# Pore structure and adsorption properties of stone active carbons prepared by physicochemical and chemical activation methods

**T. G. Lupascu,[a] G. A. Petukhova,[b]★ P. I. Nastas,[a] and N. S. Polyakov[b]†**

[a]*Institute of Chemistry, Academy of Sciences of the Republic of Moldova,*
*3 ul. Akademicheskaya, 2028 MD Chisinau, Moldova.*
*Fax: (3732 2) 73 5490. E-mail: tlupascu@mail.md*
[b]*A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences,*
*31 Leninsky prosp., 119991 Moscow, Russian Federation.*
*Fax: +7 (495) 952 5308. E-mail: larin@phyche.ac.ru*

Active carbons (ACs) with diverse microporous and developed mesoporous structures were prepared by chemical and phisochemical activation methods from walnut shells, fruit stones, and grape seeds. The surface chemistry was studied by chemical titration and spectroscopy in the IR, UV, visible, and near-IR regions. The ACs prepared by chemical activation contain carboxyl and phosphate groups, which impart acidic properties to the surface. Basic functional groups are mainly formed on the ACs prepared by physicochemical activation. The AC surface has a complicated chemical composition, which results in high adsorpion activity.

**Key words:** stone active carbons, physicochemical and chemical activations, pore structure, surface chemistry, adsorption properties.

Active carbons (ACs) obtained from walnut shells, fruit stones, and grape seeds find wide use in the purification of drinking water and detoxication of the human organism.[1—6] They are usually characterized by favorable sorption properties and mechanical strength and low ash and sulfur levels. These characteristics provide prospects for using the stone ACs in multicycle adsorption—desorption processes, for example, in food industry and medicine. As a rule, the ACs prepared from stone raw materials have rather uniform microporous structures. In the present work, we attempted to prepare the ACs containing a wide set of internal pores and study their physicochemical and adsorption properties.

## Experimental

Walnut shells, plum and peach stones, and grape seeds were used as raw materials for the preparation of active carbons. The initial raw materials are characterized in Table 1.

Active carbons were prepared by physicochemical and chemical activation procedures under laboratory conditions. The physicochemical activation of the carbonizate was conducted in a laboratory setup, whose scheme is given in Fig. 1. The carbonizate of fruit stones or walnut shells was placed into reactor *6*. The temperature regime was specified by control desk *8*. Activation was carried out for 2 h at 850—900 °C. Rotation of the reactor was initiated by electric engine *5* with a specified rate, usually being 20—25 rpm. The activating fluid was heated in glass flask *2* using burner *1*. Aqueous solutions (5%) of sulfurous anhydride or ammonia were used as the activating fluid. The vapor that formed passed through the reactor where the carbonizate was activated. The consumption of the fluid per weight unit of the carbonizate was 5 : 1. Using this procedure we prepared the ACs CAP-7 (from peach stones by activation with a 5% ammonia solution) and CAP-8 (from peach stones by activation with a 5% solution of sulfurous anhydride).

Chemical activation was carried out as follows. Walnut shells, plum stones (fractions 2—4 mm), or grape seeds were placed in a glass. Concentrated orthophosphoric acid was added, and the sample was impregnated with periodical stirring of the suspension for 48 h. The resulting material was heated for 2 h in a muffle furnace at 350 °C. Then the obtained AC was washed off from a residue of orthophosphoric acid in the Soxhlet apparatus until the removal of phosphate ions was complete. The washed-off AC was dried to constant weight in an oven at 120 °C. The active carbons CAN-7 (from walnut shells), CAPr-1 (from plum stones), and CAS-4 (from grape seeds) were thus prepared.

The ACs were studied by different methods to determine physical, physicochemical, chemical, and pore structure characteristics of ACs. The elemental analysis data, yields, and ash levels of the samples under study are given in Table 2.

As can be seen from the data in Table 2, the yield of the prepared AC product is fairly low, being 38—48%. The prepared ACs can be classified as low-ash (their ash content is not higher than 7%). This provides prospect for their use in diverse adsorption processes that require special purity of the adsorbent, because the ash and its ingredients (mineral admixtures) catalyze many undesirable reactions. The data in Table 2 show that phosphate groups were incorporated into the AC matrix during acti-

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† Deceased.

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**Table 1.** Characteristics of the initial plant raw materials for the preparation of the active carbons

| Name of initial raw materials | Moisture content | Ash level | Elemental composition* (%) | | |
|---|---|---|---|---|---|
| | % | | C | H | N |
| Walnut shells | 5.2 | 0.50 | 47.41 | 6.07 | — |
| Plum stone shells | 7.0 | 0.25 | 46.75 | 6.47 | — |
| Peach stone shells | 9.9 | 0.30 | 43.91 | 5.73 | — |
| Grape seeds | 5.2 | 2.77 | 51.85 | 6.53 | 3.62 |

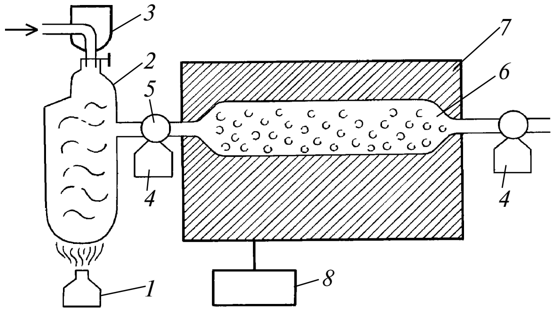


**Fig. 1.** Scheme of the laboratory setup for the preparation of active carbons: *1*, gas burner; *2*, glass flask for activating fluid; *3*, vessel for activating fluid; *4*, metallic support; *5*, electric engine; *6*, quartz or stainless-steel reactor; *7*, electric furnace; *8*, control desk.

vation with orthophosphoric acid, activation with sulfurous anhydride resulted in the incorporation of sulfur-containing groups, and nitrogen disappeared completely when ACs were prepared from grape seeds.

The parameters of the AC pore structure were determined from isotherms of equilibrium adsorption of the benzene vapor at 293 K. The isotherms of benzene vapor adsorption were measured in a sorption setup[2] in an interval of relative pressures of $10^{-6}$—1.0. All samples were pre-evacuated at 673 K and $10^{-4}$ Pa to constant weight.

Since the ACs contain mineral components and surface oxygen-containing carbon compounds, they can exert a considerable effect on the pH of aqueous systems. In medicine and food industry ACs are used for the treatment of various pH-sensitive substances and, hence, we determined the hydrogen factor of aqueous solutions of ACs as an important criterion for the purposeful choice of the region of application of adsorbents. The AC surface contains chemically bound oxygen, which, depending on the methods and conditions of preparation, forms surface chemical compounds of different acidity. The method of inverse titration[7] was used to characterize different functional groups of the acidic ($N_t^A$) and basic character ($N_t^B$). To obtain a more detailed characterization of the nanopore distribution in the ACs, the pore structure was estimated by comparing the results of measurements with benzene and other adsorptives. Adsorption of methylene blue, whose molecule have relatively large linear sizes, and iodine provides evidence of the fraction of the AC surface formed by pores exceeding 1.5 nm in diameter. Methylene blue was adsorbed according to a standard procedure[8] from a 0.15% solution of the dye, and the methylene number (M.N.), which is the amount of methylene blue (mg) adsorbed by 1 g of the AC upon the decolorization of the solution, was determined. The amount adsorbed of iodine was measured using a standard procedure.[8] The iodine number of an AC (I.N.) implies the amount of iodine (mg) that can be adsorbed by 1 g of the powdered AC from a dilute aqueous solution of iodine; the residual equilibrium concentration of iodine is 0.02 mol $L^{-1}$. It is assumed that at this equilibrium concentration iodine is adsorbed as a monolayer. Therefore, there is a dependence between the I.N. of the AC and its specific surface, which can be determined by the BET method. The results are presented in Table 3.

The chemistry of the AC surface was studied by spectroscopy in the IR, UV, visible, and near-IR regions. IR spectra were recorded on a JASCO FT-IR 620 spectrophotometer (Japan). Specta in the UV, visible, and near-IR regions were obtained on a JASCO UV—Vis—NIR V570 instrument. The spectra of the CAP-7 active carbon are shown in Figs 2 and 3. The frequencies of selected absorption bands for the AC samples under study were detected by IR spectroscopy and examined according to Ref. 9.

**Table 2.** Characteristics of the active carbons

| AC sample | Yield | Ash level | Elemental composition* (%) | | | |
|---|---|---|---|---|---|---|
| | % | | C | H | S | P |
| CAN-7 | 42.7 | 2.45 | 83.01 | 2.68 | — | 0.51 |
| CAPr-1 | 41.5 | 1.23 | 82.70 | 2.21 | — | 0.42 |
| CAS-4 | 38.2 | 6.18 | 75.88 | 3.30 | — | 0.65 |
| CAP-7 | 45.7 | 6.75 | 76.50 | 1.90 | — | — |
| CAP-8 | 48.5 | 3.09 | 87.50 | 0.62 | 3.47 | — |

* No nitrogen was found in the samples.

**Table 3.** Values of pH, number of acidic ($N_t^A$) and basic ($N_t^B$) functional groups, and methylene (M.N.) and iodine (I.N.) numbers of the active carbons

| AC sample | pH | $N_t^A$ ($N_t^B$) mequiv. g$^{-1}$ | M.N. | I.N. |
|---|---|---|---|---|
| | | | mg g$^{-1}$ | |
| CAN-7 | 3.0 | 1.87 | 257 | 858 |
| CAPr-1 | 4.2 | 1.98 | 200 | 712 |
| CAS-4 | 3.5 | 2.12 | 10 | 370 |
| CAP-7 | 8.75 | (0.95) | 280 | 988 |
| CAP-8 | 8.35 | (0.58) | 270 | 1060 |

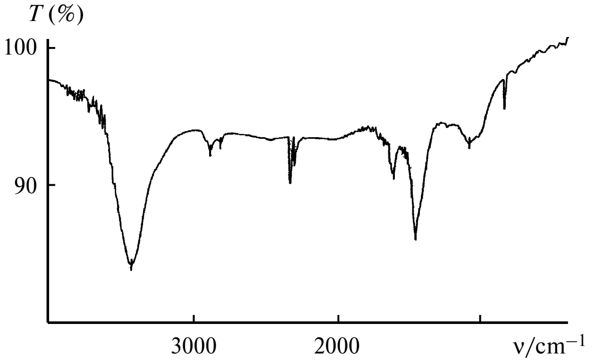


**Fig. 2.** IR spectrum of the CAP-7 active carbon.

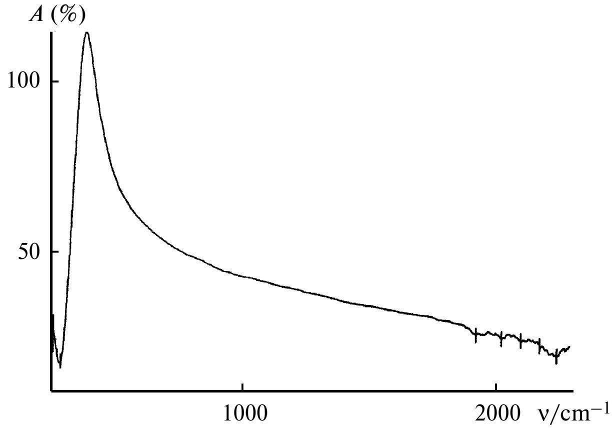


**Fig. 3.** Spectra of the CAP-7 active carbon in the UV, visible, and near-IR regions.

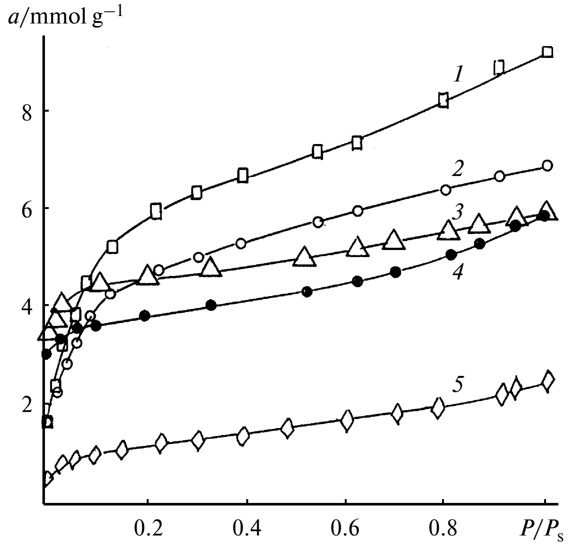


**Fig. 4.** Adsorption isotherms of the benzene vapor at 293 K on CAN-7 (*1*), CAPr-1 (*2*), CAP-7 (*3*), CAP-8 (*4*), and CAS-4 (*5*).

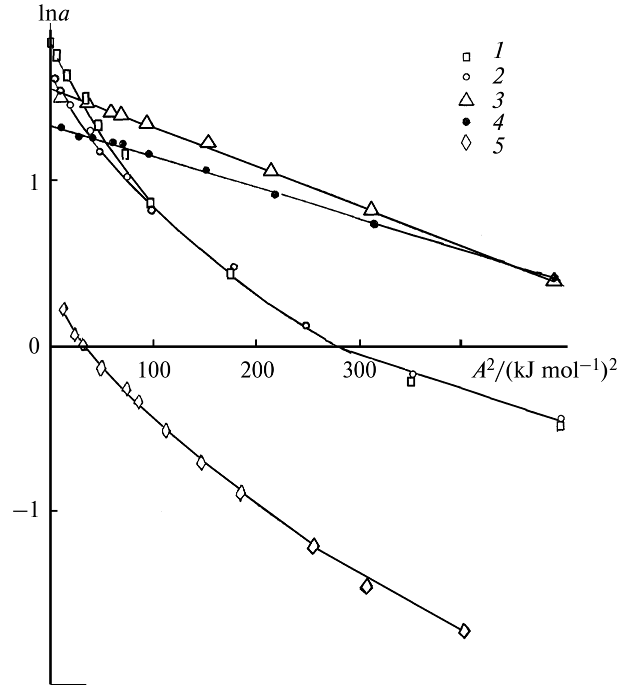


**Fig. 5.** Adsorption isotherms of the benzene vapor expressed as the linear plot of the VMFT equation on CAN-7 (*1*), CAPr-1 (*2*), CAP-7 (*3*), CAP-8 (*4*), and CAS-4 (*5*).

## Results and Discussion

Detailed information on the pore structure of the ACs accesible to adsorptives was obtained from the adsorption isotherms of the benzene vapor. The adsorption isotherms of the benzene vapor on the ACs (Fig. 4) are described by the general equations of the volume micropore filling theory (VMFT)[10] with a high accuracy in an interval of relative pressures of $10^{-6}$—0.3. The adsorption isotherms in the linear form of the VMFT equations are shown in Fig. 5. They demonstrate clearly that the one-term Dubinin—Radushkevich equation (DR-1) is applicable for the CAP-7 and CAP-8 ACs prepared physicochemically

$$W = W_0 \exp\{-[A/(\beta E_0)]^2\}, \qquad (1)$$

where $W$ is the volume of the adsorbed standard benzene vapor expressed as a liquid volume of benzene; $W_0$ is the limiting adsorption volume of micropores; $E_0$ is the characteristic adsorption energy of the standard benzene vapor; $\beta$ is the similarity factor of characteristic curves; $A$ is the differential molar work of adsorption.

The adsorption isotherms of the benzene vapor on the CAN-7, CAPr-1, and CAS-4 ACs prepared by chemical activation are described by the two-term Dubinin—Radushkevich equation (DR-2)

$$W = W_{0,1}\exp[-(A/E_{0,1})^2] + W_{0,2}\exp[-(A/E_{0,2})^2]. \qquad (2)$$

Here the corresponding parameters $W_{0,1}$ and $E_{0,1}$ characterize true micropores, and $W_{0,2}$ and $E_{0,2}$ characterize supermicropores. The specific surface of mesopores $S_{\mathrm{me}}$ was determined by the $\gamma$-method[11] from the region of the adsorption isotherm of the benzene vapor corresponding to an interval of relative pressures of 0.4—0.75. The mesopore volume $V_{\mathrm{me}}$ was calculated as the difference of the limiting adsorption volume $V_{\mathrm{S}}$ corresponding to a relative pressure of ~1 and the adsorption volume of micropores (or the sum of the volumes of micro- and supermicropores).

The characteristics of the pore structure of the ACs determined from the adsorption of the benzene vapor are presented in Tables 4 and 5. As can be seen from the tabulated data, the difference in the activation methods results in the formation of two types of ACs with different pore structures. The micro- and mesoporous ACs are prepared by the physicochemical activation, while the chemical activation produces the ACs with a broad pore size distribution of the micropore volume. The volume of supermicropores in these ACs exceeds the volumes of the true micropores and mesopores that are comparable. In all ACs, mesopores are developed to almost the same extent. The exception is the CAS-4 sample prepared from grape seeds and characterized by poorly developed micro-, supermicro-, and mesoporous structures. Thus, by varying the activation methods, one can prepare ACs based on plant raw materials with the pore structure changing in a wide range. As it is known, the main criterion of the quality of ACs is their sorption capacity under static conditions, which is usually determined with benzene. The dynamic activity characterizing the behavior of the adsorbent in real adsorption processes is proportional to the static activity. The kinetic and aerodynamic factors only determine the efficiency factor of using the static activity (or sorption capacity) of the adsorbent layer under the dynamic conditions. The limiting sorption volume of pores responsible for adsorption (true micropores, supermicropores, and mesopores) of the ACs ranges from 0.52 to 0.81 cm$^3$ g$^{-1}$, which indicates a high sorption capacity of the carbons. These values are close to the limiting sorption volume (0.7—0.9 cm$^3$ g$^{-1}$) of the industrial Russian carbon (MeKS trade mark) that was prepared by gas-vapor activation from stone raw materials but showed the uniform microporous structure. Unlike MeKS, carbons CAN-7 and CAPr-1 are characterized by heterogeneous microporosity with the predominant fraction of the supermicropore volume. That makes it possible to predict prospect of using these solids for the adsorption of substances, whose molecular diameter changes in a wide range.

The values of the hydrogen factor (pH) of aqueous solutions of the ACs and results of chemical titration (see Table 3) suggest that acidic functional groups are formed on the surface of the ACs prepared by chemical activation, while basic functional groups are formed on the surface of the ACs obtained by physicochemical activation.

The methylene numbers of all ACs, except for CAS-4, are rather high. This indicates that the AC structure contains transition pores. High I.N. values corresponding to the values of the specific surface according to BET in an

**Table 4.** Parameters of the pore structure of the active carbons prepared by physicochemical activation

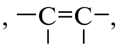
| AC samples | $W_0$ /cm$^3$ g$^{-1}$ | $E_0$ /kJ mol$^{-1}$ | $x_0$ /nm | $V_{\mathrm{s}}$ | $V_{\mathrm{me}}$ | $S_{\mathrm{me}}$ /m$^2$ g$^{-1}$ |
|---|---|---|---|---|---|---|
| | | | | cm$^3$ g$^{-1}$ | | |
| CAP-7 | 0.43 | 20.48 | 0.49 | 0.53 | 0.10 | 110 |
| CAP-8 | 0.35 | 22.91 | 0.44 | 0.52 | 0.17 | 140 |

**Table 5.** Parameters of the pore structure of the active carbons prepared by chemical activation

| AC sample | $W_{0,1}$ | $W_{0,2}$ | $E_{0,1}$ | $E_{0,2}$ | $x_{0,1}$ | $x_{0,2}$ | $V_{\mathrm{s}}$ | $V_{\mathrm{me}}$ | $S_{\mathrm{me}}$ /m$^2$ g$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| | cm$^3$ g$^{-1}$ | | kJ mol$^{-1}$ | | nm | | cm$^3$ g$^{-1}$ | | |
| CAN-7 | 0.17 | 0.44 | 20.81 | 7.78 | 0.48 | 1.29 | 0.81 | 0.20 | 170 |
| CAPr-1 | 0.17 | 0.32 | 20.81 | 7.91 | 0.48 | 1.27 | 0.61 | 0.12 | 110 |
| CAS-4 | 0.08 | 0.06 | 17.09 | 7.49 | 0.58 | 1.34 | 0.22 | 0.05 | <50 |

interval of 700—1000 $m^2 g^{-1}$ confirm that the pore structure of the samples contains micropores and larger supermicropores along with mesopores. This agrees with the data on equilibrium benzene adsorption.

The results obtained by spectroscopy make it possible to analyze the chemical state of the surface of carbon adsorbents in more detail.

An analysis of the IR spectra indicates that the carbon surface of the carbon adsorbents contains groups CH, $CH_2$, $CH_3$,  $-\underset{|}{C}=\underset{|}{C}-$, and C=O, carboxyl groups COOH, and phenol groups from alcohols or phosphate groups.

All AC samples under study (prepared by both the chemical and physicochemical methods) show an enhanced adsorption capacity to water vapor as can be concluded from the high intensity of the absorption band (~10%) at ~3430 $cm^{-1}$ and the presence of carbon dioxide (~5% of the adsorbent weight according to the intensity of two absorption bands at 2360—2400 $cm^{-1}$). The IR spectra of all samples under study exhibit absorption bands $\nu$(CH) at ~2925 and 2850 $cm^{-1}$, $\delta_s(CH_2)$ at ~1460 and 1380 $cm^{-1}$, and $\rho$(CH) at ~810 and 700 $cm^{-1}$, which is a convincing proof for the presence of the CH, $CH_2$, or $CH_3$ groups in the composition of the ACs.

The spectra also contain absorption bands at ~1570, 1480, and 640 $cm^{-1}$ assigned to benzene rings. If we take into account that an interval of 1650—1750 $cm^{-1}$ contains several absorption bands of weak or medium intensity attributed, most likely, to $\nu$(C=O) (R—CHO, R—COOH, and others), then it becomes clear that the surface chemistry of the ACs under study is extremely complicated. This is just one of the reasons for the high adsorption activity of the ACs.

Although the structures and adsorption properties of the ACs under study, which were obtained by both chemical ($H_3PO_4$) and physicochemical ($SO_2$ or $NH_3$) activations, are very similar, their IR spectra exhibit some differences in position and intensity of the main absorption bands. The appearance of absorption bands belonging to phosphorus-containing groups (~1050, 610, and 470 $cm^{-1}$) was detected for the ACs prepared by chemical ($H_3PO_4$) activation. Therefore, we can speak about individuality of each AC, which is also confirmed by both the physicochemical characteristics and adsorption properties.

An analysis of the UV and visible spectra of the carbon samples indicates the presence of an absorption band at 268—276 nm, which should be assigned to phenol structures.[12] The absorption bands in a region of 1910—2300 nm, which is close to the IR range, can be attributed to the CH and OH groups in the structure and on the surface of the ACs.[13]

Thus, an analysis of the spectra in the IR, UV, visible, and near-IR regions shows that the surface of the ACs prepared by both physicochemical and chemical activations has a complicated chemical composition and contains many functional groups and structures. The active carbons prepared by chemical activation contain carboxyl and phosphate groups, which endow the surfaces with acidic properties.

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