

ADSORPTION PROPERTIES OF BIFUNCTIONAL SORBENTS
OBTAINED BY MICROWAVE CARBONIZATION
OF APRICOT KERNEL SHELLS

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The results of studying the physicochemical and sorption properties of bifunctional sorbents obtained by chemical and electrochemical oxidation of the surface of carbonizates of apricot kernel shells are presented. It was shown that sorbents based on carbonizates obtained by microwave carbonization of shells, in comparison with sorbents obtained in the traditional way, are characterized by a more uniform pore distribution and a larger specific surface area and adsorption capacity.

Keywords: microwave carbonization, bifunctional sorbents, oxidized coals, sorption of heavy metals.

Introduction. Adsorption and ion exchange processes, along with traditional fields of application, are now widely used in the food industry – for cleaning various biological fluids from toxins, neutralizing wastewater and in other areas [1, 2]. Currently, many methods have been developed to produce a variety of carbon sorbents based on vegetable raw materials, having a high sorption capacity and selectivity with respect to certain adsorbents. Considering that as global environmental degradation and environmental pollution by various technogenic emissions – pesticides, compounds of heavy metals and other toxins, the demand for new cheap and highly selective sorbents has increased sharply, questions about the development of new multi-functional carbon highly selective sorbents are in the sphere of interest not only to researchers, but also to other food specialists, pharmacists, ecologists and others.

This report presents some research results on the development of a new method for producing bifunctional carbon sorbents from the shell of fruit and berry seeds, which are a large-tonnage waste of the food industry, in particular in Armenia.

Materials and Method. Carbonization of pre-washed with water, dried at a temperature of 120°C and crushed (particle size of about 1 mm) apricot kernel shells (AKS) was carried out as a direct heating method in an electric furnace in a rotating quartz reactor in a stream of air or nitrogen (flow rate 0.1–0.5 L/min with a programmed heating mode at a speed of 50°C/h in the temperature range 200–700°C) [3], and in a microwave oven Samsung CE1073AR brand, redesigned for chemical processes in a stream of air, nitrogen or other gas (Fig. 1). The microwaves frequency is 2.45 GHz, and the microwave power is 900 W. After reaching the required temperature, the samples were removed from the reactor, cooled in a desiccator to room temperature, weighed and determined by mass loss.

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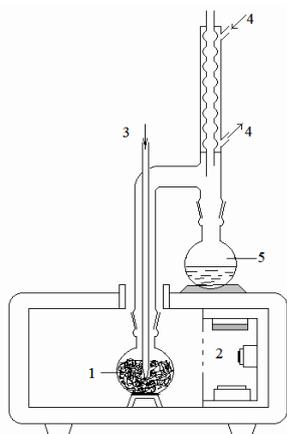


Fig. 1. The scheme of the installation for producing carbonizates microwaves: 1 – Shredded raw materials; 2 – node microwave radiation; 3 – supply of gas or air; 4 – reflux water condenser; 5 – resin collector.

The AKS carbonizates were oxidized with 10–50% hydrogen peroxide solutions at room temperature with vigorous mixing with a magnetic stirrer. After drying the samples at 105°C, the content of oxygen-containing surface functional groups on the surface of oxidized coals was determined by selective neutralization according to the procedure described in [4].

IR absorption spectra were obtained with a SPECORD 75 IR spectrophotometer in the region of 4000–400 cm^{-1} . Samples of sorbents in the form of thin plates were obtained by pressing a mixture with KBr in a mass ratio of 1: 200.

Sorption of Cu^{2+} ions under dynamic conditions was carried out by passing through a layer of 10 g of a sorbent of a solution with a concentration of Cu^{2+} ions of 5 mmol/L at pH 5.

Results and Discussion. Tab. 1 shows the data describing the dynamics of the mass loss of

the original AKS during heating in the usual way (in a rotary kiln) and in a microwave oven with reflux condenser. As evidenced by the data, at all heating temperatures, the mass loss during heating in a microwave oven is much lower. As a result, the yield of the final carbonizate at 500°C is 31.6 and 53.2%, and at 700°C it is 23.5 and 35.2%, respectively.

Table 1

The dynamics of mass loss during heating of the original AKS

$t, ^\circ C$	m_0, g	After heating, m_1, g		$\Delta m, g$		Mass loss, %	
		electric oven	microwave oven	electric oven	microwave oven	electric oven	microwave oven
200	10.00	9.48	9.85	0.52	0.15	5.2	1.5
300	9.48	4.50	6.48	5.50	3.52	55	35.2
400	4.50	3.48	5.32	6.52	4.68	65.2	46.8
500	3.48	3.16	4.15	6.84	5.85	68.4	58.5
600	3.16	2.54	3.85	7.46	6.15	74.6	61.5
700	2.54	2.35	3.52	7.65	6.48	76.5	64.8

Table 2

The main physical and chemical characteristics of AKS carbonizates, obtained in a stream of nitrogen at 700°C

Characterization	Carbonization Method	
	ordinary	microwaves
Aranovich specific surface area, m^2/g	175 ± 5	215 ± 5
The average pore diameter, nm	14 ± 3	18 ± 3
Pore volume in water, cm^3/g	0.35 ± 0.05	0.48 ± 0.05
Mechanical crushing strength, kg/cm^2	32 ± 3	43 ± 3
Bulk density, kg/m^3	420 ± 5	415 ± 5
Sorption capacity for iodine, mg/g	30 ± 3	35 ± 2
Sorption capacity according to methylene blue, mg/g	15 ± 2	17 ± 3
Ash content, %	2.1 ± 0.2	2.8 ± 0.2

The resulting carbonizates also differ significantly in the basic physico-mechanical and sorption characteristics (Tab. 2). As evidenced by the data, surface area, pore volume, and sorption capacity of carbonizates obtained by heating the feedstock in a microwave oven are significantly higher compared to carbonizates obtained by heating in a conventional rotary kiln.

Table 3

The results of oxidation of the surface of AKS carbonizates, obtained at 700°C, with hydrogen peroxide solutions

H ₂ O ₂ , %	The content of functional groups, mmol/g							
	total		-COOH		lactone		phenolic	
	AKS carbonization method							
	ordinary	microwaves	ordinary	microwaves	ordinary	microwaves	ordinary	microwaves
10	0.50	0.56	0.15	0.08	0.17	0.28	0.18	0.20
15	0.54	0.55	0.25	0.15	0.12	0.19	0.17	0.21
30	0.68	0.55	0.43	0.22	0.11	0.15	0.14	0.18
45	0.56	0.50	0.45	0.25	0.08	0.10	0.03	0.15
50	0.51	0.44	0.43	0.24	0.08	0.12	0.04	0.08

It should be noted that during the carbonization of vegetable raw materials in the microwave oven, not only is the weight loss significantly reduced compared to heating in the usual way, but the amount of tar released is also reduced.

Tab. 3 shows comparative data on the specific content of various functional groups on the surface of carbonizates obtained by conventional heating and heating in a microwave oven. The results obtained indicate that when oxidized with a 30%

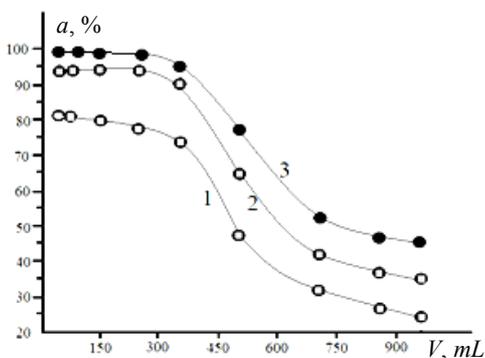


Fig. 2. Dependence of the degree of extraction of Cu²⁺ ions by various sorbents on the volume of the solution passed through the sorbent layer:

- 1 – carbonizate obtained in the usual way;
- 2 – microwave carbonizate;
- 3 – oxidized microwave carbonizate.

hydrogen peroxide solution, the content of functional groups contained on the surface of the carbonizate obtained by conventional heating reaches 0.68 mmol/g, and in the case of carbonizate obtained in the microwave up to 0.55 mmol/g. Moreover, while in terms of the content of surface acid groups, the carboxyl groups obtained by ordinary heating are to a certain extent superior to carboxyl groups obtained by microwave heating of AKS, then in terms of the content of surface lactone and phenolic groups, they are significantly inferior to them. This regularity is also preserved during oxidation of the surface of ordinary and microwave carbonizates (Tab. 3). In the oxidation of microwave carbonizate with a 10% hydrogen peroxide solution, the content of lactone and phenolic surface groups is 0.28 and 0.20 mmol/g, and in the case of ordinary carbonizates, they are 0.17 and 0.18 mmol/g, respectively. As a result of this, the bifunctional oxidized sorbents obtained by microwave treatment of AKS, in terms of the dynamic sorption of Cu²⁺ ions (Fig. 2), significantly exceed the sorbents obtained by the traditional method.

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According to the IR spectra of the microwave carbonizate (Fig. 3), the oxidized sorbent before and after sorption of Cu^{2+} ions, the presence of aromatic fragments on their surface is typical.

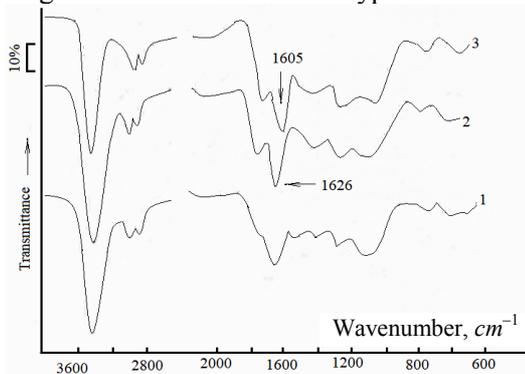


Fig. 3. IR spectra of AKS carbonizate (1), after oxidation of its surface with hydrogen peroxide (2) and after limiting sorption of Cu^{2+} ions on an oxidized sorbent (3).

This is evidenced by the presence of an absorption band (a.b.) at 2927 cm^{-1} , characteristic of stretching vibrations of $-\text{C}-\text{H}$ groups, as well as a.b. at 1034 and 1054 cm^{-1} , characteristic of deformation vibrations of the $\text{C}=\text{C}$ groups of the aromatic nucleus. In addition, a.b. at 1626 cm^{-1} , characteristic of $-\text{C}=\text{O}$ carbonyl groups of aromatic and aliphatic acids, esters and lactones. All spectra contain fairly intense a.b. at 3431 cm^{-1} , characteristic for stretching vibrations of surface $-\text{OH}$ groups.

An analysis of the above IR spectra reveals that the oxidation of carbonizates by various oxidizing agents does not lead to significant changes. However, a significant increase in the number of surface functional groups (aromatic and aliphatic acids, their esters and lactones) does not appear in the IR spectra, since their concentrations are quite small. In the case of sorption of Cu^{2+} ions, the intensities of a.b. $-\text{C}=\text{O}$ is shifted toward lower frequencies (about 1605 cm^{-1}). This may indicate that the sorption of Cu^{2+} ions proceeds mainly due to the formation of complexes with surface carboxyl groups. Apparently, sorption of Cu^{2+} ions due to exchange with acidic surface protons does not occur, since no changes in the IR spectrum are observed in the absorption region of surface $-\text{OH}$ groups.

Thus, based on the data obtained, it can be concluded that carbon bifunctional sorbents obtained by microwave carbonization of vegetable raw materials, in particular the shells of fruit and berry seeds, are not only characterized by the best physicochemical and sorption properties, but also are easily susceptible to surface – oxidation by conventional oxidizing agents, and oxidation by the electrochemical method [3].

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REFERENCES

1. Pyanova L.G. Carbon Sorbents in Medicine and Proteomics. *Chemistry for Sustainable Development*, **19** (2011), 113–122 (in Russian).
2. Kamalyan O.A., Sargsyan A.V., Kamalyan T.O. *Activated Carbons from Grape Seed as Sorbents for Wine Purification*. Int. Conf. “Chemistry and Complete Processing of Forest Biomass”. Abstracts Dokl. Conf. St. Petersburg (2010), 44 p. (in Russian).
3. Mkhitarian S. Preparation and Study of Sorption Properties of Oxidized Sorbents from the Ossicles of Fruits and Berries. *Bulletin of Armenian National Agrarian University*, **4** (2018), 79–82.
4. Boem H.P. *Chemical Identification of Surface Groups*. In Book: Stereochemistry and Mechanisms of Catalytic Reactions. M., Mir (1968), 186–288 (in Russian).