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Inverse Liquid Chromatography Investigation of Adsorption on Heterogeneous Solid Surfaces: Phenylalanine on Activated Carbon

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Inverse chromatography was used to study the adsorption and desorption behavior of phenylalanine (pollutant model molecule) at the solid−liquid interface of a porous activated carbon with heterogeneous surface. The general isotherm form was obtained by the frontal analysis method in a wide range of phenylalanine concentrations. The method of frontal analysis by characteristic point was used to obtain the isotherms with a large number of points (about 3000) from single desorption chromatographic profiles. These isotherms were submitted to a mathematical treatment by the derivative isotherm summation analysis to obtain the insight into the energetic sites involved in phenylalanine-activated carbon interactions. The low-pressure quasi-equilibrium volumetric adsorption of argon was used to confirm the existence of the different energetic sites.

Introduction

As water quality standards have become more stringent, there has been increasing interest in the use of activated carbon for water purification. Activated carbons are unique and versatile adsorbents because of their extended surface area, microporous structure, universal adsorption effect, high adsorption capacity, and high degree of surface reactivity. Activated carbon can remove organic molecules formed from natural organic compounds such as humic acids that are responsible for water color and taste as well as pesticides, phenolic compounds, or other anthropic organic pollutants.[1,2] Pollutant release from activated carbon tanks can be observed sometimes in treatment plants as a "random" phenomenon and represents a problem for operators. A precise knowledge of the surface interactions is essential for proper development and improvement of activated carbon applications. Problems arising from the heterogeneity of adsorbents may have considerable importance in practical applications; still, they are poorly understood from a fundamental point of view.

Activated carbon production and its properties are well-known and described.[2] During the pyrolysis of organic compounds most non-carbon elements are eliminated as volatile gaseous products. The residual elementary carbon atoms are grouped into stacks of flat aromatic sheets cross-linked in a random manner. The arrangements of these aromatic sheets are irregular with free interstices—pores. This porous structure is enhanced during the activation process when the spaces between the aromatic sheets are cleared of various carbonaceous compounds and unorganized carbon. These interstices give rise to pores, which make activated carbons excellent adsorbents. Besides the physical structure, the adsorption capacity is strongly influenced by the chemical structure. The random ordering of the aromatic sheets results in the creation of unpaired electrons and incompletely saturated valences. Activated carbons contain heteroatoms such as oxygen and hydrogen, which can be associated with atoms of chlorine, nitrogen, and sulfur. Thus, the surface of activated carbons is extremely heterogeneous, which explains their universal adsorption properties.

Many sophisticated methods such as X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and radiometric studies contributed significantly to a more precise knowledge about the surface chemical groups.[2] The surface heterogeneity is revealed by the variation of the heats of adsorption ΔH_a with the coverage degree of an adsorbate; the adsorption energy ΔH_a decreases steeply as the adsorbate coverage increases, according to the site energy distribution function. These observations suggest that information on surface heterogeneity can be extracted from the analysis of the isotherm shape. Extensive reviews were published on the determination of surface heterogeneity from adsorption measurements by Rudzinski and Everettt[3] or Jaroniec and Madey.[4]

Specific techniques were developed in our laboratory for analysis of surface heterogeneity of porous and nonporous materials.[5] One of them is the low-pressure quasi-equilibrium volumetry (LPQEV) that allows to continuously and precisely determine adsorption iso-

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therms at quasi-equilibrium pressures of studied gaseous adsorbate. A total of 2000−3000 experimental points can be collected for one isotherm; the expansion of the isotherm using a logarithmic scale reveals inflection points. Because of the large quantity of experimental data points, the derivative of the adsorbed quantity as a function of the logarithm of relative pressure can be calculated accurately.[5,6] The derivative of the adsorption isotherm provides the full spectrum of the adsorption interactions between the molecular probe and a heterogeneous solid surface. Villiéras et al.[5−7] developed the derivative isotherm summation (DIS) analysis by which they were able to find different adsorption domains. The total adsorption isotherm was then defined as the sum of a limited number of local adsorption isotherms; different local isotherms could be used to simulate adsorption in micropores (limited adsorption) or on external surfaces (multilayer adsorption). In the case of a porous and fibrous clay mineral, the DIS analysis permitted to distinguish adsorption in structural micropores, in interfiber micropores, and on external surface area of the particles. For talc, a nonporous clay mineral, the most energetic adsorption sites could be attributed to −OH groups located at the center of the hexagonal cavities of the basal surfaces.[8]

A detailed study of mechanism of adsorbate/adsorbent interaction can be made using an adequately chosen solute (so-called molecular probe). Balard[9] proposed gas chromatography as a method for the determination of the adsorption energy distribution functions of ground mica computed from the isotherm obtained from a chromatographic signal at finite concentrations. Single-component adsorption isotherms can be determined by chromatographic methods evaluating breakthrough curves or elution profiles. Conder and Young[10] reviewed gas chromatographic fundamentals for solid−gas isotherm measurements and Guiochon et al.[11] for solid−liquid isotherm measurements. Two typical methods exploiting breakthrough curves are frontal analysis (FA) and frontal analysis by characteristic point (FACP).

FA can be performed in one-step or multistep versions. A large advantage of the FA method is that it is possible to obtain by integration of the breakthrough curves the adsorbed amount at equilibrium, which does not depend on kinetic phenomena in the column such as axial dispersion, intra- and extraparticle mass transfer, or adsorption/desorption kinetics. One-step method is based on the adsorption of a solute on an adsorbate-free column up to the equilibrium followed by the desorption using a pure solvent. To get the whole adsorption isotherm, one-step experiment must be repeated for a number of times. In multistep method the adsorption (or desorption) is conducted by a stepwise increase (or decrease) of inlet solute concentration after equilibrium was achieved in a previous step. The main advantage of a multistep method to one-step method is that it saves time and material. On the other hand, it is more prone to systematic errors.[12]

FACP is based on the measurement of either a single desorption curve (for concave isotherms) or a single adsorption curve (for convex isotherms). Each point of the curve gives one point of the isotherm.[10,11] Using modern acquisition techniques, the FACP method allows obtaining thousands of data points. The principal limitation of the application of FACP method is that the chromatographic curve can be affected by kinetic phenomena. Therefore, a credible isotherm can be obtained only if the adsorption/desorption process in the column is controlled by the thermodynamics, and the effects of transport phenomena are negligible. There exists a rich discussion in the literature about the conditions for achieving the equilibrium regime in the column. In general, long columns, small particle size, higher velocity, and low viscosity of the fluid are recommended. However, no unambiguous criteria for these quantities can be given since they strongly depend on the shape of adsorption isotherm and affinity of solute to the adsorbent.[13] The most common procedure used is to check the overlap of profiles measured at different solute concentrations.[10,11,14]

We tried to extend the above-mentioned concept relating the isotherm shape to the adsorbent heterogeneity on the solid/liquid interface in order to study the interactions of water pollutants with solid activated carbon. The phenylalanine was chosen as a model molecule representing the building unit of natural organic polymers, humic acids.

Experimental Section

Activated Carbon. The adsorbent used in this study was a porous graphitic carbon Filtrasorb F400 provided by Chemviron (Feluy, Belgium). Prior to use, the adsorbent was gently ground in an agate mortar. The mean diameter of the obtained powder was 12.0 μm, and the BET specific surface area, derived from nitrogen adsorption at 77 K, was 1200 m^2/g, corresponding mainly to adsorption in micropores (equivalent micropore surface area around 1000 m^2/g).

Low-Pressure Argon Adsorption at 77 K. High-resolution argon adsorption isotherms were recorded on a lab-built automatic low-pressure quasi-equilibrium volumetric (LPQEV) setup.[5−8] The experimental conditions were as follows: sample mass of about 0.060 g, outgassing at 0.001 Pa at a temperature of 120°C, the gas used was argon N56 (purity > 99.9996) supplied by Alphagaz (France). In this method a slow, constant, and continuous flow of adsorbate was introduced into the adsorption cell. From the recordings of quasi-equilibrium pressure vs time, the adsorption isotherms were derived. The data were then treated using the derivative isotherm summation (DIS) procedure to examine the surface energetic heterogeneity of the samples. The total derivative adsorption isotherm on a heterogeneous surface is modeled by considering two scales of heterogeneity: in the case of crystalline minerals, the surface can be divided in i different crystal faces (patchwise distribution); each face having its own heterogeneity continuously distributed around a mean value (random distribution). The resulting adsorption isotherm can be written as follows:

$$\theta_t = \sum_i X_i \theta_{it} = \sum_i X_i \int_\Omega \theta_i(\epsilon)\, \chi_i(\epsilon)\, d\epsilon \qquad (1)$$

where θ_t is the total adsorption isotherm, θ_{it} is the adsorption isotherms on the different energetic domains of the surface, X_i is its fractional contribution to θ_t, ϵ is the adsorption energy, Ω is the physical domain of ϵ, $\theta_i(\epsilon)$ is a "local" theoretical adsorption isotherm, and $\chi_i(\epsilon)$ is the dispersion of ϵ on the ith domain. The experimental curve is then fitted using theoretical local isotherms derived from one layer and multilayer adsorption formalisms.[6]

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The local adsorption isotherm used in that study was the Bragg−Williams−Temkin equation.[6,7]

Chromatographic Experiments. *Equipment.* Chromatographic experiments were performed on HP 1081B liquid chromatograph equipped with a UV−vis HP 1040A detection system (2 nm resolution) and with a computer data acquisition system HP ChemStation (Hewlett-Packard, Palo Alto, CA). The detector was calibrated directly by flushing the cell with phenylalanine solutions of different concentrations at three flow rates (0.5, 1.0, and 1.5 mL/min) used in further experiments.

Columns. The stainless steel chromatographic minicolumns (20 mm long, 1.9 mm i.d.) (Upchurch Scientific Inc., Oak Harbor, WA) were packed manually with activated carbon powder by shaking the column against its bottom. Sixteen columns with the same carbon powder were prepared with the mass of about 37 mg (mean value: 36.9 mg ± 0.2); this small dispersion proves that the column packing procedure was reproducible. After the packing was completed, the column was flushed overnight with ultrapure water (checked by a UV−vis table spectrophotometer (Shimadzu 2100) for absence of any UV−vis absorption bands). The dead retention volume, V_0, of the system was measured 20 times with KNO_3 (10 g/L) solutions at 0.5 and 1.0 mL/min flow rate and was 0.0765 mL. This value was used in further calculations.

Mobile Phase and Chemicals. Ultrapure water (18 MΩ, station Millipore Milli-Q Plus) and solutions of DL-phenylalanine (purity of 99%, Merck, Germany) in ultrapure water of different concentrations (10, 20, 50, 150, 200, 250, 300, 500, 1000, 2000, 3500, 5000, and 5200 mg/L) were used to feed the columns. The phenylalanine solubility in water, c_0, is 14.1 g/L at 25 °C.[15]

Procedures. After the column was packed and flushed overnight with ultrapure water, the phenylalanine solutions were pumped. Three flow rates (0.5, 1.0, and 1.5 mL/min) were used to check whether phase equilibrium was reached rapidly. This was confirmed by equal q values (mass of adsorbed phenylalanine/mass of activated carbon) in all cases. For further measurements the mobile phase flow rate of 1.0 mL/min was used. The UV detector was set at 257 nm. (This is not the absorption maximum, but the detector saturation at higher phenylalanine concentrations was avoided.) The raw data were acquired with the HP ChemStation program.

An adsorption experiment was performed in a column with fresh activated carbon that was fed with a phenylalanine solution at a given concentration up to equilibrium. Desorption one-step experiments were made by ultrapure water. Since the desorption front was very diffuse when approaching the baseline, the end of experiment in one-step desorption was arbitrarily chosen after 4 h. The desorbed amount was evaluated from the desorption curve as given below, and for the verification, the desorbed phenylalanine solutions were collected and analyzed by a table spectrophotometer. It was found that both procedures gave the same results. The step-down desorption experiment was conducted by feeding the column with a phenylalanine solution whose concentration was progressively lowered after an equilibrium was reached. The last step was made with pure water:

The data processing was done according to the following procedures:[10,11]

Frontal Analysis (FA) Method. For the one-step method, the adsorbed amount q was calculated from the breakthrough curve using the following formula,

$$q = \frac{1}{m_a}[c_i(V_F - V_0) - \int_{V_0}^{V_F} c\, dV] \qquad (2)$$

where m_a is the mass of adsorbent in the column, c and c_i are the outlet and inlet solute concentrations, V is the elution volume, and V_F is the final elution volume. The integral on the right-hand side of eq 2 was computed using the trapezoidal rule. The same principle was applied in the multistep method where the adsorbed amounts in two successive steps j and $j + 1$ amounts had to be summed,

$$q_{j+1} = q_j + \frac{1}{m_a}[c_{i,j+1}(V_{F,j+1} - V_{Fj}) - \int_{V_{Fj}}^{V_{F,j+1}} c\, dV] \qquad (3)$$

At one-step desorption, the desorbed amount was obtained from the relationship

$$q = \frac{1}{m_a}\int_{V_0}^{V_F} c\, dV \qquad (4)$$

At multistep desorption, an analogous formula to eq 2 was used,

$$q_{j+1} = q_j + \frac{1}{m_a}[\int_{V_{Fj}}^{V_{F,j+1}} c\, dV - c_{j+1}(V_{F,j+1} - V_{Fj})] \qquad (5)$$

Frontal Analysis by Characteristic Point (FACP) Method. The chromatographic curve was recorded with about 3000 points. Each experimental point of this curve (c', V') was used to evaluate the corresponding value of q as follows:

$$q = \frac{1}{m_a}[c'(V' - V_0) - \int_{V'}^{V_F} c\, dV] \qquad (6)$$

Thus, the calculated isotherm had the same number of experimental data points as the chromatographic curve.

Results and Discussion

The phenylalanine interaction with activated carbon in a wide concentration region of 0−5200 mg/L was studied. As has been mentioned above, an isotherm obtained by the FACP method is very useful for the analysis of surface heterogeneity, but it can be biased by the presence of kinetic phenomena. For that reason, the FA method was used to obtain the isotherm independently. Simultaneously, the hysteresis of adsorption/desorption process was examined using the FA method.

Adsorption and Desorption Isotherms by the FA Method. All one-step adsorption procedures were performed on columns prepared with a fresh activated carbon coming from the same batch. After the equilibrium was achieved, the column feed was switched to pure water, and one-step desorption data were collected. The adsorbed amounts per unit mass of adsorbent were evaluated by the procedures described above. The results for both adsorption and desorption, presented in Figure 1, show a good coincidence. The isotherm has a very high initial slope with a slightly rising "plateau" in the region of 1000−3500 mg/L, followed by an inflection point (near 4000 mg/L). This feature reminds one of the isotherms obtained at the solid−gas interface with gas condensation near saturation (type II). In our case, it can be supposed that, at low concentrations, the first molecules are adsorbed on highly energetic sites (e.g., microporosity with optimum size for phenylalanine adsorption, or functional groups existing at the edges of the carbon aromatic sheets and specific to alanine stump, or π-interactions of phenyl group with carbon). The rising "plateau" could be explained by the formation of the second layer, and the last part of the S-shaped form would be caused by multilayer adsorption or mesopore filling at high phenylalanine concentrations. S-shaped isotherms with two inflection points were found at the adsorption of phenyl-*n*-alkanes on porous carbon, which were explained by two different adsorption mechanisms:[16,17] (1) the adsorption of phenyl-*n*-alkanes on sites highly selective of the *n*-alkyl groups and covering a very small fraction of the adsorbent surface; (2) strong adsorbate−adsorbate interactions between alkyl chains.

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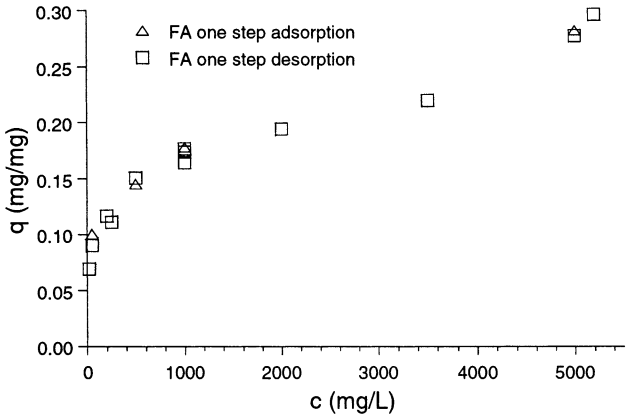

Figure 1. Adsorption isotherms of phenylalanine (0−5200 mg/L) on fresh activated carbon F400 obtained by FA one-step adsorption and desorption.

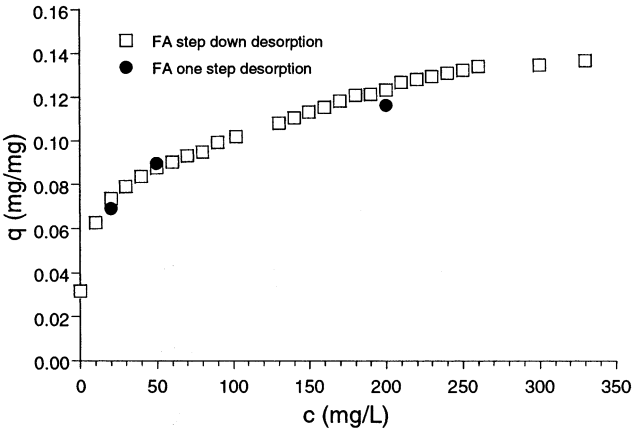

Figure 2. Comparison of desorption isotherms of phenylalanine obtained by the step down and one-step FA methods.

A detailed study of phenylalanine desorption in the low concentration range of 0−400 mg/L was made by the multistep method (Figure 2). Figure 2 shows that no significant differences were observed among the isotherm points obtained by multistep and one-step methods. All the results presented in Figures 1 and 2 confirm a good reproducibility of obtained points and general shape of the isotherm.

Figure 1 shows that the FA method did not give the evidence about the hysteresis. We have, however, found that, if the same columns were reused in adsorption/desorption cycles, the adsorbed amounts were slightly lower in the second cycle but remained the same in the third cycle. This suggests that the most energetic sites retained phenylalanine strongly during the first cycle (at least in conditions of elution with pure water).

Study of Adsorption Mechanism by LPQEV Analysis. To elucidate the adsorption mechanism, we submitted the fresh carbon and the carbon previously equilibrated with phenylalanine solutions (100, 1000, and 5200 mg/L) to LPQEV analysis with argon. Argon as an inert and nonpolar gas will interact by the van der Waals forces with adsorbent sites. The derivative argon adsorption isotherm (Figure 3a) could be described by five local isotherms with three main peaks (local isotherms II, III, and V) which represent different energetic sites of the activated carbon interacting with argon. The argon local isotherms repartition corresponds to the pore sizes repartition.[18] The adsorption energy is a parabolic function of the ratio of the pore size diameter d_p and molecule diameter d_m; the optimum interaction (highest adsorption energy) is when d_p/d_m is about 1.7 according to Pelekani and Snoeyink.[19] It was found that the argon repartition in carbon pores corresponded also to that of phenol molecules.[18,20] This was explained by a sheet form of phenol molecules (easily stackable in carbon pores) occupying the same pores volumes as the less stackable spherical argon molecules; thus, the phenol adsorption and argon adsorption take place on the same sites.

Extending the same arguments to the phenylalanine adsorption, we compared the available adsorption sites present on fresh carbon and on carbon with different q (equilibrated with different phenylalanine solution). The LPQEV and DIS analysis revealed the presence of less and less available adsorption sites for argon adsorption as a function of the rising amount of adsorbed phenylalanine (Figure 3b). In the case of F400 carbon equilibrated with 100 mg/L phenylalanine solution, sites I and partially sites II corresponding to the steep part of phenylalanine isotherm were missing in the region of $\ln(P/P_0)$ from −12 up to −18. This corresponds to the saturation of these sites by phenylalanine, which were not anymore available for argon adsorption. When the carbon was equilibrated with the 1000 mg/L phenylalanine solution, sites I and II ($\ln(P/P_0)$ from −18 up to −10) were missing completely, and site III was only slightly available for argon adsorption. In the case of carbon equilibrated with the 5200 mg/L phenylalanine solution, the situation was nearly the same as in the previous case. The three sites I, II, and III (region of $\ln(P/P_0)$ from −18 up to −4) were blocked. It confirms that, at high phenylalanine concentrations, the adsorption occurred on all energetic sites; only sites V remained partially available. It can also be suggested from these experiments that the small adsorption/desorption irreversibility of phenylalanine was due to the highly energetic sites of domains I and partially II.

To confirm this hypothesis, we submitted to the argon adsorption an already used F400 carbon and "desorbed" by pure water. The comparison of argon derivative isotherms obtained on fresh and "desorbed" F400 carbon is shown in Figure 4. The left side of the diagram (high-energy region) was modified in shape and amount, which suggests that the remaining adsorbed phenylalanine was blocked on high-energy adsorption sites. Additional differences were also observed at the low-energy region as the derivative was shifted toward lower intensities. This could result from a pore-blocking effect in porous network or errors in the determination of outgassed mass.

Desorption Isotherms Obtained by the FACP Method. One-step adsorption experiments were followed by desorption procedures by pure water, and the desorption chromatographic profiles were recorded and used for FACP evaluation (Figure 5). The desorption profiles of column beds equilibrated previously with phenylalanine solutions of 20, 50, 150, 300, 500, 1000, and 3500 mg/L were well superposed, which was not true at higher concentrations (5000 and 5200 mg/L). The desorption isotherms calculated from single chromatographic profiles are presented in Figure 6. The FACP isotherms are very smooth, which is inherent in the method. The isotherms, obtained from profiles in the range of concentrations of 0−1000 mg/L, were perfectly overlapping. The isotherm obtained from the chromatographic profile at the initial concentration of 3500 mg/L was slightly shifted to higher q values, while those obtained from the profiles at 5000 and 5200 mg/L were significantly shifted. Figure 6 also shows for com-

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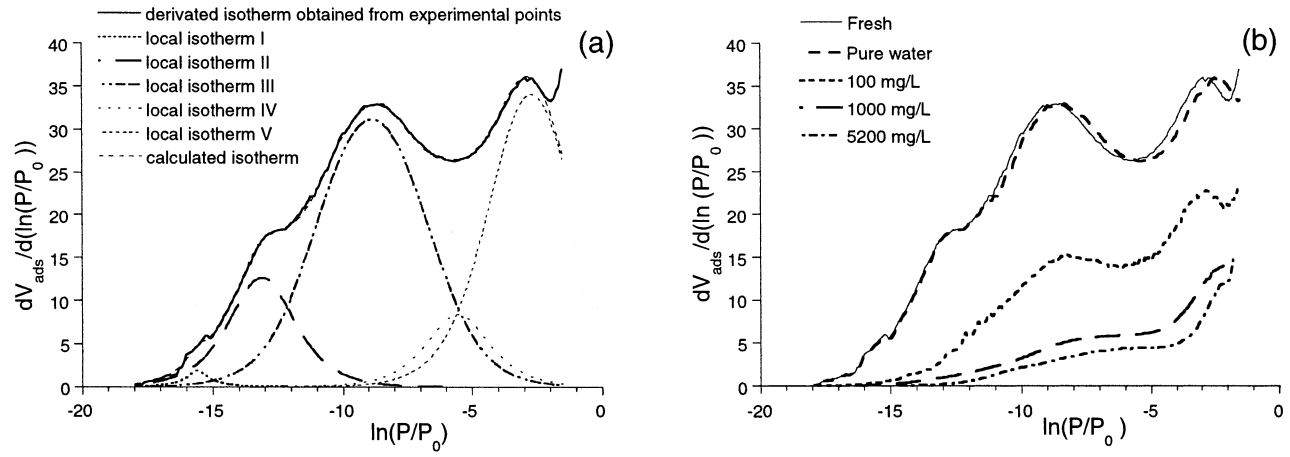

Figure 3. LPQEV: Derivative argon adsorption isotherms: (a) on fresh activated carbon F400; (b) on the same carbon equilibrated with different phenylalanine solutions: 100, 1000, and 5200 mg/L.

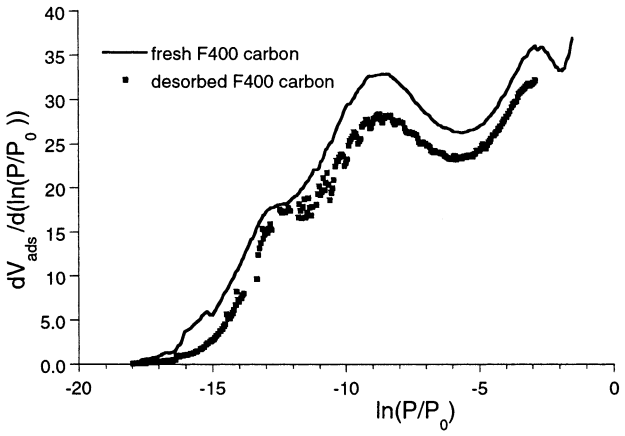

Figure 4. Comparison of argon adsorption derivative isotherms obtained on a fresh and "desorbed" activated carbon F400.

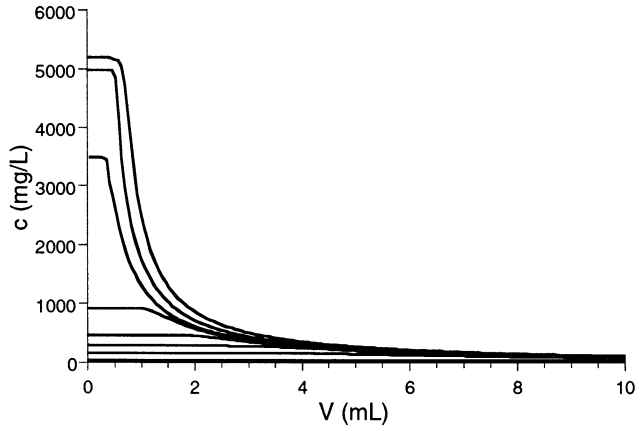

Figure 5. Desorption profiles of phenylalanine from activated carbon F400 with initial concentrations of 20, 50, 150, 300, 500, 1000, 3500, 5000, and 5200 mg/L.

parison the data obtained by the FA one-step desorption. It is obvious that, up to a concentration of 3500 mg/L, the isotherms obtained by different methods agreed very well; therewith, the general shape of the isotherm was confirmed.

The overlap of desorption profiles and agreement of isotherms obtained by FA and FACP methods confirmed that the nonthermodynamic phenomena influencing the chromatographic profiles (axial dispersion, kinetics) were not significant in our system when c was up to 3500 mg/L. The isotherms obtained by FACP were sufficiently accurate and contained a large number of points so we could use them to study the interaction mechanism of phenylalanine with the carbon.

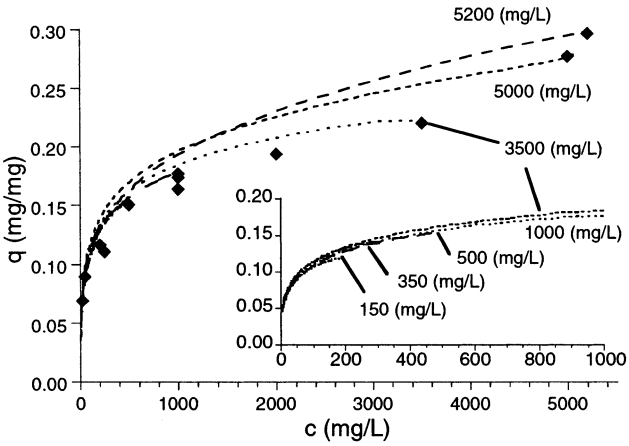

Figure 6. Phenylalanine desorption isotherms obtained by the FACP method on activated carbon F400 from chromatographic profiles at initial concentrations of 20, 50, 150, 300, 500, 1000, 3500, 5000, and 5200 mg/L. The diamonds represent the experimental data obtained by the one-step desorption presented in Figure 1.

All isotherms $q = f(c)$ obtained by FACP were transformed to the normalized form $q = f(\ln(c/c_0))$, and they are presented in Figure 7a (c_0 is the phenylalanine solubility, 14.1 g/L). The derivative form, $dq/d(\ln(c/c_0)) = f(\ln(c/c_0))$, is shown in Figure 7b. The derivative isotherms were modeled using the DIS procedure.[6] Figure 8 illustrates the fits for selected derivative isotherms. The obtained results showed the presence of four energetic regions, A, B, C, and D. Figure 8 further shows that the peak positions and intensities for sites A, B, and C were independent of the initial solute concentration. The means and standard deviations of the peak positions and adsorption capacities of individual sites were calculated from the fits of all nine derivative isotherms (Table 1). Very low values of the standard deviations (except of that for domain D) confirmed that the experimental data points of the breakthrough curves had low random errors, that the measurements at different initial solute concentrations were reproducible, and, finally, that the model with four energetic regions was adequate.

If we take into account that the desorption was not perfect and that the most energetic sites were not revealed by the above method, it is possible to conclude that five sets of energetic sites were involved in the interaction of

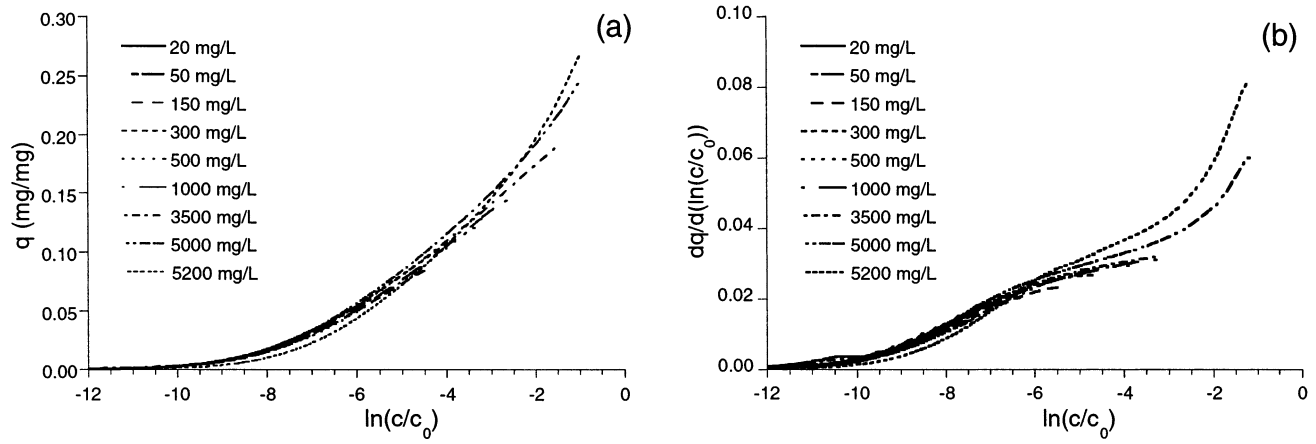

Figure 7. FACP isotherms from Figure 6 in two normalized forms: (a) $q = f(\ln(c/c_0))$; (b) $dq/d(\ln(c/c_0)) = f(\ln(c/c_0))$.

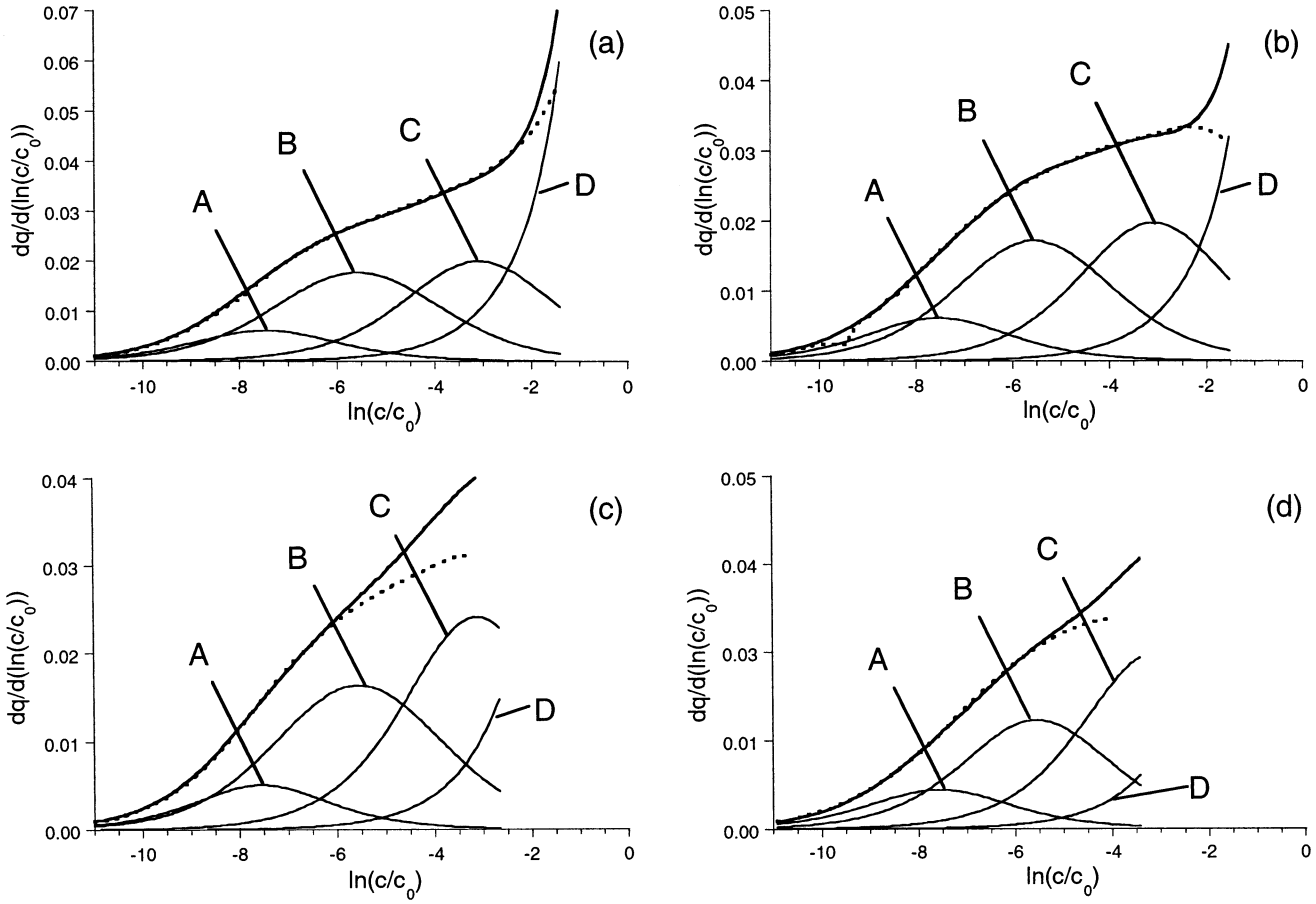

Figure 8. Selected results of the DIS analysis of the FACP isotherms obtained from chromatographic profiles at the following initial concentrations: (a) 5000, (b) 3500, (c) 1000, and (d) 500 mg/L. A, B, C, and D represent different local adsorption isotherms.

Table 1. Means and Standard Deviations of Peak Positions and Adsorption Capacities Obtained by the DIS Analysis of Phenylalanine FACP Isotherms

domain	peak position	adsorption capacity (mg/mg)
A	-7.55 ± 0.04	0.022 ± 0.006
B	-5.55 ± 0.03	0.074 ± 0.007
C	-3.11 ± 0.01	0.095 ± 0.012
D	-1.84[a]	0.099 ± 0.041

[a] No peak available for D; this was a set value.

water solutions of phenylalanine with activated carbon. If a comparison with the argon adsorption isotherm (Figure 3) is made, it may be assumed that the three main peaks of the argon isotherm (local isotherms II, III, and V) correspond to the domains A, B and C of the phenylalanine isotherms. These three domains probably represent three different types of micropores. The shift of the isotherms obtained at 5000 and 5200 mg/L to higher values (Figures 6 and 7) can be explained by the fact that at those concentrations phenylalanine was adsorbed in multilayers or in mesopores (domain D). If adsorption takes place in bottle-form pores, during the desorption, the pore-blocking effect can be responsible for the shift as often observed (adsorption−desorption hysteresis) at the solid−gas systems. This also explains a lower accuracy of the estimate of adsorption capacity of the domain D.

Conclusions

The adsorption of phenylalanine on activated carbon was studied by different methods of inverse liquid chro-

matography. The study permitted to check the possibility and limits of these methods for adsorbent surface characterization. Its major contribution is that the FACP method applied for the experiments made in carbon minicolumns gave meaningful isotherms. It is a very rapid method, giving accurate isotherms with many points, and it can be used to characterize adsorption from solution on heterogeneous solid surfaces. If combined with other approaches, such as LPQEV and DIS, it can be a powerful tool to investigate the mechanism of adsorption processes, namely, the information about interaction sites. The FACP can also be a good screening method to investigate the influence of a solid surface heterogeneity on adsorption phenomena on solid−liquid interfaces and allowing a deeper insight into the adsorption mechanism. Its limitation is that no information can be obtained about the most energetic sites (nonreversible adsorption).

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