

Obtaining Procedure and Properties of the Sorbents from Plant Raw Material

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Abstract

Physicochemical parameters of the synthesis of carbonized sorbents based on plant raw material are investigated along with the properties of these sorbents. The data of IR Fourier, ESR spectroscopy and electron microscopy are reported. It is stated that carbonized sorbents possess high specific surface and porosity. Carboxylic, carbonyl, hydroxyl groups are detected on the surface of the synthesized sorbents. It is assumed that high sorption ability with respect to Co, Ni, Pb, Cd, Cu ions is connected with the formation of chelate complexes.

INTRODUCTION

Carbonaceous adsorbents are widely used in various processes involving the purification and recovery of valuable substances from liquid and gaseous media. Active carbon is used in oil processing, petroleum chemistry, wine making, butter and fats production, *etc.* They are increasingly widely used in medicine, for example, to remove some components from physiological liquids and to purify blood [1, 2].

The urgency of ecological problems has increased the interest to the development of accessible adsorbents based on active carbon. Raw material for cheap carbonized samples (CS) of sorbents can be agricultural wastes, including kernels of fruit and nut shells. The production of CS is ecologically safe; the sorbents are easily recovered [3]. Kernel activated carbon is distinguished by perfect sorption properties; it is low-ash (ash content being ~0.2 %), contain small amount of sulphur (less than 0.1 %) *i. e.* meet the requirements to ecologically safe products [4–7]. Features of the structure of active carbon obtained from fruit kernel are almost

unknown. The goal of the present work is obtaining and investigation of carbonized sorbents based on the walnut shells (WS), grape (GK) and apricot (AK) kernel.

EXPERIMENTAL

We investigated the dependence of carbonization of walnut shells, grape and apricot kernels on temperature, nature of gas and of activating agent. The samples were carbonized according to the procedure developed at the Laboratory of Hybrid Technologies in the Institute of Combustion Problems, using a flow set-up within temperature range 250–900 °C in Ar flow (50–90 cm³/min) [8]. It is discovered that the major mass loss (Fig. 1) occurs within temperature range 200–500 °C; the largest amount of volatile and liquid products I released within the range 100–250 °C.

Physicochemical characteristics of the sorbents were investigated by means of modern methods (IR Fourier, ESR spectroscopy, X-ray phase analysis, electron microscopy). IR

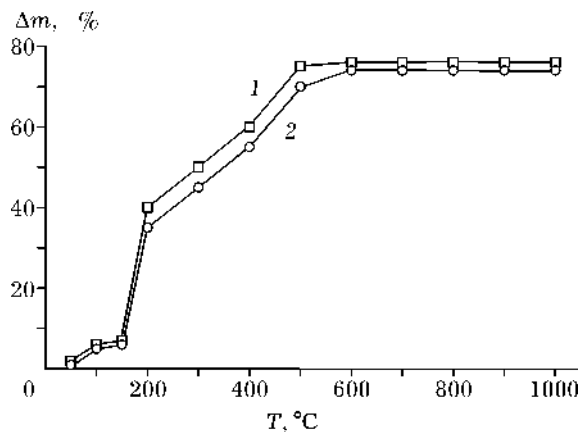


Fig. 1. Dependence of carbon mass loss on carbonization temperature: 1 - walnut shells, 2 - grape kernels.

spectra of the samples under investigation were recorded with UR-20 and Mattson IR spectrometers (USA) with Fourier transform, in tablets pressed with KBr [9, 10].

X-ray phase analysis (XPA) of carbonized samples was performed with DRON-3M diffractometer at the accelerating voltage of 35 kV, using tubes with copper cathode. Recording was performed at a rate of 2 deg/min within angle range 5 to 50°. The samples were crushed into powder and placed on glass cuvettes greased with Vaseline.

The specific surface of sorbents was determined by thermal desorption procedure based on the measurement of thermal conductivity of gas flow (helium or argon) passing through the tubes with the samples [11]. The apparent porosity was determined according to the procedure described in [12].

Electron microscopic investigation of the samples was performed with EM-125K instrument at the accelerating voltage of 75 kV. The instrument allows investigating samples at high voltage. A substrate film was prepared to be viewed in electron microscope. The powder was deposited onto the substrate film by two procedures: as a suspension, and by dry deposition. The samples were placed in sample holder and then in the electron microscope.

The absorption of heavy metal ions by carbonized samples was investigated by means of atomic absorption analysis (AAS-IN spectrometer). Propane-air mixture was used as a fuel-oxidizer system. The error was 2-3 %.

ESR spectra were recorded with IRS-1101 spectrometer of the homodyne type operating

in a 3 cm range (the frequency of magnetic field modulation was 500 kHz, the sensitivity of the instrument was 10^{11} spins per sample. The spectra were recorded at the modulation amplitude of magnetic field of 3 Oe, amplitude or magnetic field scanning 3500 Oe, scan time 10 min, accuracy 3 %.

RESULTS AND DISCUSSION

Investigation of carbonization process

It was discovered that the IR spectra of the liquid and solid phases formed during the carbonization of WS and GK contained characteristic absorption bands in the region of C=C bending vibrations of the aromatic ring (833 and 1050 cm^{-1}), absorption bands related to the stretching vibrations of the aromatic ring (1600, 1578, 1510 cm^{-1}), and the bands related to C-H stretching vibrations of the aromatic ring (3053, 3030 cm^{-1}). An increase of carbonization temperature leads to a sharp increase of the intensity of absorption bands related to aromatic condensed systems. This means that carbonization of agricultural wastes results in substantial changes in the structure of samples. The intensity of characteristic absorption bands related to C-H stretching vibrations of benzene ring at 730, 1380 and 1460 cm^{-1} increases by a factor of 3 with increasing carbonization temperature (from room temperature to 900 °C). A similar picture is observed in the region of the stretching vibrations of carbonyl, carboxyl (860-1299 cm^{-1}) and phenol (3200-3400 cm^{-1}) groups, bending vibrations of C-H groups of the aromatic ring (670 cm^{-1}) and C-CH₃ group (1365-1380 cm^{-1}). Absorption bands corresponding to the stretching (2870-2930 cm^{-1}) and bending (15530-1650 cm^{-1}) vibrations of NH₂ group have lower intensity at low carbonization temperature (by a factor of 2) than at 500 °C; after carbonization at 900 °C, the intensity of the corresponding bands increases by a factor of 3.

The IR spectra of the carbonized samples correspond to the compounds with carbonyl, carboxyl, phenol and amine groups, similarly to activated carbon. The IR spectra of the liquid phase and non-carbonized walnut shell have

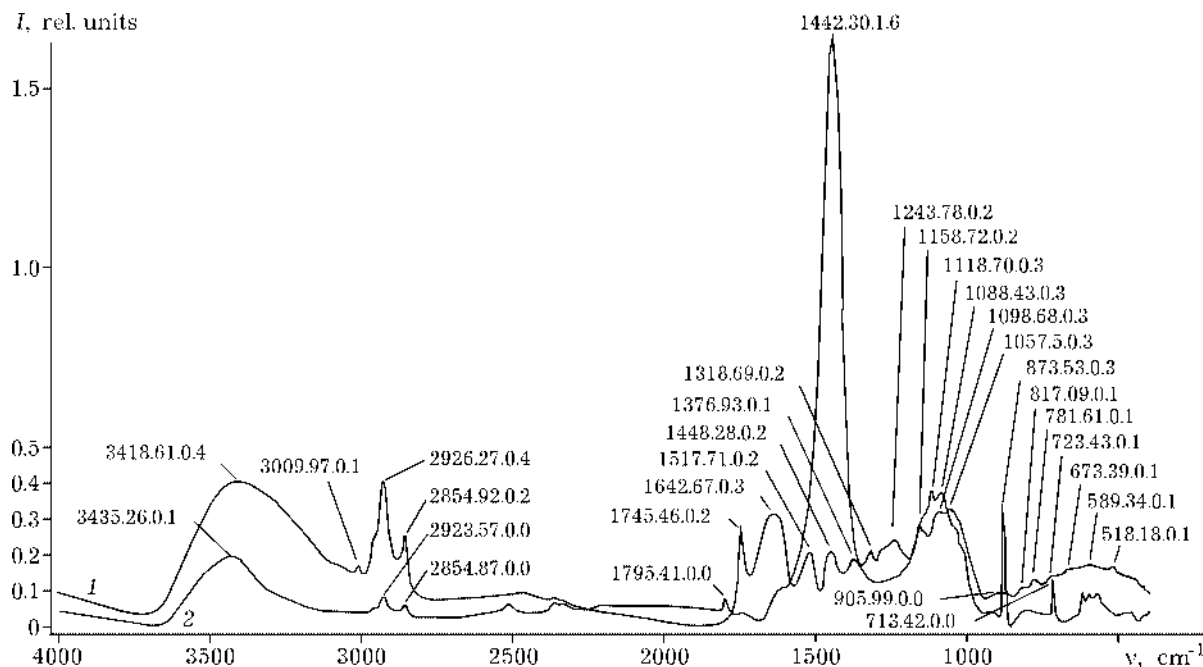


Fig. 2. IR spectra of grape kernels (1) and carbonized sorbent ($T = 850\text{ }^{\circ}\text{C}$) based on them (2).

intensive bands at 920, 940, 1120, 1180, 1200, 1280–1300 and 1360 cm^{-1} , corresponding to the characteristic absorption bands of the carbonyl group and disappear when carbonization temperature is increased from 500 to $900\text{ }^{\circ}\text{C}$. This confirms that the evolution of CO_2 occurs in this temperature region, *i. e.* carbonyl group decomposes.

The IR spectrum of CS obtained at $500\text{ }^{\circ}\text{C}$ on the basis of GK contains intensive absorption bands at 1340, 1380, and 1460 cm^{-1} , corresponding to the characteristic absorption bands of the stretching vibrations of C–H bonds of the aromatic ring, as well as the bands corresponding to bending (1590 and 1660 cm^{-1}) and stretching (2900 – 2970 cm^{-1}) vibrations of the NH_2 group. Thus, the spectrum of the carbonized sorbent based on grape kernel (at $500\text{ }^{\circ}\text{C}$) differs from the spectrum of CS of WS by the presence of more intensive bands corresponding to NH_2 group and C–H of the aromatic ring. It is stated that the intensity of absorption bands of C–O–C, COOH, C=O, CH_3 and CH_2 of the aromatic ring increases with increasing carbonization temperature. An increase of carbonization temperature leads to the increase of the intensity of bands related to the aromatic condensed systems.

Investigations performed with Mattson spectrometer showed that the spectrum of the

initial GK sample contained characteristic bands of OH and NH_2 groups in the region 3418.6104 cm^{-1} , and Ar– CH_3 groups in the region 3009.9701 cm^{-1} . Absorption bands at 2926.2704 and 2854.9202 cm^{-1} are related to the vibrations of symmetrical and asymmetrical CH_2 groups to C=O groups, 1517.7102 to COO, 1448.2802 to CH_2 , 1376.9301 to CH_3 , 1243.7802 and 1158.7202 to COOR, 1098.6803 and 1057.5703 to C–O–C (Fig. 2).

When GK is carbonized at a temperature of 600 – $850\text{ }^{\circ}\text{C}$, a sharp (10-fold) drop of the intensity of characteristic bands of OH and NH groups is observed. The intensity of characteristic C–O–C bands increases; bands related to CO_3^{2-} groups appear and increase the intensity substantially with temperature increase. We also observe the bands related to CO_2 group in the region 2486.1903 cm^{-1} .

Carbonization of apricot kernel proceeds similarly but the intensity of the corresponding bands is much lower.

Investigation of the structure of carbonized sorbents

It is stated by means of IR spectroscopy that the basis of the structure of carbonized sorbents is formed by aromatic condensed sys-

TABLE 1

Specific surface and pore size in carbonized samples at different temperature

Sorbent	T, °C	Size, μm			S_{sp} , m^2/g
		Macropores	Mesopores	Micropores	
WS	300	25	12	1.8	250
	500	30	13	2.3	770
	600	30	16	2.4	780
	700	30	16	2.3	800
	800	28	14	1.7	830
	850	29	15	2.4	800
GK	300	18	12	3	200
	600	22	14	6	500
	700	27	15	7	530
	800	25	13	5	540
	850	26	14	6	500

tems. Investigation by means of XPA shows that the dimensions of microcrystallites increase with temperature increase to 950 °C (crystal height increases from 7.62 to 8.56 Å crystal length increases from 34.54 to 41.76 Å); interplane distance decreases from 4.1 to 3.84 Å. This proves the destruction of cellulose structure in the walnut shell and grape kernel during their thermal treatment; this is also evidence of densifying the carbonizate structure.

It is demonstrated that the size of macro-, micro- and mesopores increases and specific surface increases with rising carbonization temperature. Carbonized sorbents based on walnut shell and grape kernel possess macro- and mesoporous structure (Table 1), which is preferable for the adsorption of large molecules [13].

The obtained results are in agreement with the data of Bulgarian scientists [2, 14]. One

can see in electron-microscopic images (Fig. 3) that carbonization can allow one to obtain a developed structure with larger specific surface and porosity than that of the initial samples. An electron microscopic image of the GK sample carbonized at 800 °C is shown in Fig. 3, a; the porous structure of the sample is seen. The images of WS impregnated with copper and cadmium solutions are shown in Fig. 3, b, c. Carbon fibres with metal inclusions are observed.

According to the data reported in [2], the highest specific surface was exhibited by active carbon based on apricot kernel (820 m^2/g); micropore volume was 0.46 cm^3/g , mesopore volume was 0.04 cm^3/g (macropores were absent in this case). One can see in Table 1 that the specific surface and size of pores increase with increasing carbonization temperature to 700 °C; however, further increase of tempera-

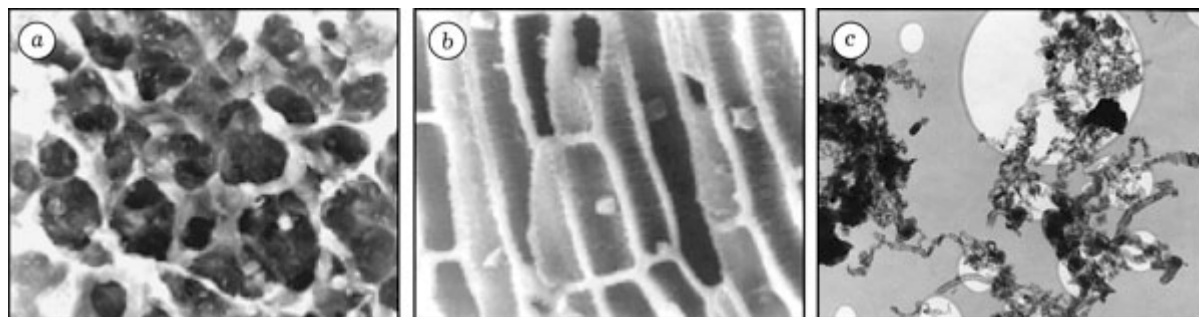


Fig. 3. Electron-microscopic images of carbonized sorbents: a - GK (magnification 1000); b - WS + Cu^{2+} (magnification 120 000); c - WS + Cd^{2+} (magnification 120 000).

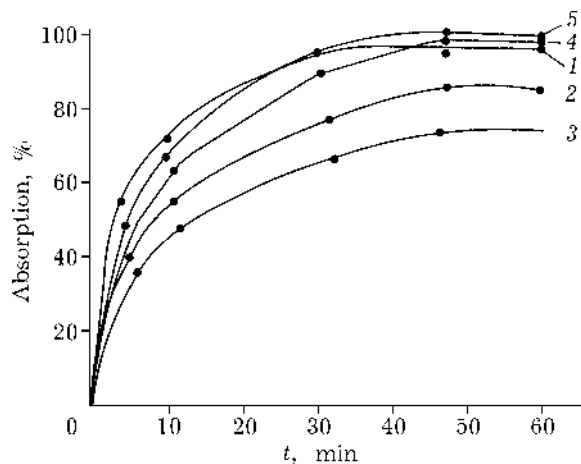


Fig. 4. Curves of metal ion absorption by carbonized sorbent based on WS: 1 - Pb^{2+} , 2 - Co^{2+} , 3 - Ni^{2+} , 4 - Cd^{2+} , 5 - Cu^{2+} .

ture causes the decrease of these parameters. A decrease of specific surface is connected with the increase of the density of carbonized sample according to the data of [14].

Sorption ability of carbonized samples

We investigated sorption of heavy metal ions: Pb^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Cu^{2+} . After contact for 30 min, sorption reaches its maximum about 100 % (except nickel and cobalt) (Fig. 4) and comes to a plateau. An important characteristics of the sorbents is their ability to ab-

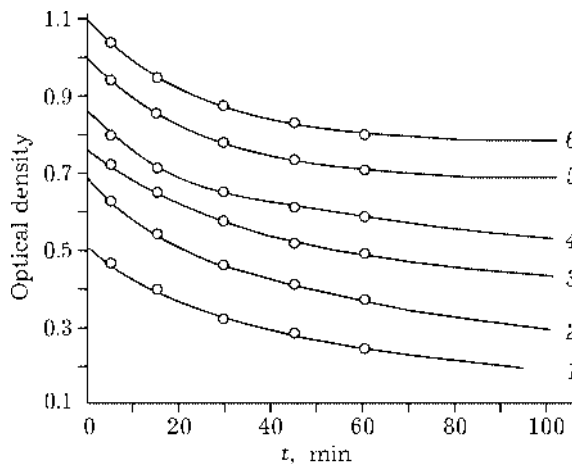


Fig. 6. Dynamics of carotene absorption by WS-based carbonized sorbent from solutions with different concentrations. H_2O /carotene, ml: 0.5 : 9.5 (1), 1 : 9 (2), 2 : 8 (3), 3 : 7 (4), 4 : 6 (5), 5 : 5 (6).

sorb iodine, methylene blue (Fig. 5) and carotene (Fig. 6). Sorption activity with respect to iodine was determined using the procedure described in [15]. One can see in Figs. 5, 6 that the sorption ability of samples increases with increased carbonization temperature. The obtained carbonized sorbents based on plant raw material are characterized by large iodine number and high bleaching ability.

The carbonized sorbent activated with acid possesses high sorption ability to iodine and methylene blue. Table 2 shows the adsorption

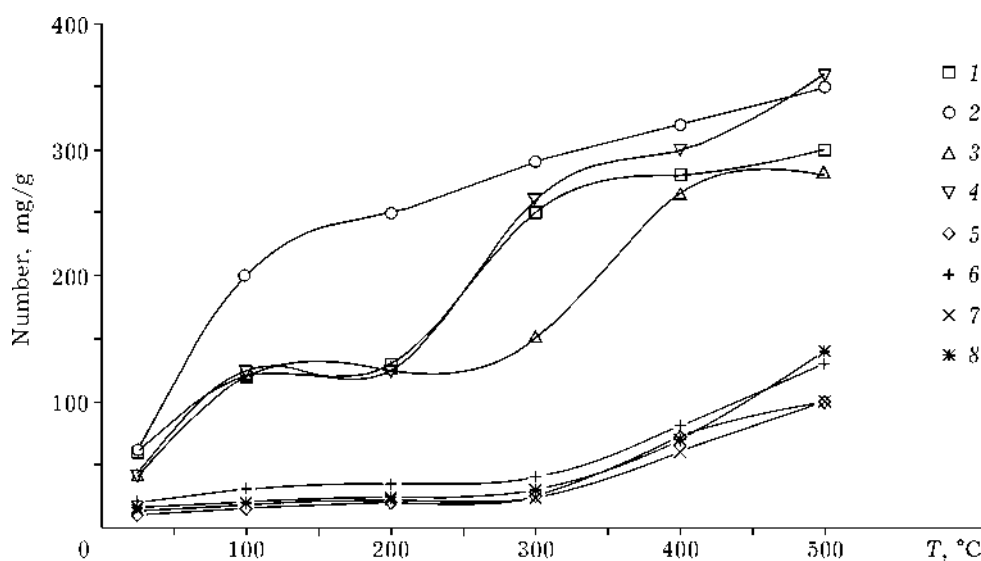


Fig. 5. Absorption of iodine and methylene blue by carbonized sorbents based on GK (1, 4, 5, 7) and WS (2, 3, 6, 8) without (3, 4, 7, 8) and after (1, 2, 5, 6) treatment with acid: 1-4 - iodine number, 5-8 - methylene number.

TABLE 2

Adsorption characteristics of CS based on apricot kernels

T_{carb} , °C	Time, h	S_{sp} , m ² /g	Iodine number, mg/g	Methylene number, mg/g
600	1	310	350	30
600	2	475	505	80
600	3	575	600	135
650	1	520	490	145
650	2	710	665	160
650	3	735	730	185
700	1	645	600	190
700	2	820	895	285
700	3	785	880	205

characteristics of carbonized sorbents on the basis of apricot kernel.

High sorption ability is determined by large specific surface and porous structure of sorbents (the presence of a large number of macro-, meso- and micropores), as well as by chemical interaction with the surface functional groups present in carbonized samples. Poorly dissociated compounds (surface complexes of chelate type) shown in Fig. 7 can be formed by the substitution of hydrogen ions in one, two

or three closely located carboxyl or carbonyl and phenol groups.

One can see comparing the obtained experimental data that the highest sorption ability is exhibited by CS based on walnut shells, while the lowest one is exhibited by the CS based on apricot kernel, which is likely to be connected with high density of samples. CS based on apricot kernel can be used to absorb chlorine and iodine ions, which is the subject of further investigations.

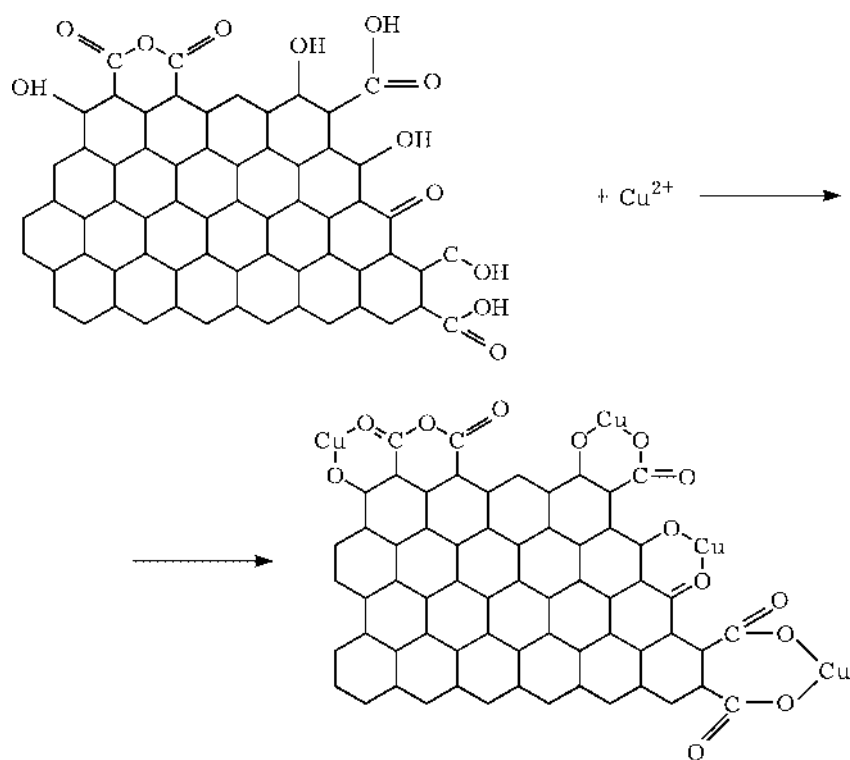


Fig. 7. The chelate complex.

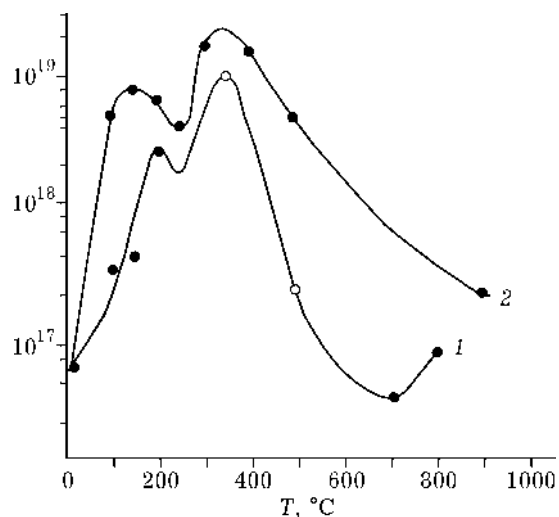


Fig. 8. ESR spectra of carbonized sorbents based on GK (1) and WS (2).

Paramagnetic properties of carbonized samples

We recorded ESR spectra of walnut shells, grape and apricot kernel, and their carbonized samples. It is stated that the carbonized samples possess paramagnetic properties. The sorbent based on apricot kernel exhibits high intensity of the signal with line width of $\Delta H = 5.1\text{--}72$ Oe. The concentration of paramagnetic centers in initial samples is approximately the

same $((2.5\text{--}3.0) \cdot 10^{16}$ spin/g). Thermal treatment at 300°C increases it by three orders of magnitude ($1.4 \cdot 10^{19}$), while at 400°C it is increased insignificantly. Further increase of temperature causes a decrease of the concentration of paramagnetic centers (Fig. 8).

The ESR spectrum of carbonized sorbent with the absorbed copper ions contains two lines. One of them is broad; it relates to the complex of metal with carbon ($\Delta H = 230$ Oe and $N = 1.6 \cdot 10^{19}$ spin/g), while the second one is narrow; it is due to the free radicals of carbon remaining unbound after the formation of complex ($\Delta H = 8$ Oe and $N = 4.6 \cdot 10^{16}$ spin/g). The ESR spectrum of carbonized sorbent with cadmium ions adsorbed in it contains two lines, too: a broad one with $\Delta H = 140$ Oe and $N = 1.1 \cdot 10^{19}$ spin/g (complex) and a narrow one with $\Delta H = 5.6$ Oe and $N = 4.7 \cdot 10^{16}$ spin/g (carbon radicals) [16].

The IR spectrum of carbonized sample of grape kernel after the sorption of Co^{2+} ions for 60 min is shown in Fig. 9. An increase of the intensity of characteristic bands related to the absorption by chelate complexes in the region of 2924.50 and 2853.89 cm^{-1} confirms the data of ESR spectra and is evidence of chemical interaction during the sorption of metal ions

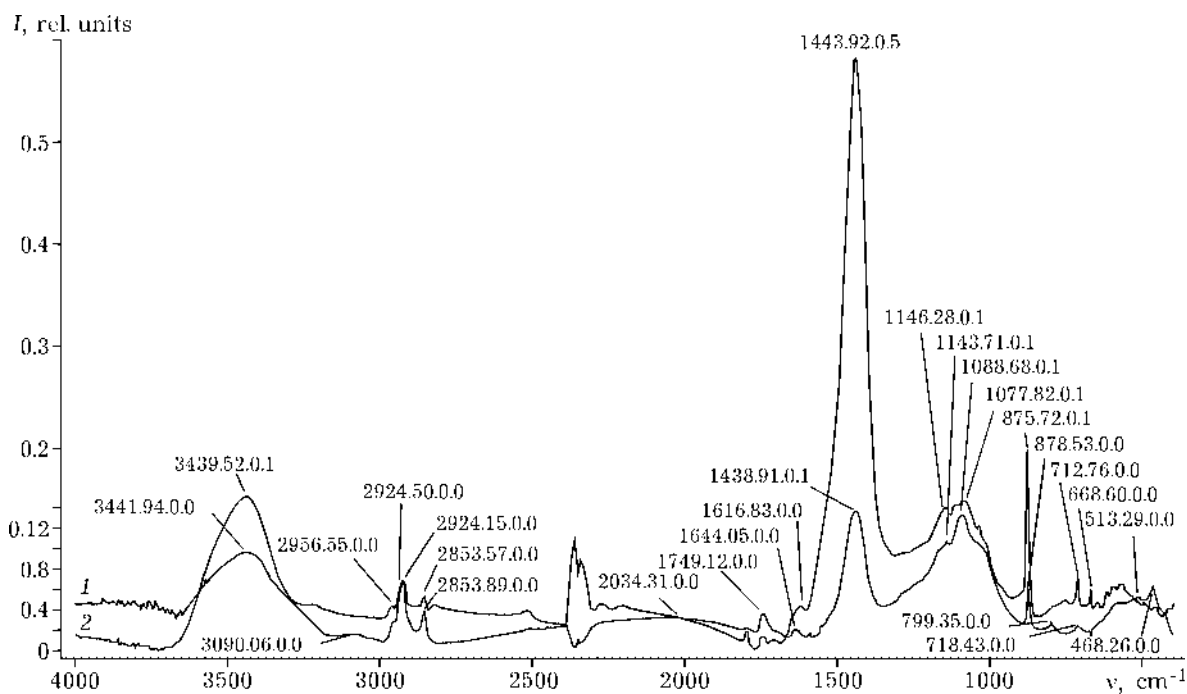


Fig. 9. IR spectra of the GK-based carbonized (750°C) sorbent (1) and the chelate complex (2)

by carbonized sorbents, *i. e.* the formation of chelate complexes.

CONCLUSIONS

Thus, the investigations confirm the possibility to obtain efficient carbonized sorbents from agricultural wastes of plant origin. Carbonized sorbents based on walnut shells, grape and apricot kernels are efficient absorbers for heavy metal ions and organic compounds since they possess large specific surface, high porosity, and have reactive surface groups including carboxyl, carbonyl, phenol, amine, hydroxyl ones.

An advantage of the considered method of obtaining the sorbents is the use of agricultural wastes of plant origin, ecological safety and high sorption ability of the carbonized sorbents.

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