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Investigation of Structural and Adsorptive Characteristics of Various Carbons

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Abstract. Structural and adsorption properties of carbon sieves, activated carbons and graphitized carbon blacks were studied using adsorption of nitrogen, water, and high molecular organics. Several types of pore models were used to study the pore size distributions (PSD) of the adsorbents. The interfacial behavior of water adsorbed in the presence of organics depends on both the surface chemistry of an adsorbent, its structure and the characteristics of organics. A smaller size (1–10 μm) of particles of microporous Carboxen 1010 than that of Carboxen 1003 (150–200 μm) provides initially faster adsorption of lipopolysaccharide (LPS) molecules by the first carbon. However, the LPS adsorption on micro/meso/macroporous Carboxen 1003 becomes greater with time since this carbon has broad pores appropriate in size for the adsorption of large biopolymer molecules in contrast to Carboxen 1010, which adsorbs LPS mainly on the outer surface of the particles.

Keywords: carbon adsorbents, structural and adsorption characteristics, interfacial water, polymer adsorption

1. Introduction

Carbon adsorbents are widely used in industrial applications, environmental protection and medicine (Bansal et al., 1988; Jankowska et al., 1991; Fenelonov, 1995). High adsorptive capacity of activated carbons is attributed to their large surface area (up to 3000 m^2/g), significant porosity (0.5–1.5 cm^3/g or larger), and to various surface functionalities. Characterization of surface composition and adequate determination of pore size distribution (PSD) of adsorbents are of importance from the practical point of view. These characteristics of activated or graphitized carbons, carbon sieves or fibers can substantially differ. Characterization of adsorbents cannot be considered as complete if their surface energetic properties (e.g. adsorption potential or adsorption energy for target compounds) are not determined. For adequate description, these properties should be linked to topological features (as adsorption potentials in narrow micropores and large mesopores can strongly differ) and chemical characteristics (e.g., nature of surface functionalities) of a surface. Fractal dimension of adsorbents provides topological information, which is useful for analysis of the particle surface

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topography (surface fractality) or textural features of pores (pore fractality) and structural heterogeneity. The latter could be of interest for dipper understanding of adsorption of macromolecules. The aim of this work is to study the relationships between different structural and energetic characteristics of several types of carbon adsorbents using low-temperature nitrogen adsorption data treated using different adsorption isotherm equations solved using regularization procedure, and analysis of the properties of interfacial water by ^{1}H NMR method with layer-by-layer freezing-out of liquid water at $T < 273$ K.

2. Materials and Methods

Activated carbons of natural origin A2PS-x (HPSD, Hajnówka, Poland) prepared from plum stones, MAST carbons (MAST Carbon Ltd., Guildford, UK) produced from phenolic resin precursors with different degree of burn-off (shown in carbon's code MAST-xx as percentage (xx) of burn-off in Table 1), carbon sieves (Carboxen 569, 1002, 1003, 1010, 1012 and 1016) and graphitized carbons Carbopacks B, F, and X (Supelco, Inc.) were studied using low-temperature nitrogen adsorption-desorption measured using Micromeritics ASAP 2010 and 2405 N adsorption analyzers. Certain carbon samples were studied by ^{1}H NMR method (using a high-resolution WP-100 SY (Bruker) NMR spectrometer) with freezing-out of adsorbed water (Turov et al., 2002) and by adsorption of organics. The nitrogen adsorption-desorption isotherms were analyzed using an overall isotherm equation based on the modified Kelvin equation and the statistical adsorbed film thickness with a regularization procedure (Gun'ko and Do, 2001) to compute the pore size distributions both differential $f(x)$ and incremental (IPSD) (Gun'ko and Mikhalovsky, 2004). Notice that the IPSD functions calculated using DFT and present method are close, for instance, for active carbons (Gun'ko and Bandosz, 2003; Melillo et al., 2004) and silica gels (Gun'ko et al., 2002). Additionally, the PSDs of porous silicon determined from the TEM image and calculated

Table 1. Structural characteristics of carbon adsorbents.

Carbon	S_{BET} M^2/g	V_p cm^3/g	V_{mic} cm^3/g	V_{mes} cm^3/g	V_{mac} cm^3/g	S_{mic} m^2/g	S_{mes} m^2/g	$\mathrm{S_{mac}}$ m^2/g	Δw
Carboxen 569	457	0.51	0.114	0.265	0.130	178	44	3	0.471
Carboxen 1002	1177	0.97	0.454	0.188	0.323	821	54	10	0.160
Carboxen 1003	1168	0.85	0.451	0.222	0.137	820	66	6	0.147
Carboxen 1010	953	0.46	0.367	0.035	0.058	697	26	1	0.143
Carboxen 1012	1375	0.64	0.590	0.048	0.003	968	36	0	0.041
Carboxen 1016	74	0.44	0.011	0.238	0.191	28	28	6	0.205
Carbopack B	99	1.02	0.015	0.276	0.730	25	42	19	0.151
Carbopack F	6	0.02	0.001	0.010	0.011	2	2	0	0.275
Carbopack X	225	0.47	0.105	0.245	0.120	164	41	3	0.073
A2PS	1054	0.720	0.425	0.286	0.009	866	188	0	0.350
A2PS-O1	1149	0.723	0.409	0.291	0.022	911	237	1	0.566
A2PS-O2	1162	0.713	0.407	0.297	0.009	928	234	0	0.540
A2PS-H	1201	0.733	0.438	0.283	0.013	980	221	1	0.571
MAST-37	1150	1.15	0.50	0.65	0	911	137	0	0.099
MAST-48	1340	1.32	0.56	0.73	0	994	175	0	0.181
MAST-58	1820	1.72	0.73	0.99	0	1167	265	0	0.285
MAST-65	1840	1.73	0.73	0.98	0	1187	271	0	0.262
MAST-75	2330	2.12	0.80	1.30	0	1243	435	0	0.328
Norit RBX	1029	0.51	0.41	0.08	0	756	48	0	0.279

Note. S_{BET} is the specific surface area, V_p is the total pore volume, V_{mic}, V_{mes}, $V_{\mathrm{mac}} S_{\mathrm{mic}}$, S_{mes}, and S_{mac} are the pore volumes and specific surface area of micro-, meso-, and macropores, respectively, calculated by integration of the PSDs over the corresponding ranges of pore half-width of 0.2–1.0 nm, 1.0–25.0 nm and 25.0–100.0 nm. $\Delta w = S_{\mathrm{BET}}/S_{\mathrm{slit}} - 1$.

using the mentioned method are very close (Gun'ko and Mikhalovsky, 2004).

3. Results and Discussion

Among the studied carbons, only microporous Carboxens 1010 and 1012 possess relatively simple PSDs (Fig. 1), since other adsorbents are characterized by complex polymodal PSDs including pores from half-width $x < 1$ nm up to $x > 25$ nm. This texture leads to a complex shape of the adsorption potential distribution, especially for non-graphitized carbons (Fig. 2). Graphitization significantly reduces not only structural non-uniformity of carbons but also the energetic heterogeneity of their surfaces (Figs. 1 and 2). The values of $\Delta w = S_{\mathrm{BET}}/S_{\mathrm{slit}} - 1$ (where S_{slit} is the specific surface area determined from $f(x)$ using the slitshaped pore model) (Table 1) related to the deviation of the pore shape from the slitlike model show that practically all the studied carbons do not have ideal slitshaped porosity, especially initial A2PS, oxidized A2PS-O1 and A2PS-O2 (oxidized by H_2O_2 (30%) at 523 and 623 K respectively for 6 h) and A2PS-H (reduced by H_2 at 1073 K for 8 h) since $\Delta w > 0.35$. A complex model of pores with contributions of slitshaped and cylindrical pores and gaps between spherical particles gives substantially smaller Δw values for carbon adsorbents (Gun'ko and Mikhalovsky, 2004; Melillo et al., 2004) that can be considered as evidence of the complexity of the texture of carbon adsorbents. The structural characteristics (Table 1) and the PSDs show that the studied carbons (with exception of Carboxens 1010 and 1012) can be used as adsorbents for large biomacromolecules.

The difference in the structural characteristics of two types of carbon adsorbents (with and without broad pores) reflects in the adsorption of lipopolysaccharide (LPS) molecules (Fig. 3). Carboxen 1010 adsorbs the LPS faster initially because of smaller particles (1–10 μm in diameter) and larger their outer surface area

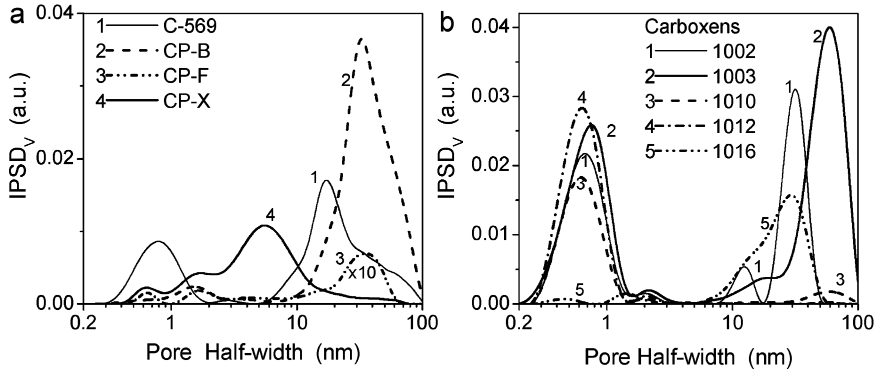

Figure 1. Pore size distributions of (a) Carboxen 569 (C-569), Carbopacks (CP) B, F, and X, and (b) Carboxens 1002, 1003, 1010, 1012, and 1016.

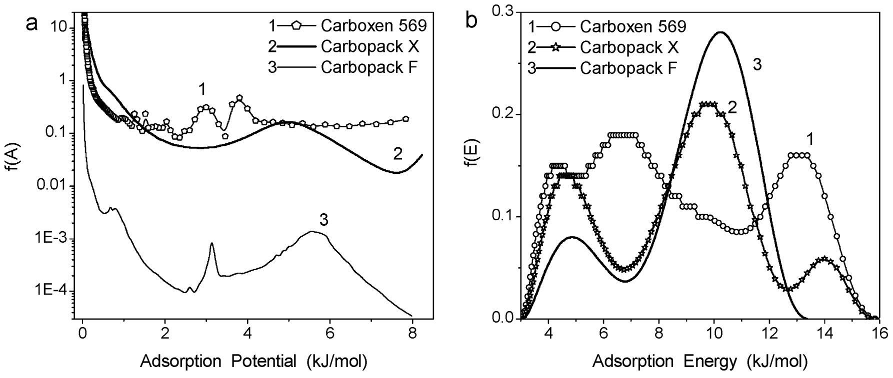

Figure 2. Nitrogen (a) adsorption potential and (b) adsorption energy distributions for Carboxen 569 and Carbopack X and F.

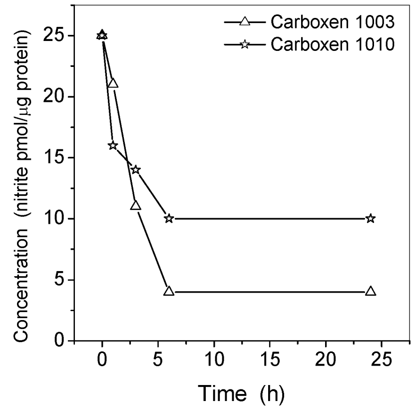

Figure 3. Comparison of the adsorptive capacity of Carboxen 1003 and Carboxen 1010 with respect to LPS.

than that of Carboxen 1003 (150–200 μm). However, Carboxen 1003 adsorbs more LPS with time because of its textural features, since it has larger surface area and pore volume (with greater contribution of pores at $x > 10$ nm) than that of Carboxen 1010. This results in greater adsorption of large LPS molecules and their complexes (LPS complexes can be up to 10^6 Da and 30 nm in size) on Carboxen 1003 than on Carboxen 1010. Carboxen 1003 removes 90% of LPS from the solution, whereas Carboxen 1010 removes only 20% at the concentration ratio $C_{\text{LPS}}/C_{\text{carbon}} = 0.01$. This equilibrium adsorption corresponds to changes in the Gibbs free energy (ΔG) on the LPS adsorption approximately –5.2 kJ/mol for Carboxen 1003 and $\Delta G = -2.7$ kJ/mol for Carboxen 1010. Since the chemical nature of these carbons is close, the difference in ΔG may be caused by the steric factor; e.g., the inaccessibility of narrow pores of Carboxen 1010 for large biopolymer molecules diminishes the adsorption. A simple estimation of the outer surface of carbon particles as $S_{\text{out}} = 6000/(d\rho)$ gives approximately 2–3 m^2/g for Carboxen 1010; i.e., about 0.2–0.3% of the total surface area. This S_{out} value can provide the LPS adsorption observed for Carboxen 1010. However, in the case of Carboxen 1003, the S_{out} value is significantly lower because of a larger size of particles but the LPS adsorption is higher. This effect may be explained only by the LPS adsorption in large pores characteristic for Carboxen 1003. The experiments show that the LPS adsorption is complete in 24 h, and a minimum time to reach the state close to equilibrium is 6 h since the response for 6 h and 24 h is very close. The time of the equilibrium adsorption is long because of slow penetration of large biopolymers into carbon pores even in the case of Carboxen 1003 having broad pores. Long time of the equilibrium adsorption of LPS on the outer surface of Carboxen 1010 can be caused by changes in conformation of the LPS molecules and their complexes in the adsorption layer, e.g., due to slow decomposition of large LPS complexes and unfolding of LPS molecules in the adsorption state in consequence of strong adsorption interaction with the carbon surface functionalities. Additionally, very low amounts of LPS can penetrate into pores of Carboxen 1010 that can cause so long equilibrium time.

The structural factor (see PSDs of MAST carbons and Norit RBX in Fig. 4, and parameters in Table 1) affects the adsorption of a low molecular compound (ibuprofen) in the presence of bovine serum albumin (BSA) (Fig. 5) (Melillo et al., 2004). Broad pores existing in particles of MAST carbons provide near the same adsorption of ibuprofen in the presence BSA. However, in the case of Norit RBX having narrow pores, the ibuprofen adsorption significantly decreases in the presence of BSA which can easily block these narrow pores. It should be noted that oxidation or reduction of the carbon surface can cause significant changes in the interfacial behavior of water (Fig. 6(b)) filling carbon pores with near the same PSDs (Fig. 6(a)). Interaction between water and other adsorbates in pores play an important role in both equilibrium adsorption (Tuvov et al., 2004) and dynamic adsorption (Palijczuk et al., 2002) of organic compounds. These features of interfacial water should be considered on interaction of both polar and nonpolar organics with carbon adsorbents, since the solubility and the miscibility of water and organics can significantly differ in narrow pores in

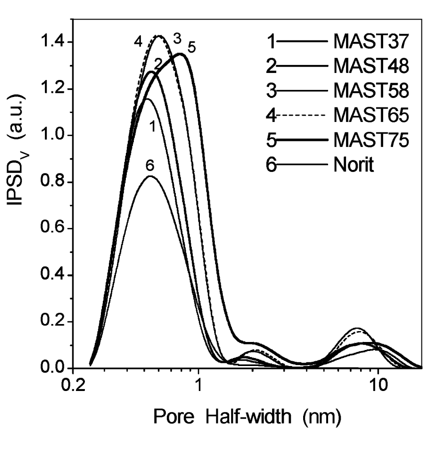

Figure 4. PSDs of MAST carbons and Norit RBX.

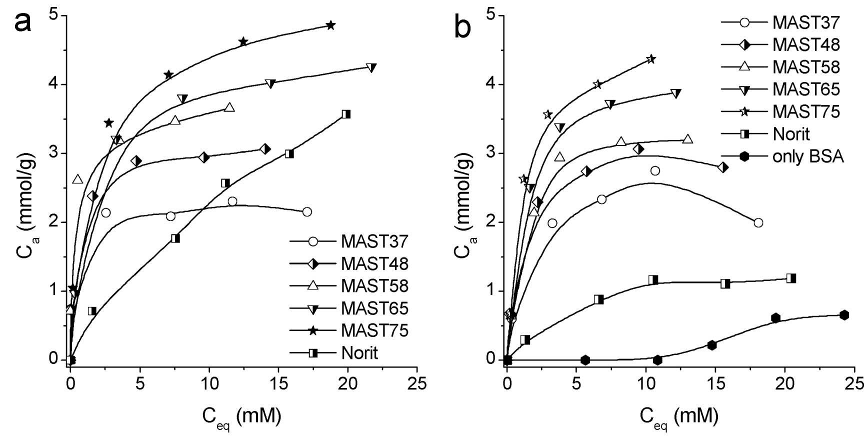

Figure 5. Ibuprofen adsorption isotherms from (a) protein free solution and (b) the solution with BSA on carbons; interaction between ibuprofen and BSA without carbon is shown (b).

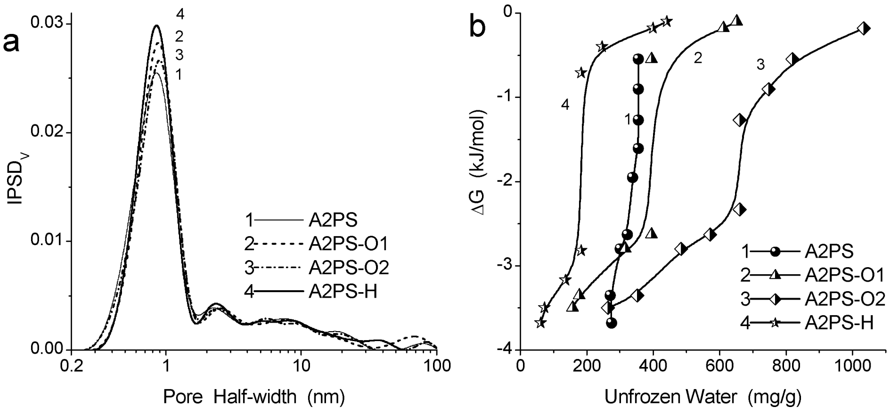

Figure 6. (a) Pore size distributions for A2PS-x carbons, and (b) changes in the Gibbs free energy of water adsorbed onto these carbons and which is nonfreezable at $T < 273$.

comparison with bulk solutions or broad pores (Tuvov et al., 2004).

4. Conclusion

A model of slitshaped pores may be too simplified for many of activated carbons. In the wide sense, any model of pores for any adsorbent gives always simplified picture. A proposed criterion of deviation of the pore shape from the model is useful for estimation of the trustworthiness of the applied model. Adsorption of low and high molecular compounds depends not only on the pore size distribution of carbon adsorbents but also on the particle size distribution and the nature of the particle surface. Macromolecules can affect the adsorption of low molecular compounds stronger with lowering contribution of broad meso- and macropores. MAST carbons and other carbon adsorbents with significant contribution of broad pores can effectively adsorb not only low molecular compounds but also macromolecules, or small organic molecules such as ibuprofen in the presence of biomacromolecules. These effects are of importance on the application of carbon adsorbents in haemoperfusion column technique and other applications in medicine and biotechnology.

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