predominance of the recombinative and condensative processes which lead to the stable structures of the carbonizates at high temperatures. The final process in the formation of the adsorbent structure is probably complete above 700°C; this is supported by the still considerable level of PMCs at that temperature. The results of the study of PMC concentration and g-parameter show that the initial samples contain stable organic free radicals. In the untreated apricot stones, the g-values of the free radicals are quite high, indicating that the unpaired electron is somewhat delocalized on a heteroatom (oxygen) and that the species is probably an *ortho*- or *para*-semiquinone, which is coexistent with quinhydron and quinone moieties [14,15]. These results are important because they give experimental support to the free-radical mechanism in various processes. The value of the g-parameter falls to 2.0028 after thermal treatment; this value is characteristic of pure aromatic radicals [14,15]. The peak-to-peak linewidth, ΔH_{pp}, of the free radical signals in the case of apricot stones is 6.2 mT, narrowing after thermal treatment to 4.5 mT. Because the width of the EPR adsorption is determined primarily by hyperfine interactions between the unpaired electron spin of the carbon radical and the protons on the host molecule and adjacent molecules, reduction in the density of such protons as a result of dealkylation should reduce this line broadening.

The results of the investigation of the pyrolysis of almond shells are presented in Table 3 and Fig. 2. The mechanism of the change in PMC concentration and the formation of a porous structure in the temperature range 600–700°C have a similar dependence to that of apricot stones. The concentration of PMCs is highest at 600°C; the value obtained is higher than that of the apricot stones. A temperature increase to 700°C reduces the number of PMCs and results in an increase in S_{25}, with a tendency to reduce the relative number of the pores with small dimensions. The value of the g-parameter of almond shells, 2.0028, shows that the heteroatom (oxygen) does not participate in the molecular orbit of unpaired electrons to any

Table 3
EPR and adsorption parameter measurements of activated carbons prepared from almond shells

Temperature in °C	$N \times 10^{-17}$ in spin g^{-1}	g (± 0.0001)	ΔH_{pp} (± 0.01 mT)	$S_{sp}25$ in $m^2 g^{-1}$	$S_{sp}100$ in $m^2 g^{-1}$
Initial	4.20	2.0028	0.59	–	–
600	228.00	2.0025	0.54	156.0	17.5
650	36.00	2.0026	0.56	59.7	9.7
700	4.10	2.0025	0.56	246.0	15.2

considerable extent. Thermal treatment reduces the g-parameter to 2.0025, which is an indication of the formation of radicals of aromatic hydrocarbons.

The results in Table 4 and Fig. 3 present the process of the formation of an active adsorbent surface from grape seeds. They show that thermal treatment to 600°C leads to a great increase in the PMC concentration, which is considerably higher in comparison with almond shells and apricot stones at the same temperature. As distinct from the previous two adsorbents, increasing the temperature over 600°C considerably reduces the intensity of the destructive processes forming radical products because a sharp decrease in PMC concentration takes place at 650°C and

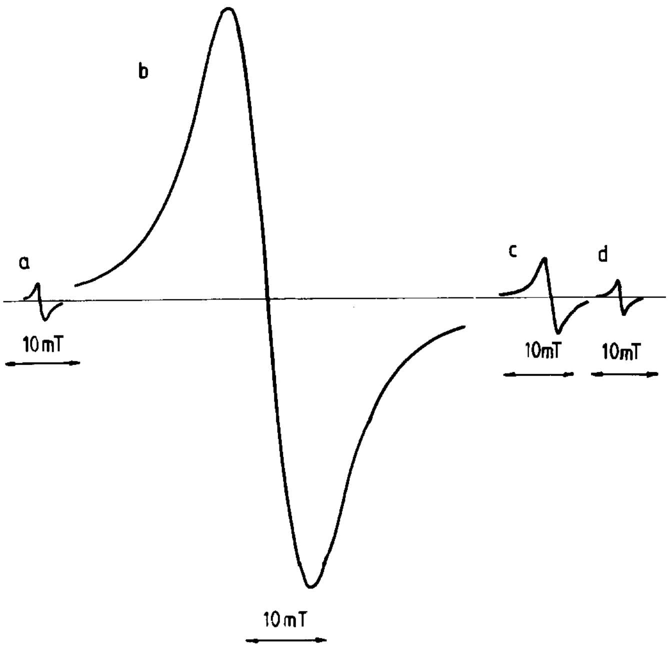

Fig. 2. EPR spectra of activated carbon prepared from almond shells: a, initial sample; b, at 600°C; c, at 650°C; d, at 700°C, under the following conditions: CF, 340 mT; M, 0.16 mT.

Table 4
EPR and adsorption parameter measurements of activated carbons prepared from grape seeds

Temperature in °C	$N \times 10^{-17}$ in spin g^{-1}	g (± 0.0001)	ΔH_{pp} (± 0.01 mT)	$S_{sp}25$ in $m^2\ g^{-1}$	$S_{sp}100$ in $m^2\ g^{-1}$
Initial	0.76	2.0037	0.60	–	–
600	320.00	2.0025	0.54	158.0	55.1
650	18.00	2.0026	0.54	25.0	84.0
700	19.20	2.0024	0.54	106.0	32.0

is unchanged to 700°C. The results of the investigation of the porous structure obtained from grape seeds reveal that the solid product obtained by pyrolysis up to 600°C is characterized by a larger pore volume and a larger specific surface area ($S_{25} + S_{100}$) compared to the products obtained from the other starting materials. It is obvious that the thermal destruction of the grape seeds in the presence of water vapor proceeds quite differently from that of the other materials. One of the reasons for the difference in the mechanism of the change in PMCs and the development of the porous structure of grape seeds in comparison with the previous two adsorbents might be the different cellulose and lignin contents in the initial materials, which, in the pure state, yield solid residues of various structures and adsorption characteristics. The content of lignin in grape seeds is 20% higher than that of cellulose. In the other raw materials these components are either equal or that of lignin is 10% larger. The value of the g-parameter is 2.0038, which shows that the oxygen is present in the molecular electronic orbit. After thermal treatment, the value of the g-parameter falls to 2.0028, and ΔH_{pp} decreases from 0.60 to 0.54 mT, which is a result of the formation of proton-poor aromatic structures.

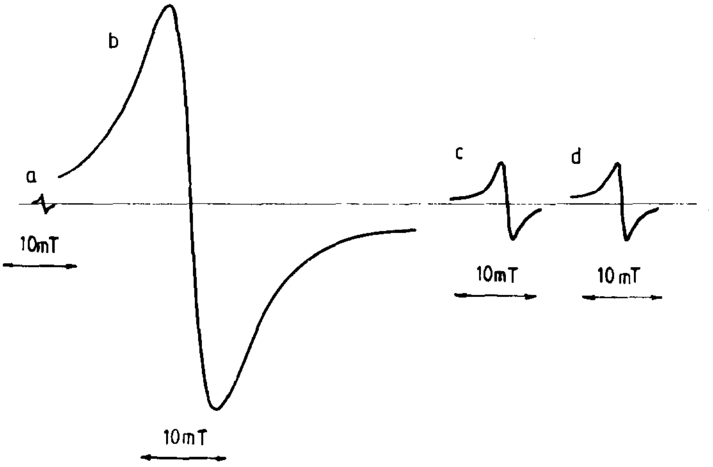

Fig. 3. EPR spectra of activated carbon prepared from grape seeds: a, initial sample; b, at 600°C; c, at 650°C; d, at 700°C, under the following conditions: CF, 340 mT; M, 0.125 mT.

Table 5
EPR and adsorption parameter measurements of activated carbons prepared from nuts

Temperature in °C	$N \times 10^{-17}$ in spin g^{-1}	g (± 0.0001)	ΔH_{pp} (± 0.01 mT)	$S_{sp}25$ in $m^2 g^{-1}$	$S_{sp}100$ in $m^2 g^{-1}$
Initial	3.80	2.0027	0.57	–	–
600	194.00	2.0026	0.54	252.4	91.8
650	389.00	2.0025	0.54	246.0	30.0
700	42.00	2.0024	0.52	333.0	19.3

Table 5 and Fig. 4 show the results of the pyrolysis of nuts in a stream of water vapor. The data from the change in PMCs show that the carbon material is very reactive with water vapor over a wider temperature range. Thus the highest PMC concentration is measured at the higher pyrolysis temperature, 650°C, and is twice as high as that at 600°C (comparable with almond shells and apricot stones). The same dependency was established for the development of the porous structure. The data reveal a considerable development of porous structure and the formation of a large surface area. The variations of S_{25} with the increase in temperature differ markedly from those of other adsorbents. At 600°C, S_{25} grows considerably and continues to show the largest value over the whole temperature interval compared to those from the other starting materials.

The data from EPR and the adsorption investigation for the sample of coconut are presented in Table 6 and Fig. 5. They show that this material possesses the highest reactivity, evidence for which are the largest concentration of PMC and the more developed porous structure. The measured PMC concentration of coconut

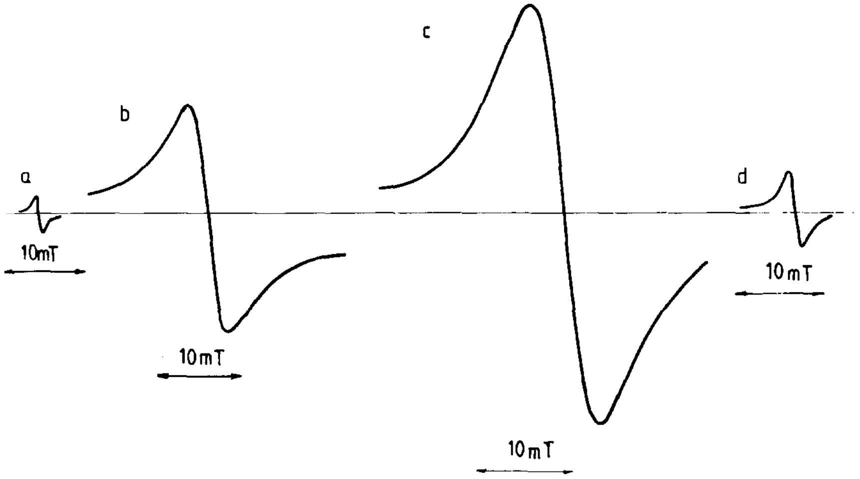

Fig. 4. EPR spectra of activated carbon prepared from nuts: a, initial sample; b, at 600°C; c, at 650°C; d, at 700°C, under the following conditions: CF, 340 mT; M, 0.125 mT.

Table 6
EPR and adsorption parameter measurements of activated carbon prepared from coconuts

Temperature in °C	$N \times 10^{-17}$ in spin g^{-1}	g ($\pm$0.0001)	ΔH_{pp} ($\pm$0.01 mT)	$S_{sp}25$ in $m^2\ g^{-1}$	$S_{sp}100$ in $m^2\ g^{-1}$
Initial	3.10	2.0029	0.55	–	–
600	772.00	2.0026	0.47	186.0	16.7
650	194.00	2.0027	0.50	114.0	14.2
700	19.00	2.0025	0.42	469.2	15.2

shells on pyrolysis in water vapor is highest at 600°C, and it is three times the values of apricot stones, almond shells and grape seeds, and twice that of nut shells (650°C). The activated carbons obtained from coconut and nut shells exhibit high constant values of S_{25} for all pyrolysis temperatures and higher concentrations of paramagnetic centers. The activity of large amounts of radical structures, favored by the presence of water vapor, leads to the formation of well-developed porous structures inside the larger part of the grains. The g-parameter and H_{pp} of nut and coconut shells are similar to those of almond shells, and their changes during pyrolysis are also similar.

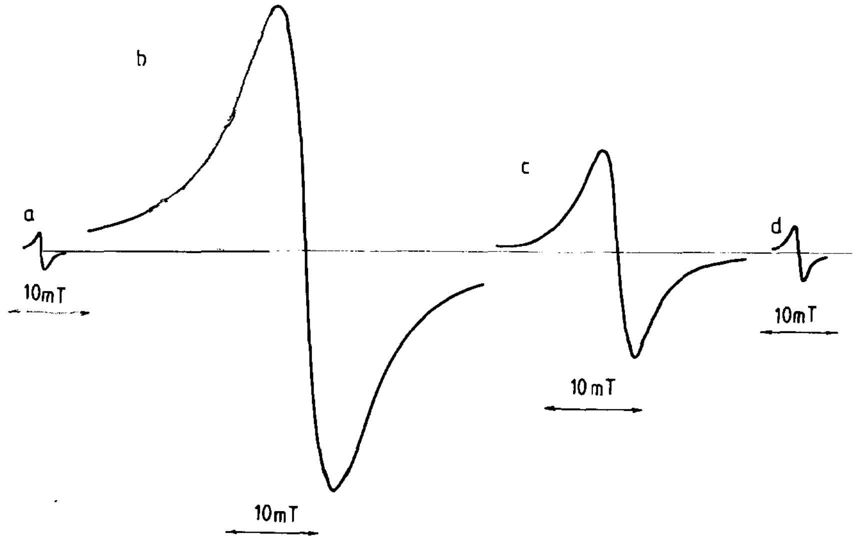

Fig. 5. EPR spectra of activated carbon prepared from coconuts: a, initial sample; b, at 600°C; c, at 650°C; d, at 700°C, under the following conditions: CF, 340 mT; M, 0.125 mT.

4. Conclusions

The present investigations on the mechanism of pyrolysis of agricultural by-products in the presence of water vapor and the active surface of the carbonizates formed show that not only are temperature and the composition of the initial material important, but that the water vapor is also a significant factor in the formation of active surfaces. Their thermal treatment in the presence of water vapor leads to physico-chemical changes in the structure of the materials, as a result of which carbonizates with aromatic structures and porous structures are formed. The results of the EPR investigations show that the samples are destroyed by aromatic radical species, which probably become stable and neutral by reaction with other radicals, non-radical particles or by transportation by the hydrogen of the water vapor. The radical reactions are progressive with the increase in temperature; the level of free radicals depends on the competitive effects of free-radical formation and deactivation of the radicals. A relation is established between the development of the porous structures and the formation and accumulation of the radicals during the process of pyrolysis in a stream of water vapor.

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