

Nanoporous active carbons at ambient conditions: a comparative study using X-ray scattering and diffraction, Raman spectroscopy and N₂ adsorption

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Abstract. Furfural-derived sorbents and activated carbonaceous fibers were studied using Small- and Wide-angle X-ray scattering (SWAXS), X-ray diffraction and multiwavelength Raman spectroscopy after storage at ambient conditions. Correlations between structural features with degree of activation and with sorption parameters are observed for samples obtained from a common precursor and differing in duration of activation. However, the correlations are not necessarily applicable to the carbons obtained from different precursors. Using two independent approaches we show that treatment of SWAXS results should be performed with careful analysis of applicability of the Porod law to the sample under study. In general case of a pore with rough/corrugated surface deviations from the Porod law may become significant and reflect structure of the pore-carbon interface. Ignorance of these features may invalidate extraction of closed porosity values. In most cases the pore-matrix interface in the studied samples is not atomically sharp, but is characterized by 1D or 2D fluctuations of electronic density responsible for deviations from the Porod law. Intensity of the pores-related small-angle scattering correlates positively with S_{BET} values obtained from N₂ adsorption.

1. Introduction

The sorption capacity and efficiency of carbon adsorbents strongly depend on pore size distribution and on structure of pore-matrix interface. Analysis of vapour adsorption isotherms is well established, widespread and important method of investigation of the porous structure. The effective pore size is usually calculated in the framework of Dubinin's volume filling theory (MVFT) [1, 2], density functional theory (DFT) [3], Kawazoe or BJH equations [4]. Complementary techniques, such as Small-Angle X-ray (SAXS) and neutron scattering (SANS) [5–10], pulsed NMR [11] and positron annihilation spectroscopy [12] are used for characterization of porous solids as well. These methods are nondestructive and rather fast compared to sorption experiments but provide information about various structural parameters and on different scales. Application of several complementary

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techniques is the only reliable way to investigate the sorbent structure in detail. In this contribution we report results of investigation of activated carbons made from furfural (FAS-type) and of activated carbonaceous fibers (ACC-type) using several complementary techniques: Small- and Wide Angle X-ray Scattering (SWAXS), X-ray diffraction, Multi-Wavelength Raman Scattering (MWRS) and N_2 adsorption. This study attempts to elucidate correlations between results obtained using different analytical methods and to improve understanding of structure of activated carbons on several structural levels.

2. Experimental

Technology of synthesis of FAS-type activated carbons (AC) was developed at SPA “Neorganika” (Electrostal, Russia). Extreme mechanical strength of these materials and high sorption capacity of this type of AC make them extremely important in applications requiring high mechanical and adsorption properties, e.g., biomedicine, radiochemistry etc. Detailed description of these ACs is given in [13], general preparation scheme is the following: 1) liquid moulding of synthetic furfural monomer at 105 °C, 2) carbonization of spheroidal sorbent grains in inert medium at 750 °C, 3) steam activation at 850 °C. The samples differ by duration of the activation process: from 5 to 15 hours. After the activation the spheroidal grains were washed in distilled water and dried. In our work the sorbents were studied in as-received state.

The carbonaceous fibers (ACC) were prepared by thermal treatment of impregnated viscose fibers.

The nitrogen adsorption characteristics were measured using ASAP-2020 Analyzer (Micromeritics). We report results obtained by MP method, since it allows determination of pore size distribution for supermicro- and mesoporous adsorbents. The obtained values can be recalculated to other comparative methods (t-, αS -, n-methods).

The samples used for the structural characterization were shelf-stored at identical conditions for comparable periods of time (at least 12 months), assuring attainment of “equilibrium” degree of moisture saturation, which, of course, is sample-dependent due to variations in pore sizes.

It is well-known that water and other adsorbents may influence structure of sorbents considerably. Kinetics of water desorption may be extremely slow even at elevated temperatures (e.g., [14-16]). This applies even to samples in high vacuum in transmission electron microscopy where physisorbed water is most likely absent, but chemically-bound fraction may well be retained. For example, investigation of loose nanodiamond powder using infra-red spectroscopy showed that even vacuum heating of the powder at 400 °C for few hours does not eliminate surface OH-groups completely [17]. Therefore, frequently employed outgasing of activated carbons at 80-100 °C “in dry air” prior to structural studies may lead to large sample-to-sample variations due to differences in pore structure and relative fraction of pores of different sizes, strongly influencing desorption kinetics of adsorbed moisture. For consistency, in this contribution we report structural peculiarities of the samples stored for prolonged period of time at ambient conditions and thus being in equilibrium with environment. Validity of this approach to the studied samples is confirmed by presented comparative studies at various temperatures and duration of storage in vacuum. The adsorption measurements were performed according to common routine after prolonged vacuum drying.

SWAXS patterns were recorded using monochromatic CuK_{α} -radiation in broad range (0.1–27 nm⁻¹) of scattering vectors, q , using dedicated diffractometer SAXSess (Anton Paar). Samples of the FAS-type activated carbons were measured in standard X-ray capillaries or between two layers of special low-scattering polymer film; the fibers-based samples were measured without packaging. Kratki collimation scheme was employed; desmearing was performed using standard software. All measurements were performed at room temperature in evacuated chamber (residual pressure 5–10 mbar); therefore, partial desorption of physisorbed atmospheric species might took place. However, due to high brightness of the setup the measurements were generally fast and total exposure of the samples to vacuum was less than 5 minutes. For comparative purposes, for some samples the scattering curves were obtained immediately after reaching the target pressure (less than one minute) and after continuous pumping for up to 24 hours and after vacuum annealing at 50 °C for up to 24 hours. The difference was found to be negligible, see below.

X-ray diffraction patterns were recorded using Empyrean (Panalytical BV) diffractometer in Bragg–Brentano geometry using Ni-filtered $\text{CuK}\alpha$ -radiation in the angular range $10\text{--}120^\circ$ (2θ). No binder was employed to exclude influence of sample humidity on sorbent structure, which is discussed in detail in [11, 14] and all reported patterns were acquired for the samples dried directly in the sample holder in hot air for several hours. However, for comparative purposes several samples were also studied in wet state.

In-depth analysis of XRD data for carbons requires fitting of the whole pattern (total scattering) [18]. In the same time, the total scattering approach is based on models of sample structure and validity of these models requires independent confirmation. For comparative purposes the diffraction patterns were deconvoluted into components assuming Pearson VII peaks shape. Since the deconvolution is always not very robust, in subsequent analysis we operate with relative intensities, rather than with areas.

Raman spectra were acquired in quasi-backscattering geometry in air at room temperature at low power of 532 and 785 nm lasers using microscope (Bruker Senterra). Absence of sample alteration by the laser beam was checked both visually and by controlling persistence of spectral features. Several scans were averaged to improve signal to noise ratio; in addition for every sample several spots were analysed for consistency. Spectral decomposition to individual components is described in corresponding part of the paper.

3. Results and discussion

3.1. Sorption

Parameters of porous structure of the activated carbons (see Table 1) were calculated from the nitrogen adsorption isotherms at 77 K using several methods. The BET method was used for calculation of S_{BET} [4]; b) the comparative MP-method [19–22] gave mesopore surface area (S_{ME}) and total surface area (S_{MP}) for samples with rather wide micropores (supermicropores); c) nanopore surface area calculated as: $S_{\text{NANO}} = S_{\text{BET}} - S_{\text{ME}}$; Dubinin's micropore volume filling theory (MVFT) [1, 2] provided micropore volume (W_0) and characteristic energy of adsorption (E_0); micropore size (x_0) calculated using Stoeckli et. al. equation [23]. Figure 1 shows the N_2 vapour adsorption isotherms for majority of the studied samples. The average isotherm for adsorption on the surface of nonporous carbon black was adopted as the reference isotherm [21, 22].

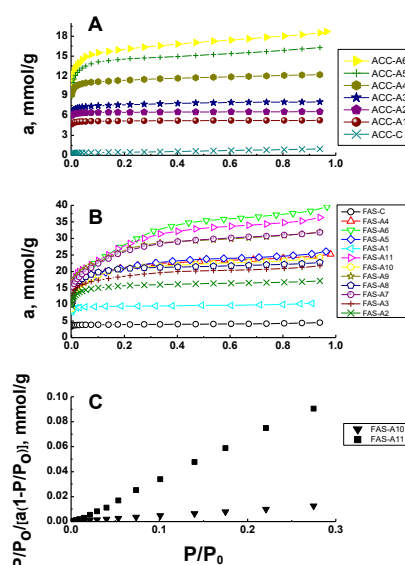


Figure 1. Nitrogen adsorption isotherms of studied samples. A – activated fibers (ACC); B – carbonizate (FAS-C) and activated (FAS-A) carbons; C – BET adsorption isotherms in linear form in the region used for calculation of S_{MP} for supermicro- and mesoporous carbons.

Table 1. Parameters of porous structure of the carbonizate (FAS-C), activated carbons of FAS-type and of activated fibers (ACC) with different degrees of activation

Sample	S_{BET} , m^2/g	S_{MP} , m^2/g	S_{ME} , m^2/g	S_{NANO} , m^2/g	W_o , cm^3/g	E_o , kJ/mol	x_o , nm	x_{BET} , nm
FAS-C	350		20	328	0.13	45	0.18	0.88
FAS-A1	680		30	650	0.32	32.4	0.29	1.06
FAS-A2	1300		70	1230	0.53	20.5	0.59	0.90
FAS-A3	1500		90	1410	0.60	20.3	0.61	1.02
FAS-A4	1660		160	1600	0.67	19.6	0.60	1.05
FAS-A5	1600		120	1480	0.60	19.4	0.64	1.1
FAS-A6	2300		290	2010	0.67	18.2	0.79	1.20
FAS-A7	1900	1800	190	1710	0.73	17.9	0.83	1.16
FAS-A8	1650	1820	80	1570	0.70	17.2	0.94	0.95
FAS-A9	2030	2100	170	1850	0.81	17.1	0.94	1.10
FAS-A10	1600	1700	140	1460	0.65	16.5	1.06	1.04
FAS-A11	1950	1950	220	1730	~1.20	15.0	1.60	~1.30
ACC-C	38		30	8	0.014	42	1.8	0.8
ACC-A1	460		3	457	0.18	39.2	0.19	0.8
ACC-A2	580		4		0.22	45.2	0.16	0.8
ACC-A3	680		50		0.27	28.0	0.33	0.8
ACC-A4	940		35	905	0.39	28.3	0.79	0.9
ACC-A5	1250		80	1170	0.52	18.3	0.79	0.9
ACC-A6	1400	1470	140	1260	0.55	19.9	0.63	0.94
ACC-A7	1459		120		0.56		0.74	0.74
ACC-A8	1530		280		0.623		0.87	0.82
ACC-10								
ACC-UT	23							
Non-porous								
Non-porous								

* $S_{NANO} = S_{E3T} - S_{ME}$, ** $x_{BET} = 4V_{tot}/S_{BET}$ (V_{tot} - the total pore volume)

3.2. X-ray diffraction

X-ray diffraction patterns of the studied sorbents are typical for nanocrystalline carbons (Fig. 2). In the $2\theta > 10^\circ$ range the patterns are dominated by broad 002 graphite peak. Formally, the corresponding interlayer spacings are between 0.36 and 0.39 nm, which are notably larger than those for ideal (0.334 nm) or even turbostratic graphite. Such spacings are encountered in non-graphitising carbons and in poorly graphitized carbonaceous substances with impurities. Application of the Debye–Scherrer formula gives crystallite sizes in the order of 1–2 nm. However, as shown in [24, 25], when the size of graphitic crystallites becomes smaller than 2–3 nm, the width and position of the 002 diffraction peak cannot be reliably used for determination of size and lattice spacing because of strong influence of detailed structure and morphology of the graphene layer stacks and surface termination.

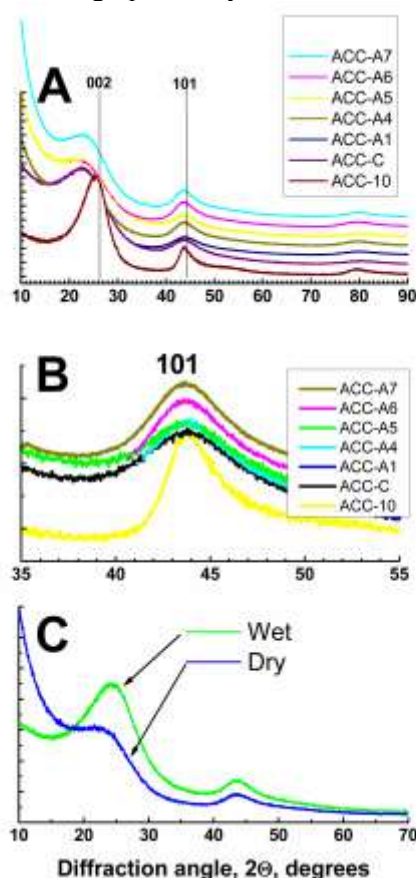


Figure 2. X-ray diffraction patterns of fibers-based sorbents (A) and close view of the 101+10 peak (B). The burn-off degree increases from bottom to top. Vertical lines indicate peak positions for ideal graphite. Diffraction from the FAS carbons are qualitatively similar. C - Comparison of X-ray diffraction patterns recorded in water-saturated and dry (several hours in flow of 40–50 °C air) states.

The patterns of non-porous materials ACC-10 and ACC-UT approach that of hexagonal graphite. Increase of the activation degree leads to gradual deterioration of graphitic structure. The peak at 42 degrees represents an overlap of 101 peak of graphitic and of two-dimensional 10 peak of turbostratic carbon.

Comparison of X-ray diffraction patterns recorded in water-saturated and dry (several hours in flow of 40–50 °C air) states (Fig. 2c) confirms very significant influence of moisture on X-ray diffraction patterns of the FAS ACs, see also [11, 13]. This effect is explained mostly by structural peculiarities of particular sample: depending on wettability and porosity of the material adsorbed water molecules may either align adjacent graphitic crystallites increasing L_a or, in contrast, may introduce disorder.

This effect is currently investigated in detail. Note that this dramatic effect of moisture is not present in SAXS data, see below.

For the activated carbon fiber samples (ACC) a fairly good positive correlation between the intensity of the ratio $I_{(101)+(10)}/I_{(002)}$ peaks and degree of activation (manifested in specific surface area (S_{BET}) and maximal adsorption volume (W_0)) is observed (Fig. 3). Note that existence of the correlation for the ACC-type samples indicates that diffraction halo of adsorbed water plays very minor role if any. In the same time, the FAS-type sorbents form another group with no or little dependence of the sorption parameters from the diffraction data. The correlation observed for ACC-samples could reflect either increase of lateral dimensions of graphitic domains with constant or decreasing thickness, or growing contribution of turbostratic carbon. The differences in morphology of the graphitic domains are partly inherited from precursors. In addition, one cannot exclude differences in gas-transport reactions during activation process which may promote lateral growth of graphene stacks (e.g., [26]).

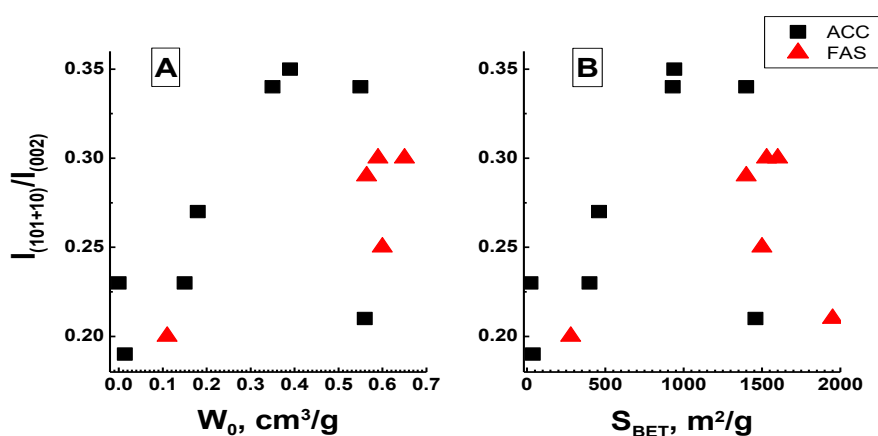


Figure 3. Relationships between sorption parameters and ratio of XRD peaks intensities. For ideal hexagonal graphite the $I_{(101)}/I_{(002)}=0.17$.

3.3. Small-angle scattering

3.3.1. Modeling of scattering curves from pores with diffuse boundaries. According to the Porod law a desmeared SAXS curve for slit-shape scatterers with sharp interfaces should be linear in coordinates $q^4 I(q) - q^2$ at high values of the scattering vector. However, for almost all samples deviations from the Porod law are clearly observed (see below), in accordance with many of previous SAS studies of sorbents of different types [5]. Several approaches to describe such deviations could be used: 1) heavily polydisperse distribution of the scatterers; 2) assumption of fractal nature of the interface [27, 28], and 3) various models of the interface boundary [29, 30]. Since Guinier plots of our samples show existence of monodisperse scatterers, the polydispersity should not play an important role. The fractal approach is very popular, but it provides little information for comparison with other techniques. It should be also kept in mind that the fractal dimension derived from experimental scattering curves is sensitive to details of background subtraction [31].

In our view the most useful approach to explain deviation of SAS curves of carbonaceous sorbents should relate the deviations from the Porod law to structural features of the material, such as finite width of the interface or short-range disorder [29, 30]. It is important to emphasise that interpretation of SAS studies of activated carbons is usually performed in assumption of atomically flat pore

boundaries of graphene layers. This assumption is largely based on two famous papers devoted to investigation of fibers-based carbons using SAS [32] and TEM [33]. However, recent high resolution TEM studies of various carbonaceous sorbents (e.g., [34, 35]) clearly show that generalization of this assumption to all carbonaceous materials is a gross oversimplification. Some of furfural-based samples discussed in the current work were analysed using TEM protocol from [34] and it is obvious that many pores cannot be approximated by a void formed by atomically flat walls [37]. For example, some of the walls are formed by stacks of ruptured graphene layers for which the formalism of “sharp” interface is not applicable. In the same time, corrugated walls are not uncommon. Below we present results of direct modeling of the scattering patterns from objects of variable roughness and show that the walls roughness may well account for observed deviations from the Porod law. Depending on exact topology of the wall its roughness may influence the scattering curve similar to mathematically-derived effects of finite thickness of the void-matrix interface or fluctuations of electron density.

To demonstrate influence of the scatterer roughness on SAXS patterns two independent computational approaches were employed.

The first approach is based on direct calculation of the SAXS curve from a scatterer with a given shape and consists of calculation of the SAS curve from a given cluster of “quasi-atoms” (QA) and is extremely successful in evaluation of SAXS data for monodisperse particles [37]. The “quasi-atoms” (QA) approach is based on filling a volume of a given shape and size with solid quasi-atoms. The size of QA is determined by user, therefore, the surface of the body can be made very smooth (very small QAs) or rough/corrugated. In order to avoid appearance of Bragg peaks from QA packing and to explicitly create variations in density of the body, the QA can be placed with variable degree of overlap. According to the Babinet principle scattering curves for a cluster of QAs and for a pore with the same shape/size and contrast will be undistinguishable.

The second approach is based on direct calculation of the scattering curve from a body with a surface layer with a gradient of the scattering density. The thickness of the layer and profile of electron density variations are user-determined as a radial density profile $\rho(r)$. The details of calculation of scattering intensity from quasi-atom models are described in [37]. Scattering from a spherically symmetric particle with a radial density profile $\rho(r)$ is computed as

$$I(q) = 4\pi \int_{s_{\min}}^{s_{\max}} \rho(r) \frac{\sin(qr)}{qr} \cdot r^2 \cdot dr \quad [38].$$

These two kinds of simulation of the surface density gradients differ in essential detail. The quasi-atom modeling may describe both scattering from inhomogeneities in a particle shell and effect of the scattering from an object with gradually changing density. The modeling by a radial density function describes only the latter case which does not influence scattering intensity at high angles in comparison to the scatterers with sharp boundaries, but may describe the scattering behaviour at intermediate angles corresponding to those used in the present study.

Using the first (quasi-atoms) approach we have modeled scattering from ellipsoidal scatterers consisting of quasi-atoms of different radii and embedded into ellipsoidal shell. Variations of the thickness and QA radii in the shell produce objects with virtually identical sizes, but with widely different surface roughness/corrugation. Examples of the modeled bodies are shown in Fig. 4. Porod plots for sets of representative models are shown in Fig. 5.

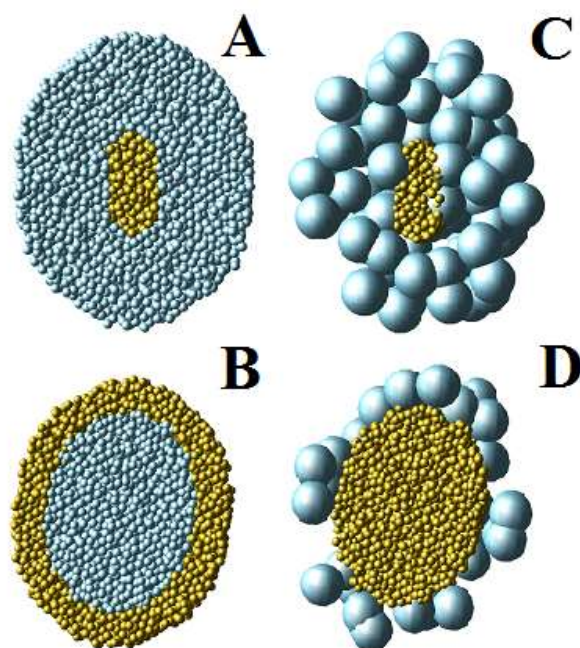


Figure 4. Examples of the bodies (cross-cuts) constructed for modeling of the scattering curves from objects with variable roughness. Different colors depict the “core” and “shell”. A, B – small quasi-atoms (smooth surface); C, D – large quasi-atoms (rough/corrugated surface. Various combinations were modeled, see text for details.

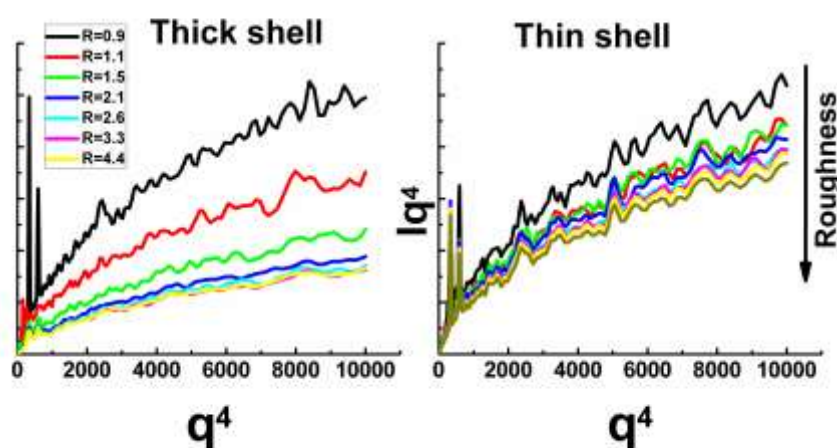


Figure 5. Porod graphs for the bodies consisting of quasiatoms of different sizes (see text and Fig. 4 for details). Radius of the shell QA’s is indicated. The curves are normalized to “dry volume” of the bodies [37].

The modeling of the scattering curves for bodies with user-defined density profiles was performed for several general cases including very sharp boundary, boundary with a smooth decay in density and a case where the density has a peak, roughly mimicking kind of an adsorbate layer, see Fig. 6c. The power of the fitting exponent of the corresponding part of the scattering curves on log-log plot (the “slope” in our notation) show clear deviations from the ideal -4 value.

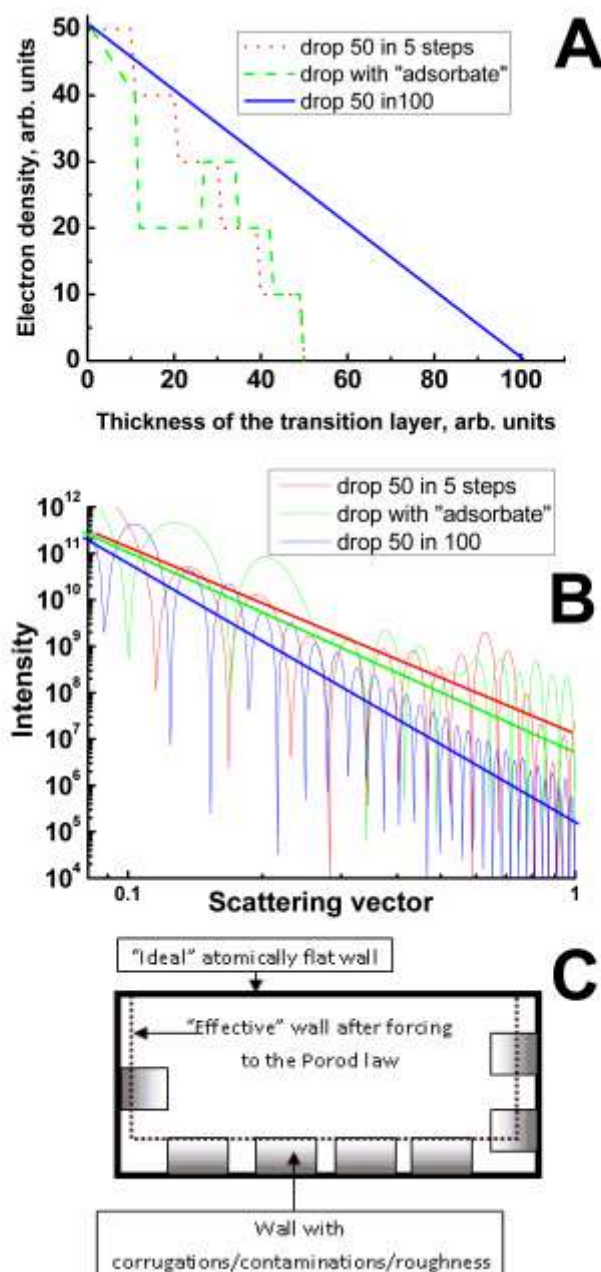


Figure 6. Simulated profiles of electron density decrease in a transition layer (A) and scattering curves from such bodies (B). Straight lines show linear fit to the data in the shown range of the scattering vectors, C – schematic image illustrating weakness of the concept of open/closed porosity evaluation from the SAS data.

The principal conclusion of these rather straightforward calculations is that subtraction of a constant background from a SAS curve to forcibly obey the Porod rule explicitly implies that the scattering pores possess atomically sharp walls, the assumption which is not always correct (see TEM results [34, 36]). Such subtraction effectively replaces a pore with rough/corrugated walls by some kind of an “effective” pore with unclear physical meaning in general case (Fig. 6c). Therefore, the combined use of SAS and adsorption results to extract “closed porosity” fraction is meaningful only in cases where the flat wall approximation is valid. Of course, subtraction of atomic scattering due to chemical elements comprising the sample is necessary, but in cases of activated carbons this contribution is typically small. Obviously, the angular region where the described deviations from the Porod plot will be manifested depends on ratio of the scatterers size and wavelength of the incident radiation and in some cases the deviations will occur in range inaccessible for SAXS instruments. However, our simple modeling as well as theoretical works by Ruland [29, 31] shows that one should be very careful prior to “standard” subtraction of a constant. Of course, background signal from atomic scattering by carbon and other important elements present in a sample should be subtracted, but in case of rather strong scattering from active carbons this contribution is usually very small.

3.3.2. Experimental data. SAXS patterns of the sorbents reveal their hierarchical structure (Fig. 7). As discussed in the Introduction, most SAXS studies of activated carbons employ some degree of degassing. The X-ray diffraction patterns of the studied carbons notably depend on amount of moisture (chapter 3.2, fig. 2c). In order to check influence of the moisture on the SAXS patterns several samples were measured in several states: 1) immediately after reaching the required conditions ($P=5-10$ mbar at $23\text{ }^{\circ}\text{C}$), 2) after pumping for 0 up to 24 hours at RT or at $50\text{ }^{\circ}\text{C}$. The measurements themselves were performed both at 25 and at $50\text{ }^{\circ}\text{C}$. The relatively low T of $50\text{ }^{\circ}\text{C}$ was chosen to minimize eventual modification of the samples with highly developed porosity. Figure 7b shows that the scattering patterns coincide within measurement error except the region corresponding to diffraction from poorly ordered graphite ($10 < q < 20\text{ nm}^{-1}$), where rearrangements of the crystallites (reversible on cooling) are observed. The discrepancy with the XRD results can be tentatively explained by two interrelated factors: 1) as shown in independent study [36 and in preparation], SAXS is sensitive mostly to pores accessible to N_2 molecules and, depending on the AC type, these pores are not necessarily serve as principal water reservoir, 2) the scattering and diffraction phenomena differ in their origin, providing complementary information: diffraction patterns are mostly determined by (relatively) ordered crystallites and their mutual arrangement, whereas the scattering is determined by contrast of electronic density and (in isotropic case) is not sensitive to spatial arrangement of the domains.

For most samples the Debye–Bueche plot ($I^{-1/2}-q^2$) is linear in range of scattering vectors corresponding to pore scattering region (Fig. 7c). This suggests applicability of the random two-phase medium approximation. However, no clear relation between fit parameters of the Debye-Bueche plot and sorption data exists.

The major fraction of the total scattering intensity is due to polydisperse large heterogeneities with sizes exceeding the resolution of the employed setup (65 nm). It is important to emphasise that the Guinier plot for the low q region is usually not linear, or the linearity range is fairly short. This observation indicates that the large scatterers do not represent a monodisperse system. These heterogeneities could be tentatively assigned to graphitic crystallites or to macropores; their role in the sorption processes is minor. The power of the fitting exponent of the corresponding part of the scattering curves on log-log plot (below we use the term “slope”) differ for the two studied types of carbons. For the furfural-based carbons the slope values cluster between -3.7 and -4.2 without clear correlation with activation degree. For the fibers-derived carbons the slopes show greater variability between -5 and -2.5 . We note here that following standard approach to treat SAXS data from activated carbons one should subtract a constant to force the scattering curve to obey the Porod law. However, as shown above (see paragraph 3.2.1) such procedure implies rather strong assumptions about structure of the material and should not be applied “by default”.

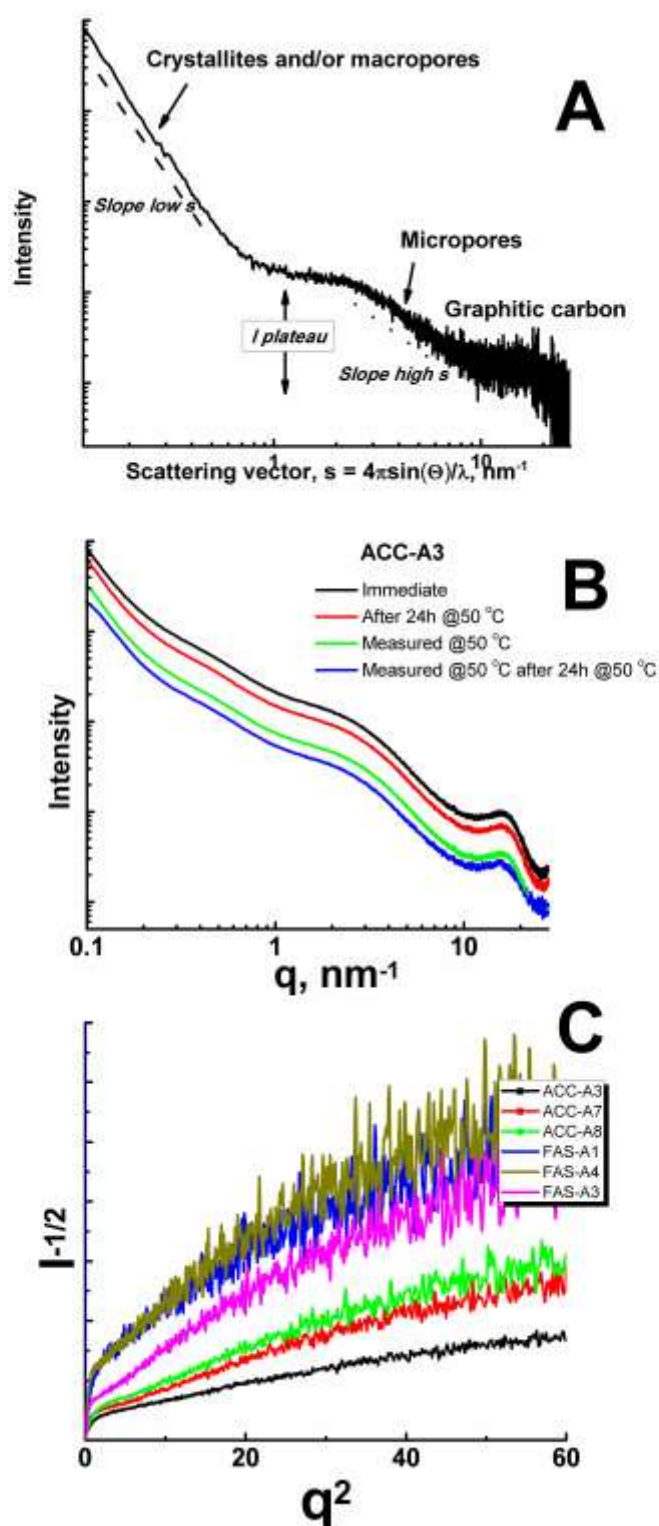


Figure 7. Small-angle scattering from the activated carbons. A – a representative SAXS curve with notations used in the text; B – Comparison of results obtained for the same specimen recorded immediately after reaching required vacuum and after various types of thermal treatment (see legend and text); C – Debye-Bueche plots for several representative samples.

A broad correlation between the activation and the slope is observed: the activation generally pushes the slope towards smaller values (-2.5) (Fig. 8). Since the drop of intensity of these regions is always not less than 1.5 orders of magnitude, with certain caution one may apply the concept of fractals, though this approach is somewhat difficult to compare with other characterization methods. Note also, that as mentioned above the scatterers are polydisperse and in case of their power-law size distribution the scattering curve will be undistinguished from fractal system (e.g. [27]).

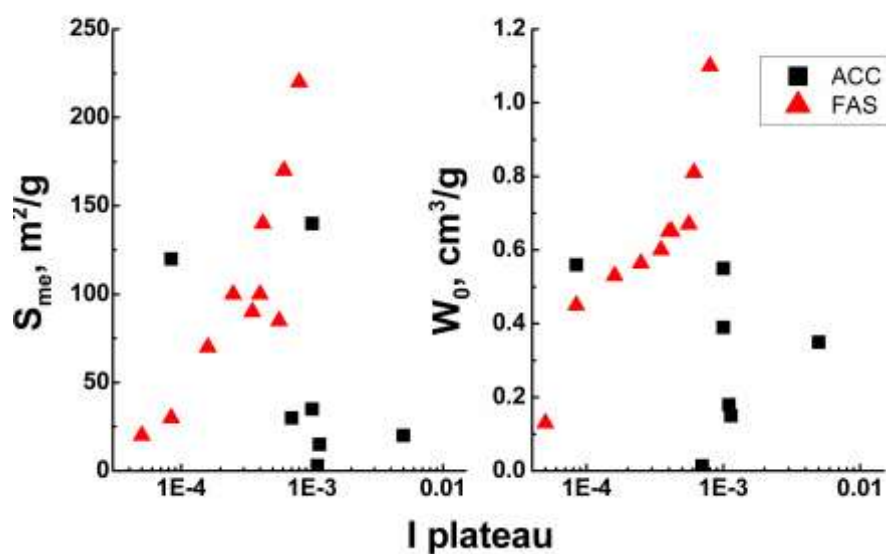


Figure 8. Sorption parameters as function of relative intensity of SAXS curve plateau. Positive correlation is observed for the polymer-based sorbents, but not for the fibers-based ones.

For the furfural-based samples we may assume presence of surface fractal. However, for the fibers-based samples the activation leads to transition from the surface to mass fractal (“perfectly rough” object corresponds to the slope -3). Since a mass fractal is a structure including branching and crosslinking of structural units to form a three-dimensional network, applicability of this concept to fibers-derived samples with rather loose structure is not unexpected. Interestingly, for few samples of both types the observed slopes are ≤ 4 . According to [29] such behavior is due to existence of a transition layer on surfaces of the scatterers. Therefore, large scale heterogeneities (crystallites or macropores) in some of the furfural-derived sorbents as well as fibers-based samples with low degrees of activation possess finite thickness transition layer on surfaces. Below we show that similar phenomenon is also observed for micropores in some samples.

At larger values of the scattering vectors (usually at $q \geq 3 \text{ nm}^{-1}$, i.e. at scales less than $\sim 2 \text{ nm}$) scattering from pores responsible for the sorption dominates. The Guinier plots ($\log(I) - q^2$) at medium to high q values ($\sim 2\text{--}8 \text{ nm}^{-1}$) contain linear region, indicating monodisperse character of the scatterers. Gyration radii are in the range $0.5\text{--}0.9 \text{ nm}$. The slope of this part of the scattering curve on double logarithmic plot ($\log(I) - \log(q)$) is roughly -2 (see below for detailed consideration). With certain caution this may be interpreted as an indication of lamellar shape of the scattering heterogeneities. Scattering curves from several samples are even more complex, possibly suggesting existence of three populations of the heterogeneities or several types of pore–matrix interfaces [30]. A clear correlation between SAXS and sorption data is observed for furfural-derived sorbents. Tentative explanation of this behaviour is given in “Discussion” section.

Intensity of small-angle scattering is proportional to product $(\Delta\rho)^2V$, where V is the volume of a scatterer and $\Delta\rho$ – contrast of electronic density between the matrix and the scatterer. Therefore, relative intensity of the plateau on the scattering curves may serve as an indication of the relative

volume of the pores, weighted with fraction of adsorbed water. For the furfural-derived samples the sorption characteristics show broad positive correlation with the plateau intensity (figure 8). Therefore, assuming that the scatterers (i.e. the pores) in the sorbents of a given type possess roughly similar electronic density, the correlation between S_{BET} and I_{plateau} is logically explained by higher volume of the pores in the samples with higher degrees of activation. In the same time, for the fibers-based sorbents such correlation does not hold. We do not have a unique explanation of such behavior, but presumably the microstructure of these materials on nanometer scale is less well-constrained due to weaker interaction between the structural units. Due to Babinet's principle the SAXS pattern acquired at a single wavelength cannot discriminate between a pore and a solid object of the same size and shape. It is therefore possible that in case of the fiber-based sorbents contributions of heterogeneities of very different nature (e.g., pore and a crystallite) to the scattering pattern are comparable. This smears the effect of activation.

The observed deviations from the Porod law are positive, i.e. the power exceeds 2. Such behaviour indicates presence of 1D and 2D fluctuations of electron density of the pore-bulk interface. Following [29] these types of the fluctuations can be explained by presence of vacancies and by variations of interlayer spacings in graphitic crystallites close to the interface. Few samples of highly activated furfural-based sorbents, but with the lowest S_{BET} values, show power law with an exponent close to 4, suggesting that the pores are approaching three-dimensional quasi-isometric shape. For the studied sorbents a correlation between the sorption characteristics with the SAS curve slope may be observed: e.g. S_{BET} increases with decreasing slope (fig. 9). The observed correlation may be logically explained by higher specific surface in materials with very rough interfaces.

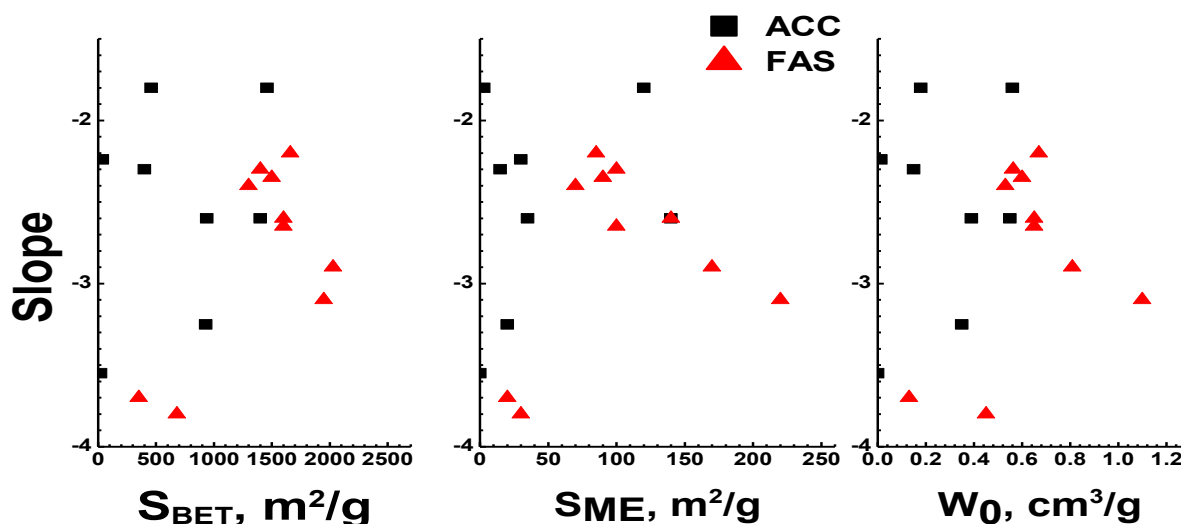


Figure 9. Relationships between parameters derived from sorption experiments and slope of SAXS curves in region related to pores.

Comparison of pores sizes obtained from sorption and SAXS data shows that x_{BET} and x_0 (Fig. 10) are broadly correlated with the Guinier radius (R_g). For the active carbons with higher degree of activation and wider micropores the pore sizes obtained from adsorption and X-ray data broadly correlated. However, no correlation is observed for activated carbons with small degree of activation.

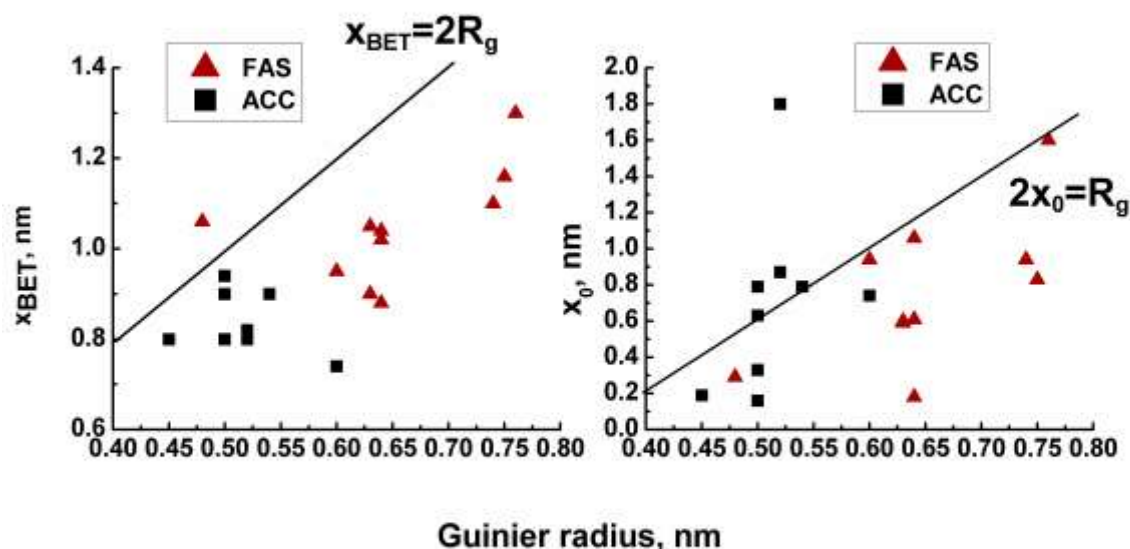


Figure 10. Correspondence between pores sizes obtained from SAXS and sorption.

3.4 Raman scattering

Raman spectra of all samples are dominated by strong broad G and D bands of sp^2 -bonded carbon. In most cases weak second order bands are also observed. Experimental spectra were decomposed into several components using Fityk software [39]; the number of potentially existing components was inferred from inflection points. Voigt profile (convolution of Gaussian and Lorentzian profiles) of the lines was assumed in order to account for various types of peak broadening. In most cases 4–5 components were needed to obtain good fit of the data. All spectra possess well-known G and D bands; the D' was poorly pronounced in most cases. Spectral decomposition employing only D and G bands often leaves a noticeable residue in the region around 1500 cm^{-1} . The fit may be partly improved by using Breit–Wigner–Fano shape taking into account extended phonon density of states (PDOS) of graphitic carbon. However, since the PDOS for the studied materials are poorly constrained due to wide variations in sizes and morphologies of graphene stacks, we employ a “phenomenological” approach and introduce an additional broad band underlining the D and G components; an example of such decomposition is shown on Figures 11a and 12. Similar decomposition was earlier used by several authors [39–43] and it was suggested that the “extra” band (G2 following notation from [43]) is related to poorly ordered sp^2 -carbon, for example, to defects outside the aromatic plane. Results of our work also support the view that this band is not purely a mathematical trick, but is indeed an important issue in Raman studies of carbon-based sorbents. Following [40] we suggest that it represents a G-band of (semi)amorphous carbons present in the samples. This assignment is based on several independent observations: 1) X-ray diffraction clearly shows presence of considerable amount of poorly ordered carbon in all studied sorbents; 2) the position of the band corresponds well to the G-

band of amorphous carbon [44]; 3) in unconstrained fit this band has almost pure Gaussian character, indicating that responsible bonds possess broad distribution of interatomic angles; 4) this band shows pronounced dispersion. Note that recent computational study [45] assign the raman intensity between 1400 and 1550 cm^{-1} to coupling of breathing modes and asymmetric stretching caused by defects within the PAH clusters and impurities.

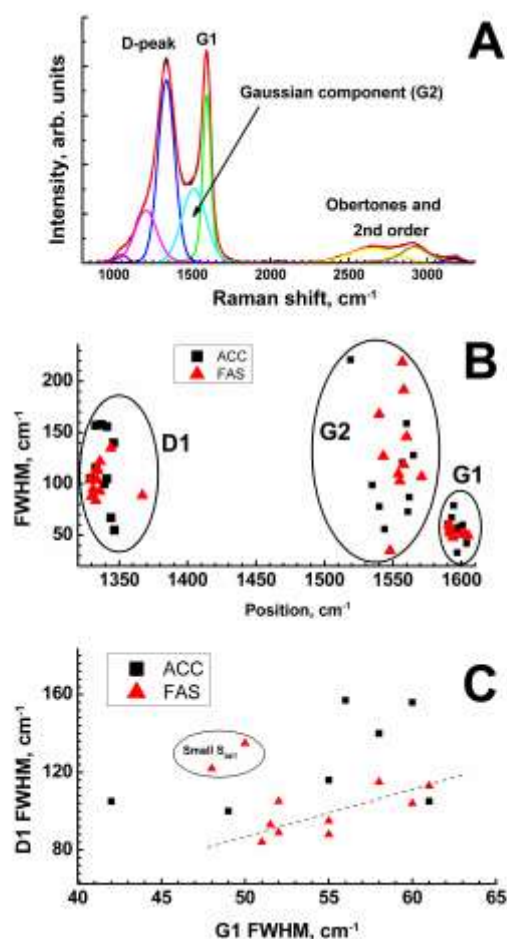


Figure 11. A - Example of spectral decomposition of Raman spectrum acquired at 532 nm excitation. A Gaussian band around 1500 cm^{-1} is clearly observed. B – position of the studied samples at FWHM-position plot, see text. C – relationships between the FWHM values of the G1 and D1 bands.

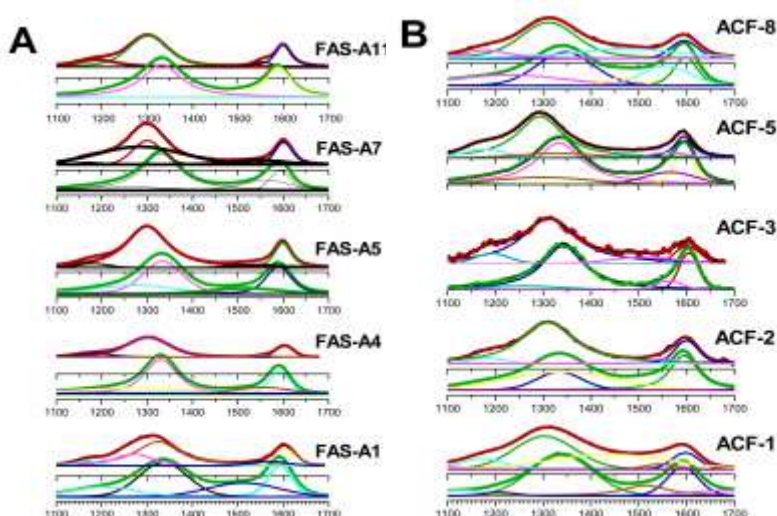


Figure 12. Raman spectra of studied sorbents. A- FAS – furfural-based active carbons; B – Activated Carbon Fibers - based sorbents. For every sample spectra excited at 532 nm (bottom curve) and 785 nm (top curve) are shown. The degree of activation increases from bottom to top.

Decomposition of the D band into several components is also possible, and example of such decomposition is shown, for instance, in [43] (their bands D1 and D2). If the assignment of the broader G2 band to disordered carbon is correct, one may expect presence of the corresponding D2 band. However, the FWHM of the D2 band is always very large (250-400 cm^{-1}) both in [43] and in our own work. In our view bands of such width are not easily ascribed to a single component, reflecting kind of a “continuum”. Subsequently, position of the maximum, FWHM and other characteristics of this band often change significantly between independent decomposition runs. Therefore, this band was not included into our evaluation. FWHM and positions of the components are shown on Fig. 11b. Decomposition of spectra recorded at 532 and 785 nm excitation gave qualitatively similar results; therefore, only the former data are shown.

A broad correlation between FWHM of the D1 and G1 peaks is observed for the FAS samples except the specimens with very low S_{BET} (fig. 11c). At present structural grounds for the correlation are not yet clear. Intensity and FWHM of the G2 band broadly correlates with porosity derived from sorption measurements, see fig. 13. For the fibers-derived samples the G2 band becomes less important with increased activation. For the FAS-samples the relation is more difficult to explain.

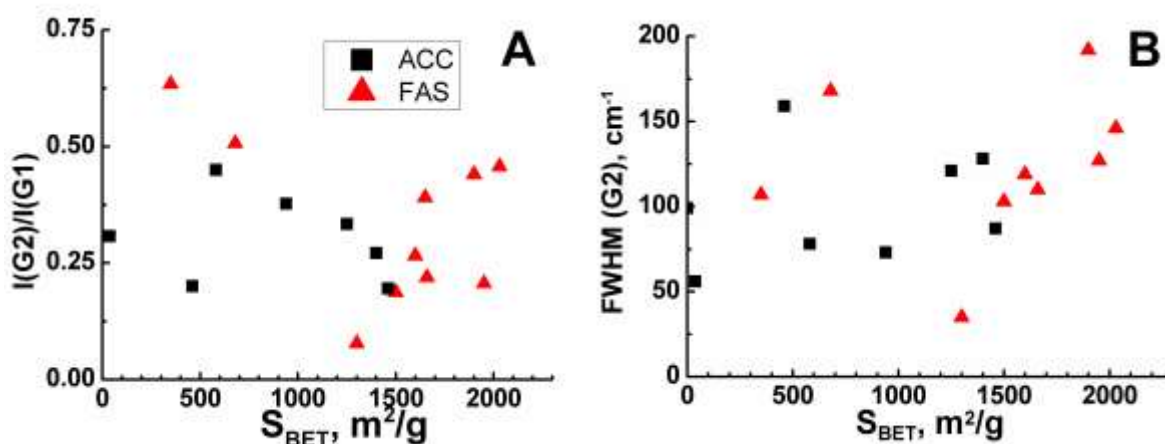


Figure 13. Relationships between intensity and FWHM of the G2 band with porosity.

Virtually all spectra show weak peak around 1180 cm^{-1} and sometimes a second feature at $1030\text{--}1060\text{ cm}^{-1}$ (figs. 11a, 12). These peaks might correspond to sp^3 -carbon, e.g. in olefinic chains [29], to transpolyacetylene (TPA) – like structures or symmetric breathing modes of PAH rings of different sizes [45]. Some support of the assignment to TPA is given by existence of a feature in pair-distribution function analysis (not shown), but persistence of the feature at 785 nm excitation weakens this assignment. Due to general weakness of the peak it is difficult to correlate it with other structural or sorption parameters. However, its intensity seems to be lower in samples with medium degree of activation.

In order to get better constraints on the structure of the samples excitation at different wavelengths was used. The dispersion of the main G1-band (close to 1600 cm^{-1}) was generally small and appears to be unrelated to the activation degree. The small dispersion implies that the responsible sp^2 -carbon is arranged into relatively large crystallites (several nm in size). In the same time, X-ray diffraction data indicates that the average crystallites are smaller than 2 nm . No clear correlation between the FWHM values for the G1 or D1 peaks or of $I(\text{D})/I(\text{G})$ ratio and X-ray-derived size (Tuinstra-König relationship) was observed. The discrepancy may be ascribed to several factors including various physical mechanisms of the signal formation in X-ray diffraction and Raman scattering [46]. In addition, these two methods are sensitive to somewhat different populations of the crystallites present in complex material such as carbonaceous sorbent. Presumably, the G-peak at 1600 cm^{-1} in Raman spectra originates mostly from relatively perfect large crystallites; the (semi)amorphous component gives rise to broad G-peak around 1500 cm^{-1} . No clear correlation between the width of the G peak or $I(\text{D})/I(\text{G})$ ratio with sorption characteristics is observed. In the same time, a weak negative correlation is observed for the D peak properties and sorption – its FWHM decreases with increasing S_{BET} , likely reflecting changes in the defects types with progressive activation.

The dispersion of the D band demonstrates high variability from sample to sample (Fig. 12). The studied sorbents can be separated into two main groups with fairly different values of the dispersion. Most of the polymer-based samples are characterized by relatively small dispersion, whereas the fibers-based ones are clustered in the region of high dispersion values.

4. Conclusions

Carbonaceous sorbents produced from furfural and from impregnated viscose fibers were characterized after storage at ambient conditions using complementary techniques permits to establish correlations between sorption parameters and some structural characteristics. The sorbents could be represented as a system comprising nanosized graphite-like crystallites of various degrees of perfection wrapped into amorphous carbon. The amorphous fraction diminishes on activation. In wet state water molecules may arrange graphitic crystallites, dramatically influencing X-ray diffraction patterns. In contrast to X-ray diffraction, moisture has only negligible influence on SAXS patterns from the studied ACs, implying that overall shape and size of pores accessible to N_2 are not strongly affected.

A correlation between the Small-Angle X-ray Scattering results and N_2 sorption data is observed for carbons obtained from the same precursor. According to SAXS the studied samples represent hierarchic structures consisting of large crystallites and fairly monodisperse pores. The relative intensity of the pore-related scattering increases with degree of activation. An important problem in interpretation of the SAXS data for sorbents is the dependence of the scattering curve slope on pore-matrix interface structure. In most samples the deviations from the Porod law are positive, suggesting presence of 1D and 2D fluctuations of electron density of the pore-bulk interface. In highly-activated carbons the pores approach three-dimensional quasi-isometric shape. The observed correlation between the SAXS curve slope and sorption parameters is due to higher specific surface in materials with very rough interfaces. Modeling using two independent approaches shows that deviations from the Porod law should not be ignored in analysis of SAS data for active carbons. For active carbons with higher degree of activation and wider micropores the pore sizes obtained from adsorption and X-ray data broadly correlated. However, no correlation is observed for activated carbons with small

degree of activation. X-ray diffraction patterns of the sorbents change considerably with humidity of the powdered sorbents, severely complicating data analysis.

Spectral decomposition of Raman spectra in addition to obvious G and D bands reveals almost pure Gaussian residue in the region around 1500 cm^{-1} . Presumably this band is due to poorly ordered sp^2 -carbon, possibly being a G-band of (semi)amorphous carbons present in the samples.

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