Estimation of the porous structure of active carbons

G. A. Petukhova,[a] N. S. Polyakov,[a] F. G. Lupashcu,[b] and L. I. Monakhova[b]*

[a]Institute of Physical Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: +7 (095) 952 5308
[b]Institute of Chemistry, Academy of Sciences of the Republic of Moldova,
3 ul. Akademicheskaya, 277028 Kishinev, Moldova.
Fax: +7 (373 2) 739 954

Active carbons from apricot, plum, peach, and grape stones were prepared. The analysis of adsorption isotherms of benzene vapor showed that the active carbons obtained from fruit stones have highly homogeneous microporous structures with W_0 ~0.30 $cm^3\ g^{-1}$, E_0 ~ 24.5 kJ mol^{-1}, and x_0 ~ 0.42 nm, and they contain ultramicropores along with micropores.

Key words: active carbons from fruit stones, porous structure, benzene.

Preparation of active carbons (AC) from fruit stones is a promising and economically profitable field of the production of sorbents. The sorbents produced have good sorption properties and mechanical strength, providing a possibility of performing multicyclic adsorption-desorption processes. Recently, the demand for ecologically pure products has been increasing all over the world. The programs of improvement and protection of the environment adopted in different countries involve requirements for manufactured AC. AC from fruit stones are noted for their high sorption properties; as a rule, they contain a low amount of ash (ash content ~0.2 %) and sulfur (less than 0.1 %). Hence, they conform to the requirements for ecologically pure products. The production of AC from fruit stones is now developing in countries where processing of fruits at canning plants is employed on a large scale.[1,2] Unfortunately, the peculiarities of the structure of active carbons obtained from fruit stones are almost unknown; therefore, in this work we attempted to investigate the porosity of these carbon adsorbents using the adsorption of benzene vapor as an example.

Experimental

Active carbons were obtained from plum stones (AC-Pl), apricot stones (AC-A), peach stones (AC-Pe), and grape stones (AC-G). The stones were pretreated with H_2SO_4 and H_2O to remove the residues of pulp. Carbonization and activation were carried out in a stream of water vapor. The porous structure was studied using adsorption isotherms of benzene vapor at 293 K. The adsorption isotherms of benzene vapor were measured on a sorption device within the interval of relative pressures from 10^{-6} to 1.0 Pa. All samples were previously evacuated at 673 K and 10^{-4} Pa until a constant weight was attained.

Results and Discussion

As a rule, equations of volume filling of micropores are widely used to describe the microporous structure of AC: the monomial Dubinin—Radushkevich (DR) equation[3] for homogeneous microporous structures and the binomial DR equation[3] and the Dubinin—Stoeckli (DS) equation for heterogeneous microporous structures.[4] The choice of equation is determined by the type of the adsorption isotherm. As a rule, isotherms of the standard vapor, benzene, are studied in order to characterize the micro- and mesoporosity of carbon sorbents. Based on their form, the adsorption isotherms obtained for carbons from fruit stones can be categorized as isotherms of type 1 according to the BDDT classification.[5] The distinguishing features are the absence of a hysteresis loop and the existence of a horizontal plateau, which approaches the axis of relative pressures $p/p_s = 1$ at an almost right angle (for AC-A, AC-Pl, and AC-Pe) or has a small rise near this axis (for AC-G). The adsorption isotherms of benzene vapor on AC in coordinates of the linear DR equation are given in Fig. 1. For AC-G, the adsorption isotherm of benzene vapor is linear in coordinates of the linear DR equation within the p/p_s interval from $1 \cdot 10^{-6}$ to 0.2 Pa, indicating the high homogeneity of the micropores. For the remaining samples, the isotherms plotted in these coordinates are convex towards the abscissa axis. Such a form of the isotherms is typical of microporous samples, in which the surface of the mesopores is developed insignificantly or is practically absent, and the sizes of the micropores are comparable with those of the molecules of the adsorbed substance. As a rule, the dispersion (δ), *i.e.*, size distribution of micropores, determined with the DS equation,[4] is negligibly small for isotherms of this type ($\delta \to 0$), which

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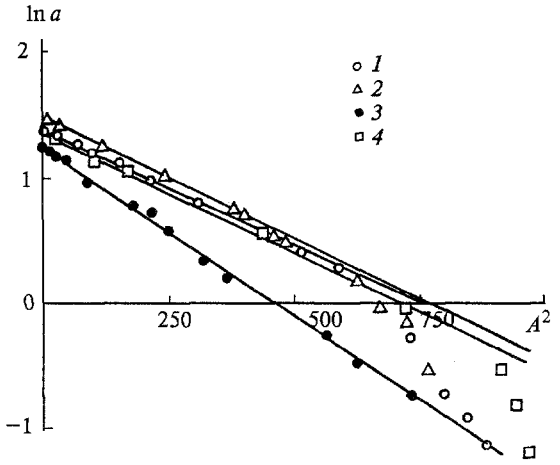

Fig. 1. Adsorption isotherms of benzene vapor plotted in coordinates of the linear DR equation [ln$a$—A^2] for samples of AC-Pl (*1*), AC-Pe (*2*), AC-G (*3*), and AC-A (*4*).

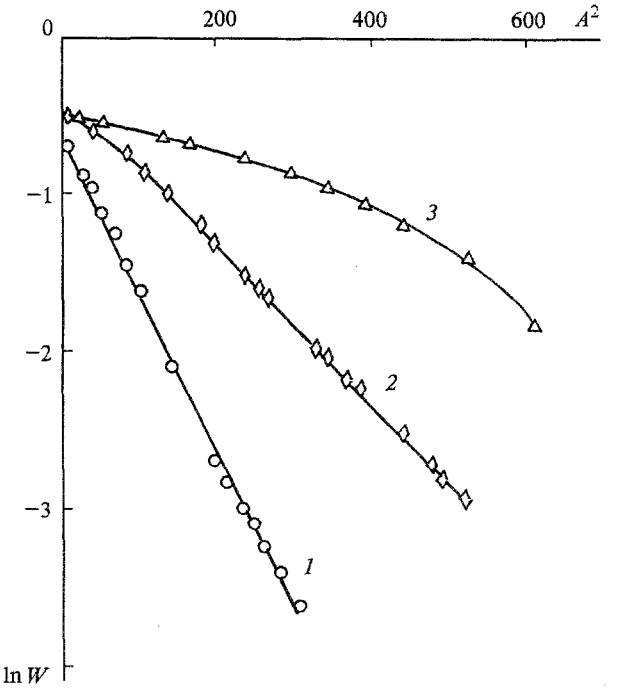

Fig. 2. Adsorption isotherms on AC of vapors of substances: SO_2 (*1*), CS_2 (*2*), and $C_2F_4Br_2$ (Freon 114B2) (*3*).

indicates the homogeneity of micropores in AC. The characteristic examples of isotherms of this type are isotherms of adsorption on AC of PAU and SKT types. Figure 2 presents adsorption isotherms in coordinates of the DR equation for vapors of substances with different molecular diameters. The isotherms were obtained on AC with homogeneous microporous structure. The adsorption isotherm of sulfur dioxide (d ~ 0.27 nm) is linear, and the isotherms become convex in the case of adsorption of larger molecules of carbon disulfide and Freon 114B2 (d ~ 0.3 and 0.6 nm, respectively). Such isotherms are more adequately described by the exponential Dubinin—Radushkevich—Astakhov (DRA) equation[6]

$$a = (W_0/V) \cdot \exp[-(A/E_0)^n]. \quad (1)$$

than by the DR and DS equations.

Extensive experimental studies showed that it is advisable to use Eq. (1) with $n = 3$ for the adsorption on AC. An increase in the exponent n in the DRA equation indicates an increase in homogeneity of microporous structure of the AC. The adsorption isotherms for the AC-A, AC-Pe, and AC-Pl samples in coordinates of the linear DRA equation with $n = 3$ are presented in Fig. 3. The plot is linear for AC-A, which allows one to estimate the microporous structure with high accuracy. However, deviations from linearity are observed for AC-Pl and AC-Pe in the region of p/p_s ~$10^{-4} \div 10^{-5}$. The AC-Pl and AC-Pe samples, along with micropores, probably contain ultramicropores, whose sizes are less or comparable to those of benzene molecules. The existence of ultramicropores shows that AC with a narrow size distribution of the micropore volume and high characteristic adsorption energies, like AC of the PAU type, can be prepared from fruit stones. One can assume that an increase in carbonization temperature or additional activation should result in an increase in the internal surface and adsorption space of the micropores.

Table 1 shows the parameters of the porous structure determined from the isotherms. The parameters of microporous structure for AC-G were estimated using the DR equation with $n = 2$, and for the remaining AC, $n = 3$. As can be seen from Table 1, the AC obtained from plum, peach, and apricot stones have high characteristic adsorption energies, E_0 ~24.5 kJ mol^{-1},

Table 1. Parameters of porous structure for AC from fruit stones

Sample	Volume of micropores, W_0/cm^3 g^{-1}	Characteristic energy, E_0/kJ mol^{-1}	Micropore half width, x_0/nm	Volume of mesopores, V_{me}/cm^3 g^{-1}	Limiting volume, V_s/cm^3 g^{-1}
AC-G	0.30	19.4	0.50	0.08	0.38
AC-Pl	0.30	24.9	0.40	0.10	0.40
AC-Pe	0.32	23.9	0.42	0.07	0.39
AC-A	0.28	25.6	0.39	0.11	0.39

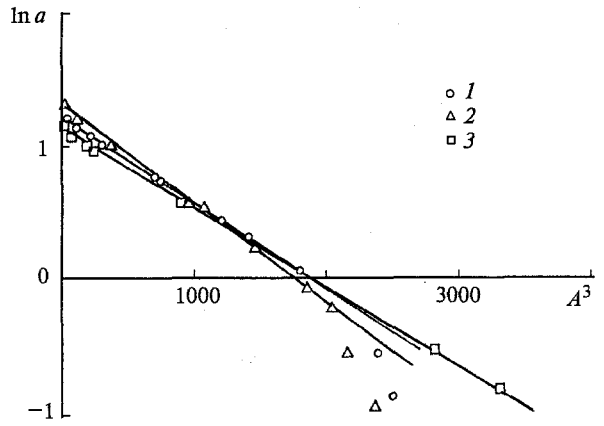

Fig. 3. Adsorption isotherms of benzene vapor plotted in the coordinates of the linear DRA equation [$\ln a$—A^3] for samples of AC-Pl (*1*), AC-Pe (*2*), and AC-A (*3*).

with micropore volume W_0 ~0.30 $cm^3\ g^{-1}$. According to the parameters of the microporous structure, these samples do not rank below the carbons of OU-A and BAU type (see Ref. 6) used for purification and preparation of medicinals in the pharmaceutical industry and for purification of water in food industry. The sample obtained from grape stones has lower characteristic adsorption energy and larger micropores (x_0 = 0.50 nm), which allows one to assume that this carbon should have high sorption activity for the vapors of various organic substances.

Hence, the AC obtained from fruit stones have a developed homogeneous microporous structure and high characteristic energies of adsorption of benzene vapor.

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