

Heterogeneity of activated carbons based on adsorption of phenols from aqueous solutions

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The heterogeneity of activated carbons (ACs) prepared from different precursors is investigated on the basis of adsorption isotherms of phenol and 2,3,4-trichlorophenol from dilute aqueous solutions at various pH values. The Langmuir-Freundlich equation as well as the Dubinin-Astakhov one have been used to estimate the parameters characterizing adsorption from aqueous phenol solutions on heterogeneous carbon surfaces. Adsorption-energy distribution (AED) functions have been calculated by using an algorithm based on a regularization method. Analysis of these functions for activated carbons provides significant comparative information about their heterogeneity. Besides, literature data on enthalpy values for the transfer of phenol from a solution to surfaces of ACs confirm the correctness of the adsorption energies obtained in our study. The AED functions for phenol on activated carbons, generated by a utilization of the regularization method have been verified. As a verification tool, the Grand Canonical Monte Carlo simulation method carried out on a square lattice has been chosen.

1. INTRODUCTION

Adsorption of phenolic compounds on activated carbons (ACs) is an important issue because of its environmental aspects [1-4]. Phenols are toxic compounds, dangerous for human health, that cause an unpleasant taste and odor even at low concentrations in drinking water.

It is known that the adsorption capacity of activated carbon (AC) for the liquid adsorption of aromatic compounds depends on [3,5]: the nature of the

adsorbent (extended pore structure, present surface functional groups, ash content); the nature of the adsorbing species (pK_a , functional groups, polarity, aqueous solubility, molecular size); and the bulk solution conditions (pH, ionic strength, concentration of compound). Important are also such factors as the type of the precursor of carbon, and oxygen availability in the solution (“oxic” or “anoxic” conditions of the adsorption process [6,7]).

The heterogeneity of AC surfaces has both a geometrical and chemical character. The geometrical heterogeneity - porosity is the result of differences in the size and shape of pores and pits, vacancies etc. The chemical heterogeneity is associated with different functional groups at a surface (mainly oxygen), and with various contaminants of the surface. Both heterogeneities contribute to the unique adsorption properties of carbons [3,8-10]. The surface groups as well as the delocalized electrons of the graphitic structure determine the apparent acid/base character of the AC surface, so they cause the surface properties of carbons to depend on the pH in aqueous solutions. The distribution of the surface functionalities is thus of great importance in the adsorption processes from liquid solutions.

The heterogeneous properties of solid adsorbents can essentially be described by their so called adsorption energy-distribution (AED) function. To obtain this function, the Fredholm integral equation of the first kind must be solved. However, this equation is numerically ill-posed [11,12], so the exclusive use of the least squares method for its solving can lead to distorted functions. A regularization method was therefore used, which substantially improves the results [9,11-17]. The adsorption energy-distribution functions for phenol on activated carbons, generated by application of the regularization method (INTEG algorithm) can be verified [9,11-21]. As an independent verification tool, the Grand Canonical Monte Carlo (GCMC) simulation technique has been chosen [22-26]. The definitive stage of the verification was a comparison of the experimental isotherms and those obtained by the employment of GCMC simulations – based on the parameters of AED functions generated by the regularization method.

The main objective in the present paper is a survey in a compact form of our selected studies which have been made lately, dealing with heterogeneity effects accompanying the adsorption of phenols from aqueous solutions on activated carbons.

2. EXPERIMENTAL

The compact characteristic of activated carbons studied is included in this section. Additionally for each carbon the sorption experiment from the dilute aqueous solutions of phenols is briefly described.

2.1. Preparation and characterization of BW and MT carbon samples

The experimental adsorption data have been taken from literature [27]. Two Australian bituminous coals, Black Water (BW) and Mt Thorley (MT) were used as precursors of activated carbons. The major difference in the ultimate analysis of both carbons was the oxygen content – 7.4 wt % for BW carbon and 11.8 wt % for the MT one. The detailed preparation, the physical properties of these carbons and the analysis of nitrogen adsorption data were reported earlier [27]. Table 1 includes the porosity characteristics of ACs studied. Each activated carbon has been designated by using the nomenclature of its coal precursor followed by the burn-off level reached in CO₂ gasification. This table includes the specific surface area, S_{BET} , volume of the pores, V_p , volume of micropores, V_{micro} , and mesopore volume V_{meso} , respectively. The last column includes the average pore diameter \bar{d} .

The average pore diameters were calculated assuming their cylindrical shape by means of the equation: $\bar{d} = 4V_p / S_{BET}$. Micropore volumes of the samples were determined from the Dubinin-Radushkevich equation. Subtraction of the micropore volumes from the total amounts (determined at $p/p_0 = 0.98$) provided the volumes of mesopores. The ACs studied were mainly microporous, as indicated by the data in the table. Table 1 shows that the surface area and the pore volume increase upon the activation process. For the BW carbons the mesopore volume, V_{meso} , and the average pore diameter \bar{d} show increase with the burn-off level, but it is less visible for MT carbons.

Tab. 1. Porosity characteristics of the ACs studied [27].

Activated Carbon	S_{BET} (m ² /g)	V_p (cm ³ /g)	V_{micro} (m ³ /g)	V_{meso} (cm ³ /g)	\bar{d} (nm)
BW17	204	0.10	0.094	0.006	2.0
BW51	300	0.22	0.1452	0.0748	2.9
MT21	321	0.17	0.1513	0.0187	2.1
MT40	528	0.29	0.2465	0.0435	2.2

2.1.1. Sorption from the dilute aqueous solutions of phenols

The adsorption isotherms were determined by the static method for BW and MT activated carbons for the phenol aqueous solution at 303 K. The details of measurement are described elsewhere [27].

2.2. Preparation and characterization of APAN and APET carbons

The APAN carbon was obtained from polyacrylonitrile (PAN) by a two-step physical activation process [28,29]. The preparation, physical properties and the analysis of the nitrogen adsorption were reported earlier, but for reminder the Table 2 shows selected data.

The surface chemical composition of the APAN carbon was determined by X-ray photoelectron spectroscopy (XPS). The distributions of carbon, oxygen and nitrogen structures (at.%) from the XP C_{1s}, XP O_{1s} and XP N_{1s} spectra, respectively, were published in tabulated form [28,30]. According to the analysis of the N_{1s} spectrum, several forms of nitrogen (e.g., quaternary nitrogen, pyrrolic-N, pyridinic-N) exist on the surface of this carbon sample. These sites reveal a basic character, and their protonation results in the formation of positive charges [28]. The XPS results showed that the surface of the APAN carbon contains 89.4 at. % carbon (of which 50.4 at.% in the form of graphitic carbon), 5.3 at. % oxygen and about 5.3 at. % of nitrogen. The comprehensive acid/base characterization of the carbon studied is included in Table 3. The carbon surface reveals a basic surface character as the initial pH value of the carbon suspension was found to be 7.8. The equilibrium Boehm titration was used to determine the number of surface groups of the granular carbon [28]. About 75 % of the functional groups are basic and about 25 % are acidic.

Tab. 2. Nitrogen adsorption data for APAN and APET carbons [9,28,31].

Precursor	Carbon	S _{BET} [m ² /g]	V _p [cm ³ /g]	V _{micro} [cm ³ /g]	V _{meso} [cm ³ /g]	\bar{r} [nm]
polyacrylonitrile (PAN)	APAN	544	0.278	0.266	0.012	1.02
polyethylene terephthalate (PET)	APET	1170	0.625	0.425	0.200	1.07

Note: \bar{r} is the average pore radius and $\bar{r} = 2V_p/S_{BET}$ (assuming cylindrical geometry of pores)

The activated carbon (APET) was obtained from polyethylene terephthalate (PET). The preparation and the physical properties, as well as the analysis of the nitrogen-adsorption data were reported elsewhere [29,31]. Table 2 includes selected characteristics of this carbon.

The surface chemical composition of the APET samples was also determined by XPS. The distributions of the carbon and oxygen structures (atomic %) derived from the XP C_{1s} and XP O_{1s} spectra, respectively, were published earlier [30,31]. The XPS results showed that the surface of the APET carbon contains

95.7 at. % carbon (of which 60 at.% of surface carbon atoms are present in graphitic form) and 4.3 at. % oxygen. The acid/base characterization of the APET carbon is shown in Table 3. The initial pH value of the carbon suspension determined in the same way as in the case of APAN carbon, was found to be 8.1. The Boehm titration method was used to determine the number of oxygenated surface groups. About 81.6% of the functional groups were basic. The acidic character arose from the phenolic (81.1%) and lactonic (18.9%) groups.

2.2.1. Sorption from dilute aqueous solutions of phenols on APAN and APET carbons

Adsorption isotherms for phenol from aqueous solutions on APAN and APET activated carbons were determined by the static method at room temperature. The details of measurement are described elsewhere [28,31]. Solutions of phenol were prepared using doubly distilled water, or the appropriate buffer solutions. The specified sample of carbon was shaken with phenol solution for 24 hrs at room temperature. Contact time was determined from preliminary kinetic measurements [32].

Tab. 3. The acid/base characterization of the APAN and APET carbons [9,28,31].

Activated carbon	pH _{ini}	Total acidity [μeq/g]	Total basicity [μeq/g]	% of the basic groups	Basic/acidic	total number of titrated groups /100 nm ²
APAN	7.8	112.9	336.3	75	2.98	74
APET	8.1	93.7	416.8	81.6	4.45	26

2.3. Preparation and characterization of the original APET carbon as well as modified ACs

Activated carbon samples were prepared from polyethyleneterephthalate (PET) by a two-step physical activation [33]. Part of the samples was treated with concentrated HNO₃ at room temperature for 3 hrs (APET3) and 6 hrs (APET6) to achieve changes of surface functionalization. Carbons were then washed in distilled water and extracted in a Soxhlet apparatus until neutral pH was obtained. An additional heat treatment at 700°C for 30 min in N₂ flow was applied to part of samples APET3 and APET6 to modify the concentration and the distribution of the surface functional groups. Carbons obtained are designated as APET3H and APET6H, respectively. The detailed preparation and

physical properties as well as analysis of low temperature nitrogen adsorption data were reported earlier [10]. Table 4 shows porosity characteristic of ACs studied.

The surface chemical composition of the samples was determined by XPS [30]. The distributions of the carbon and oxygen structures (atomic %, ± 1 %) derived from the XP C_{1s} and XP O_{1s} spectra, respectively, were published recently in tabular form [33]. The XPS results showed that the surface of the APET carbon contains 93 at. % carbon (of which 52.7 at.% of surface carbon atoms are present in a graphitic form) and 7 at. % oxygen, which leads to an O/C ratio of 0.075. The acid treatment slightly increases the O/C ratios for the granular samples APET3. However, the longer treatment (APET6) does not further increase the overall surface oxygen content. Additional heat treatment results in a further slight increase in the O/C ratio (APET3H, APET6H).

Tab. 4. The porosity characteristic of activated carbons studied [10].

Activated carbon	S_{BET} [m ² /g]	V_t [cm ³ /g]	V_{micro} [cm ³ /g]	w_{ads} [nm]
APET	1214	0.52	0.50	0.87
APET3	1320	0.57	0.53	0.86
APET6	1165	0.50	0.47	0.86
APET3H	1382	0.60	0.56	0.87
APET6H	1488	0.64	0.61	0.86

Note: $w_{\text{ads}} = (2 V_{\text{tot}} / S_{\text{BET}})$

The original APET carbon surface reveals a basic surface character (the pH value of the carbon suspension was found to be $\text{pH}_{\text{slurry}} = 7.5$), but other carbons possess an acidic surface character. The pH_{PZC} values of the carbons were measured by the so-called drift method [34]. The Boehm titration method was used to determine the number of oxygenated acidic and basic surface groups. In this aim, the carbon samples were titrated with 0.05 M NaOH and HCl solutions, respectively [35]. The comprehensive acid/base characterization of the carbons studied is included in Table 5.

Table 5. The acid/base characteristic of activated carbons studied [10].

Activated carbon	pH _{slurry}	pH _{PZC}	Total acidity [μeq/g]	Total basicity [μeq/g]	% of the basic groups	basic /acidic	total number of titrated groups /100nm ²
APET	7.5	9.25	80	420	84.0	5.25	24.8
APET3	4.0	4.45	640	196	23.4	0.31	38.1
APET6	3.8	3.81	725	193	21.0	0.27	47.5
APET3H	5.8	7.12	442	319	41.9	0.72	33.2
APET6H	5.7	7.13	380	328	46.3	0.86	28.7

2.3.1. Adsorption from dilute phenol aqueous solution

The equilibrium phenol isotherms were measured at various pH values by the batch method from their solutions prepared with doubly distilled water and the appropriate buffer solutions at ambient temperature [36]. Initial and equilibrium concentrations were determined by detecting the UV absorption of the solutes. The contact times needed to reach equilibrium were deduced from preliminary kinetic measurements [32].

3. RESULTS AND DISCUSSION

For adsorption from dilute aqueous solutions, the total fractional coverage of solute, $\theta_t(c)$, in the surface phase may be expressed in the following form [12-14]:

$$\theta_t(c) = \int_{\varepsilon_{12,\min}}^{\varepsilon_{12,\max}} \frac{\Phi x \exp(\varepsilon_{12}/kT)}{1 + \Phi x \exp(\varepsilon_{12}/kT)} \chi(\varepsilon_{12}) d\varepsilon_{12} \quad (1)$$

where $\Phi = \Phi(c, \theta_t)$ is a model-dependent function [12,13], $\chi(\varepsilon_{12})$ is the normalized AED function, $\varepsilon_{12} = \varepsilon_1 - \varepsilon_2$ is the energy difference of both components (i.e. phenol and water), $x = c/c_s$, where c_s is the solubility of the solute in water.

The program INTEG [11], based on the regularization method, was used for inverting eq. (1) with respect to the energy distribution function, $\chi(\varepsilon_{12})$. Eq. (1) can be written in a more general form:

$$g(y) = \int_{z_{\min}}^{z_{\max}} K(z, y) \chi(z) dz \quad (2)$$

where $g(y)$ is a known function; the integral kernel, $K(z,y)$, represents the local isotherm of eq. (1) and $\chi(z)$ denotes the unknown AED function.

Eq. (2) must be transformed into a system of linear equations of the type, $\mathbf{g} = \mathbf{A}\mathbf{f}$, where the one-dimensional matrices \mathbf{g} and \mathbf{f} respectively represent the functions g and f , respectively, but \mathbf{A} is a two-dimensional matrix that represents the kernel. Regularization consists in replacing the problem of minimizing the functional, $\|\mathbf{A}\mathbf{f} - \mathbf{g}\|^2$, by another one that prevents strong oscillations of the AED function. This can be done by adding an additional term to the minimization functional [11]:

$$\mathbf{S}(\mathbf{f}) = \|\mathbf{A}\mathbf{f} - \mathbf{g}\|^2 + \gamma \int_{z_{\min}}^{z_{\max}} f^2(z) dz \quad (3)$$

where, γ is the regularization parameter, which is a measure for weighting both terms in eq. (3) [9,11-14,17]. It should be emphasized that the regularization method makes no assumption about the form of the AED function.

Podkościelny et al. [17] utilized the literature experimental data by Teng and Hsieh [27] in order to investigate the heterogeneity effects in phenol adsorption from water on the bituminous BW and MT Coals. The following Langmuir-Freundlich (LF) equation was chosen as appropriate to estimate the value of the monolayer capacity [9,17,37-41]:

$$\theta_t(c) = \frac{n_a}{n_{am}} = \frac{(K' c)^\eta}{1 + (K' c)^\eta} \quad (4)$$

where $\theta_t(c)$ is the fractional coverage of the adsorbent surface, n_a is the absolute adsorbed amount of solute, n_{am} is the monolayer-adsorption capacity, c is the solute equilibrium concentration, K' is the equilibrium constant for a heterogeneous solid, and η is the heterogeneity parameter, $0 < \eta < 1$.

For illustrative purposes Figure 1 presents the AED function for the BW17 activated carbon, compared to that for the BW51 one. The peak of the AED function for BW51 with the maximum about 20.5 kJ/mol is lower, more broadened and shifted towards a higher energy in comparison to the BW17 peak (maximum at about 18 kJ/mol). As has been expected, the AED functions

proceeded to a higher energy with the increase of micropore volumes [17]. Besides, they became lower and more broadened. It coincides well with the changes of the heterogeneity parameter values in the Langmuir-Freundlich equation (i.e. η becomes smaller).

In another paper [9] activated carbons prepared from polyethyleneterephthalate (PET) [31] and from polyacrylonitrile (PAN) [28] were used to adsorb both phenol and the potential chlorinated derivative, 2,3,4-trichlorophenol, dissolved in aqueous solutions that were acidic ($\text{pH} = 3$), unbuffered and basic ($\text{pH} = 11$), respectively.

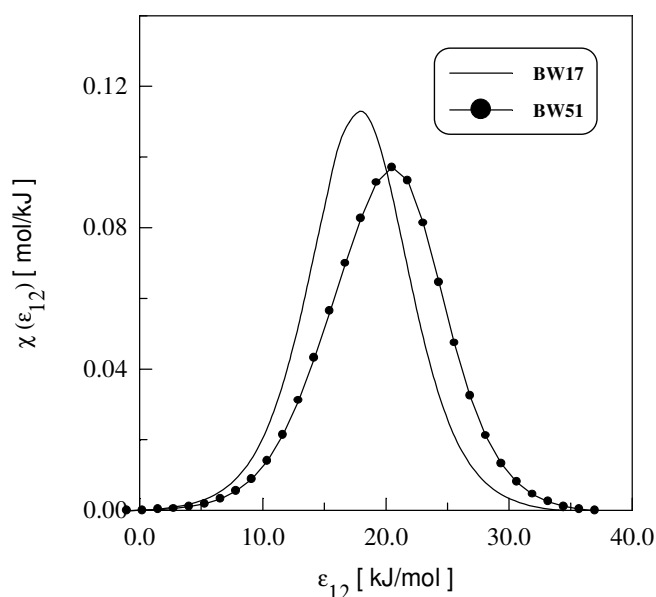


Fig. 1. Adsorption-energy distribution function for the BW17 activated carbon, compared to the distribution function for the BW51 one [17].

As an example, the results for the adsorption of both phenols on the APET carbon are shown below [9]. The experimental adsorption isotherms of phenol and 2,3,4-trichlorophenol on the APET activated carbon at an ambient temperature in $\text{pH} = 3$, unbuffered, and $\text{pH} = 11$ aqueous solutions belong to the type L2 in Giles's classification [9,42,43], except for the unbuffered 2,3,4-trichlorophenol curve – H2-type [42,43].

As before, the LF eq. (4) was utilized to estimate parameters characterizing adsorption for the systems studied. The order of the values of heterogeneity parameters, η , for phenol was as follows: unbuffered < $\text{pH} = 3$ < $\text{pH} = 11$. This means that the surface has the most heterogeneous character for the unbuffered

solution, and the least for the solution with pH = 11 (η is closer to one). In the case of 2,3,4-trichlorophenol, the sequence of η is as for phenol adsorption.

Figure 2 shows the calculated values of the AED functions for 2,3,4-trichlorophenol on the APET AC. The peak for (pH = 3) is broader and shifted towards a slightly higher energy compared to the (pH = 11) one, but the peak covering the widest range of adsorption energies ϵ_{12} is that for the unbuffered solution. The sequence of peaks correlates well with the sequence of the heterogeneity parameters, η , for the LF equation. The calculated $\chi(\epsilon_{12})$ distributions suggested that the adsorption energy of phenol on the APET carbon is stronger by about 20 kJ/mol than that of water [9]. For 2,3,4-trichlorophenol, the particular values are ca. 11-15 kJ/mol (see: Fig. 2). The literature data on enthalpy values for the transfer of phenol from the solution to the surfaces of ACs confirm the correctness of the adsorption energies obtained in our study [44-46].

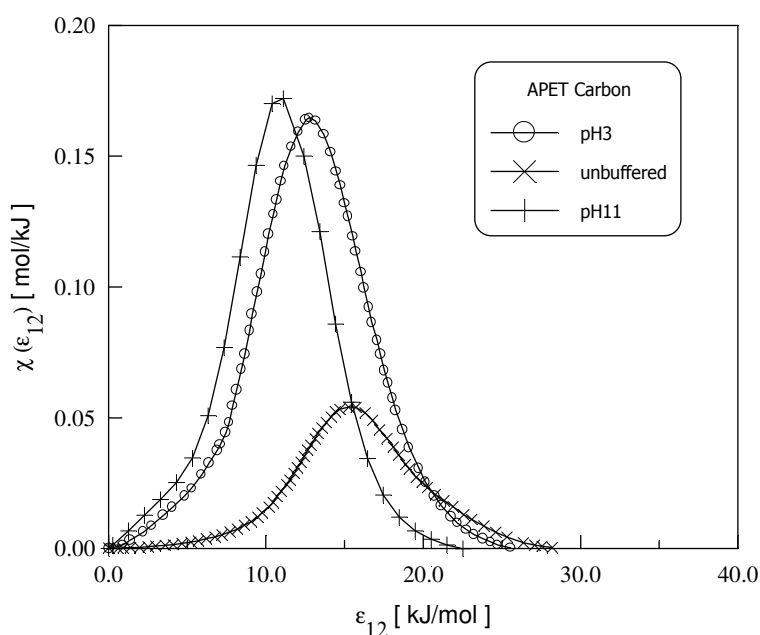


Fig. 2. Adsorption-energy distribution functions for 2,3,4-trichlorophenol on APET activated carbon [9].

The following possible interactions between the carbon surface and the phenols have been proposed [9]: (a) electron donor-acceptor interactions between the aromatic phenolic ring and the surface oxygens; (b) dispersion effect between the aromatic phenolic ring and the π electrons of the graphitic

structure; (c) electrostatic attraction and repulsion (for $\text{pH} > \text{pK}_a$). The detailed mechanisms of adsorption at value $\text{pH} = 3$, unbuffered solution and in the case of $\text{pH} = 11$ were presented earlier [9].

The activated carbon studied in our next paper was prepared from polyethyleneterephthalate (PET) by a two-step physical activation method [10]. Its various oxygen surface functionalities were systematically changed by additional nitric acid and heat treatment. Our main object in this paper was to investigate the heterogeneity effects of the original APET and modified activated carbons (APET3, APET3H, APET6H) upon the adsorption of phenol from water, at different pH values of the solution.

The Dubinin-Astakhov (DA) adsorption-isotherm equation was used for describing adsorption from dilute aqueous solutions on heterogeneous surfaces of ACs studied [2,39,46-48].

It has the following form:

$$\theta_t(c) = n_a / n_{am} = \exp\{-[RT \ln(c_s / c) / \beta_s E_{os}]^m\} \quad (5)$$

where $\theta_t(c)$ is the fractional coverage of the adsorbent surface, n_a is the adsorption capacity, n_{am} is the maximum adsorption in the micropores, β_s is the affinity coefficient (for phenol equal to 1), E_{os} is the characteristic energy of phenol adsorption, c and c_s are the equilibrium phenol concentration and the saturation concentration at temperature T , respectively.

To examine the influence of the pH on the adsorption of phenol, this phenomenon was investigated on APET carbon at room temperature from aqueous solutions with $\text{pH} = 3, 4, 5$ and from unbuffered solution [10], respectively. To investigate the influence of carbon surface chemistry, the adsorption was studied on modified carbons from $\text{pH} = 3$ and unbuffered solutions ($\text{pH} \approx 6.5$) [10].

Figure 3 shows the calculated values of the AED functions for phenol on APET carbon at different values of pH. The single peak of the energy-distribution function for ($\text{pH} = 3$) shows a maximum at about $\varepsilon_{12}^{\max} = \varepsilon_1 - \varepsilon_2 = 19.09$ kJ/mol. That for $\text{pH} = 4$ is lower, broader and shifted towards a slightly higher energy ($\varepsilon_{12}^{\max} = 20.45$ kJ/mol) compared to the $\text{pH} = 3$ peak. The lowest and the broadest peak, covering the widest range of adsorption energies ε_{12} is that for the unbuffered solution.

It has been proved that the Dubinin-Astakhov (DA) equation with a selected value of $m = 4$ is proper for the description of phenol adsorption from the aqueous solution in the narrow micropores of activated carbons studied [10]. It should be stressed that (DA) equation with parameter $m = 4$ is very useful not

only for studying the adsorption of phenol on activated carbons [2,46,49-53] but for studying adsorption of many organics besides phenol, such as paracetamol, acetanilide, aniline from aqueous solutions [52,54]. The present paper shows that increasing the pH gradually improves the strength of the interaction and adsorption performance – the uptake of phenol is always larger for the unbuffered solution than that with a lower pH. The sequence of the energy-distribution peaks $\chi(\varepsilon_{12})$ obtained by the regularization method, in the order of increasing energy ε_{12} correlates well with that of the parameter, E_{os} , of the DA equation. The strongest interactions of phenol with the surface occur for the unbuffered solution, and the weakest for the solution with pH = 3. Furthermore, the peaks are “broader” for the unbuffered solution, which indicates the largest spread of interactions between the carbon surface and phenol. The calculated $\chi(\varepsilon_{12})$ distribution suggests that the adsorption energy of phenol on APET carbon exceeds that of water for the unbuffered solution by more than 22 kJ/mol.

The way to verify energy distribution functions for phenol on activated carbons, generated by a utilization of the regularization method (INTEG algorithm) has been presented in another paper [55]. As a verification tool, the Grand Canonical Monte Carlo (GCMC) simulation method has been applied. The definitive stage of verification was a comparison of experimental isotherms and those obtained by the employment of GCMC simulations. The experimental data of phenol adsorption on activated carbons prepared from two bituminous coals BW and MT have been taken from literature [17,27].

In the first step the experimental data were analysed by INTEG to characterize the energetic heterogeneity of the adsorption systems [17]. Then, the AED functions obtained in this way were fitted by the analytical Gaussian-like energy distribution obtained by Cerofolini’s method [26,38,56]:

$$\chi(\varepsilon_{12}) = \frac{\eta \exp\{\eta(\varepsilon_{12} - \varepsilon_{12}^0)\}}{[1 + \exp\{\eta(\varepsilon_{12} - \varepsilon_{12}^0)\}]^2} \quad (6)$$

It is known that the solution of the Integral Equation Approach with the function (6) and Condensation Approximation leads to a Langmuir-Freundlich isotherm (4). The fitting of eq. (6) led to the values of the most probable adsorption energy ε_{12}^0 (corresponding to the maximum value of the fitted functions) and the heterogeneity parameter η (connected with the width of the curve (6)).

The symmetry of the energy distribution functions obtained from INTEG for our systems justifies the use of function (6).

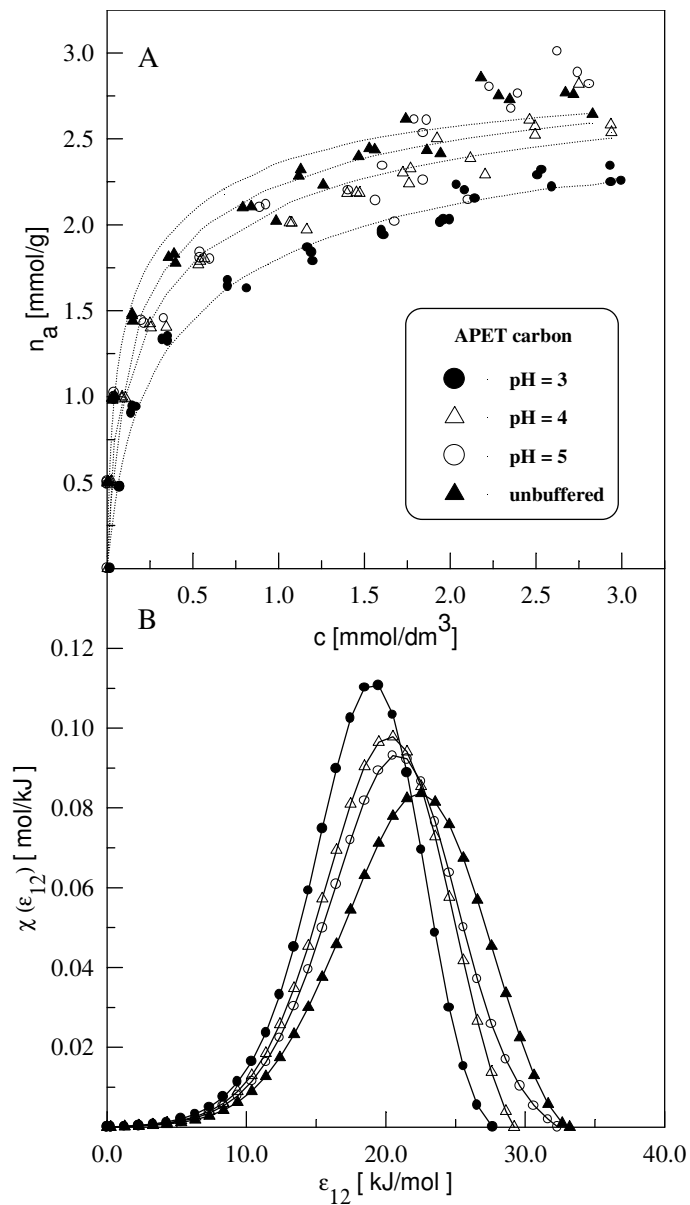


Fig. 3. (A) Adsorption isotherms from aqueous phenol solutions of various pH on APET carbon at room temperature. The symbols are the measured values of isotherm and the lines are the theoretical isotherms calculated from the DA equation (B) Adsorption-energy distribution functions for phenol on the carbon studied [10].

Next, we employed the Grand Canonical MC (GCMC) simulations that were carried out on a square $L \times L$ lattice [22-26]. All the simulations were performed for $L = 100$. The energy attributed to every lattice site had the following form:

$$\varepsilon_{12} = \varepsilon_{12}^o + \frac{1}{\eta} \ln \frac{\exp(-z \eta) + \xi \{1 + \exp(-z \eta)\}}{1 - \xi \{1 + \exp(-z \eta)\}} \quad (7)$$

where ξ is an uniformly distributed random number, $0 < \xi < 1$, η is the heterogeneity parameter; parameter “z” is connected with the width of the interval from which the adsorption energy is sampled – in other words it is a parameter of the distribution cut-off [55].

The details of the simulation technique are described earlier [55]. The simulations gave the adsorption isotherms as functions of surface coverage θ_t versus absolute activity λ .

It is known that an alternative form of LF eq. (4) is the following:

$$\theta_t = \frac{\left[\lambda \exp\left\{ \frac{\varepsilon_{12}^o}{kT} \right\} \right]^\eta}{1 + \left[\lambda \exp\left\{ \frac{\varepsilon_{12}^o}{kT} \right\} \right]^\eta} \quad (8)$$

Taking into account two forms of LF eq. a comparison of equivalent expressions, i.e. $K'c$ (eq. 4) and $\lambda \exp\left\{ \varepsilon_{12}^o / kT \right\}$ (eq. 8), is possible.

In Figure 4 we show the experimental isotherms of phenol adsorbed from water on carbons studied compared with the simulations. The experimental isotherms were plotted in the function (θ_t vs. $K'c$) whereas predictions of simulations were generated as the function (θ_t vs. $\lambda \exp\left\{ \varepsilon_{12}^o / kT \right\}$). For the reader's convenience the simulation data were connected by solid lines. We can observe a satisfactory agreement between the predictions of simulations and the experimental isotherms.

The values of surface coverage θ_t from simulations slightly overestimate the corresponding ones obtained basing on the experimental data. This can be caused by some errors which appeared during the fitting procedures. Nevertheless, the agreement of the experimental data with simulations is very close.

Bertoncini et al. [57] have used the same data in their simulations. They have presented the results of computer simulations of gas-phase adsorption of phenol

on a series of model amorphous carbons at 298 K. Their simulated adsorption isotherms have been compared with experimental isotherms of phenol adsorption from the aqueous solution. Since the trend of simulated isotherms was the same as of the experimental ones it could be concluded that the solvent effects on the carbon surface are negligible [2].

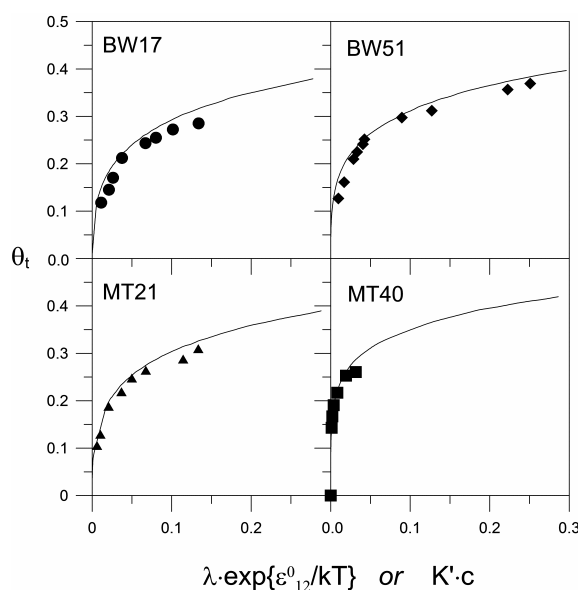


Fig. 4. Comparison between the experimental isotherms data (black symbols) and predictions of simulations plotted as solid lines [55].

4. CONCLUSIONS

The regularization method has been found to be a good procedure for characterizing activated carbon heterogeneity from experimental adsorption isotherms. The energy distribution functions are useful for comparing the heterogeneities of different carbons with respect to one selected liquid mixture – phenol/water; heterogeneity can also be investigated on the basis of isotherms from dilute water solutions of phenols at different pH on a selected original activated carbon (or a modified one). Then uncertainties in evaluating the AED function are analogous for all systems studied and significant comparative information about their heterogeneity is provided.

AED functions can be verified by utilizing the Grand Canonical Monte Carlo simulation method. The final stage of verification was a comparison of experimental isotherms and those obtained by the employment of GCMC

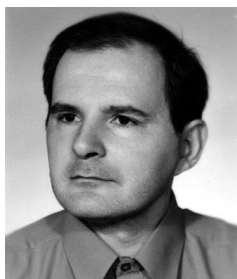
simulations - based on parameters of AED functions calculated by the regularization method. Agreement of the experimental isotherms data with predictions of simulations is very close. It confirms the reliability of energy distribution functions obtained basing on the regularization method (INTEG program) and it independently confirms the utility of this method for studying the energetical heterogeneity of carbon adsorbents.

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Przemysław Podkościelny was born in 1966, Lublin, Poland. Graduated from Maria Curie-Skłodowska University in Lublin. In 1990 he was employed in Department of Theoretical Chemistry, Faculty of Chemistry of MCS University as an assistant. In 1996 he obtained Ph.D. degree on the basis of dissertation entitled: "The methods of determination of capacity of surface phases formed onto homogeneous and heterogeneous solid surfaces". He is a member of of Polish Chemical Society. Main field of interest is theoretical description of adsorption

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Scientific activity: Synthesis, characterization and modification of nanoporous systems (activated carbon, spherical carbon, monoliths); interactions on solid/liquid interfaces, novel type sorbents for the adsorption of environmentally relevant contaminants.

Memberships: Hungarian Society of Chemists; Hungarian Academy of Sciences, commission on colloid chemistry, secretary (1993–2003) IACIS; US Air & Waste Management Association; American Carbon Society; American Chemical Society; Deutsche Kolloid-Gesellschaft.

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