SOME CHARACTERISTICS OF PHENOL ADSORPTION ON ACTIVATED CARBON

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Abstract

Some characteristics of phenol adsorption on activated carbon are discussed comparing experimental and Monte Carlo computer simulation results. Langmuir, Redlich-Peterson, Tóth, Freundlich, and BET equations are fitted to the experimental and simulated isotherms to discuss the meaning of the equations parameters. Computer simulations for the system phenol/graphite are employed as reference system. The adsorption energy distribution functions are calculated from the isotherms using a regularization algorithm and a least squares minimization procedure.

Resumen

Se estudian algunas características de la adsorción de fenol sobre un carbón activado. El análisis incluye la comparación de los resultados experimentales con simulaciones Monte Carlo. Se ajustaron las ecuaciones de Langmuir, Redlich-Peterson, Tóth, Freundlich y BET a las isotermas experimentales y simuladas con el objeto de discutir el significado de los respectivos parámetros. Los resultados obtenidos de las simulaciones del sistema fenol/grafito se utilizan como sistema de referencia. Las funciones de distribución de energía de adsorción se calculan de las isotermas utilizando un algoritmo de regularización y uno de minimización de cuadrados mínimos.

Introduction

The adsorption phenomenon is probably the most widely employed procedure as separation method, waste effluents treatment, refrigeration, environmental control and life support systems in spacecrafts, and obviously heterogeneous catalysis [1 – 6].

To describe the adsorption on solid surfaces, several models and empirical equations have been proposed. Some of them have solid thermodynamic bases and others are no more than empirical equations having at least two adjustable parameters. This kind of equation has been proposed to describe the adsorption on heterogeneous surfaces and some effort has been devoted to assign a physical meaning to the equation parameters [7, 8].

Phenol has been chosen as model adsorbate for many researchers to study the adsorption process from solution on a large variety of adsorbents. The interest is mainly due to the presence of this species and its derivates in wastewater effluents originated in many industries. Many authors have studied phenol adsorption experimentally [see for example 9 – 12]. Several characteristics of the process have been disclosed but there are still more questions that need an answer. For example, there is general agreement on the influence of the surface chemical composition on the adsorption mechanism for several compounds like phenol, aniline, nitrobenzene, etc. [13]. On the other hand, there is one crucial aspect on which there is no agreement concerning the reversibility or not, of the adsorption of phenol and phenolic compounds. There are experimental results supporting both possibilities and the problem remains unsolved as has been demonstrated by Radovic et al [6].

In previous papers we have studied the adsorption of phenol on the graphite basal plane [14] and on amorphous and porous carbons [15] using Monte Carlo computer simulations and comparing those results with experiments. Our results are in good agreement with many theoretical and experimental results previously published (see references therein). The models employed to simulate both the adsorbate and the adsorbent have been validated with our results and by other authors [16].

In this paper we present an analysis of the experimental adsorption isotherm using different equations that are widely employed to describe the process to find out if there is a relationship between the parameters of those equations and the surface heterogeneity. To achieve this goal we employ our computer simulation results as reference. This can be done since the simulations have been validated through a successful match of the calculated and experimental adsorption isotherms [15] and the agreement with quantum mechanical calculation results [16].

The adsorption energy distribution function is calculated from the experimental and simulated isotherms using a constrained regularization algorithm [17, 18] and one based on a least squares minimization procedure. The obtained distributions are compared with the one obtained from the surface energy maps generated for the model solids.

The paper is organized as follows. We first discuss the results produced by the different equations employed and analyze them using the results of computer simulations. A very brief description of how the adsorption energy distribution function is calculated is presented next. Finally all the results are compared and discussed together. Conclusions are derived concerning the characteristics of the adsorbent and the usefulness of the empirical equations.

Experimental and computational details

The adsorption isotherms of phenol on an activated granular carbon have been determined using the conventional batch technique at 298 K [15]. The sample of the solid is put in contact with a solution of known phenol concentration and let to reach the equilibrium at constant temperature. It has been determined that it is necessary approximately one week to reach the equilibrium using manual discontinue agitation (three times every day). A portion of the supernatant is extracted and phenol concentration is determined through its absorption in the UV region (272 nm). The

solution was prepared with distilled water and no pH buffer was added, thus the solution is slightly acid. The carbon sample employed is a commercial one (Stanton, made in Argentina) and has been employed as received. The analysis of the carbon indicates that it has 0.5% of impurities soluble in water, 1% of impurities soluble in acid solution, and 0.2% of impurities soluble in ethanol. The maximum content of chloride is 0.01% and 0.01% of sulfate. The BET area, determined with nitrogen at 77.5 K, is 672 m^2/g. The pore volume, determined from the real and apparent densities, is 0.29 g/cm^3.

Computer simulations were performed using the Monte Carlo method with the Grand Canonical Ensemble [19]. Each simulation run consisted of 9 x 10^8 movement and creation / destruction attempts, except the first point of each run where 2.7 x 10^9 attempts were employed. In all cases the average acceptance ratio for movements was kept constant ca. 45% and 1% for the creation / destruction attempts. A rectangular simulation box has been employed and periodic boundary conditions were effective in *x* and *y* directions. The simulation box is closed with a reflection plane conveniently located to optimize the simulation run.

The solid is described using the Bernal model as in previous papers [20]. Phenol molecule has been modeled as previously reported [14]. The interaction potentials employed take into account for gas – solid and gas – gas interactions including electrostatic interaction terms due to the dipole moment of phenol molecule. The dipole moment has been simulated by calculating partial charges on each atom of the molecule in such a way that the resulting dipole moment (1.23 D) is very close to the experimental value (1.45 D). The orientation of the molecule is treated in the usual way in terms of Euler angles [14]. A detailed description of the behavior of the employed potentials and the energies involved have been fully described elsewhere [14].

Results and discussion

The first adsorption equation employed was Langmuir isotherm in three of its versions: classical one-site equation, two-site equation, and one-site plus a non-specific term. The mathematical forms are:

$$N_{ad} = \frac{N_{max} \, C_{eq}}{k_L + C_{eq}} \tag{1}$$

where N_{ad} is the adsorbed quantity, usually expressed in mole/g, N_{max} is the maximum adsorption capacity or monolayer capacity, k_L is a constant connected with the adsorption energy, and C_{eq} is the concentration of the solution in equilibrium with the solid. The two-site equation has the following form:

$$N_{ad} = \frac{N_{max1} \, C_{eq}}{k_{L,1} + C_{eq}} + \frac{N_{max2} \, C_{eq}}{k_{L,2} + C_{eq}} \tag{2}$$

where the parameters have the same meaning than in equation 1 but referred to different sites. Finally, the third version of Langmuir equation contains a one-site term plus a non-specific one and its form is given by:

$$N_{ad} = \frac{N_{max} \, C_{eq}}{k_L + C_{eq}} + N_s \, C_{eq} \tag{3}$$

The next adsorption isotherm tested is Brunauer, Emmett and Teller equation (BET). This equation is an extension of Langmuir monolayer isotherm to the case where a multilayer of the adsorbate is formed. This equation is currently employed to determine the specific surface area of powders using nitrogen as standard adsorbate. The model underneath the equation has been criticized and its drawbacks and failures are very well known [21], thus this point will not be discussed here. The mathematical form of BET equation, in its linear form, is given by:

$$\frac{x}{N_{ad}(1-x)} = \frac{C-1}{N_m C} x + \frac{1}{N_m C} \tag{4}$$

where $x = N_{ad}/N_o$; N_{ad} is the adsorbed amount and N_o is related to the reference state, it is the vapor pressure for adsorption of vapors, and the saturation concentration for adsorption from solution. C is a parameter related to the adsorption enthalpy and taken as constant in the original model. N_m is the adsorbed amount necessary to form a monolayer on the surface. Once the monolayer capacity is known from the isotherm, it is possible to calculate the surface area of the adsorbent provided that the cross-sectional area of the adsorbate is known.

Redlich-Peterson is a three-parameter empirical equation that is widely employed to described adsorption from solution or from the gas phase. The equation is given by:

$$N_{ad} = \frac{a\, C_{eq}}{1 + b\, C_{eq}^c} \tag{5}$$

where a, b, and c are the parameters that must be determined from the adsorption isotherm. Redlich-Peterson equation is equal to Langmuir isotherm for c = 1. It is generally assumed that c is related to the heterogeneity of the adsorbent. The next empirical equation we have tested is the well-known Freundlich isotherm given by:

$$N_{ad} = k_F\, C_{eq}^{1/n} \tag{6}$$

where k_F and n are constants, the rest of the symbols have their usual meaning. The parameter n is usually associated with the heterogeneity of the surface. The last empirical equation analyzed is Tóth adsorption isotherm given by:

$$N_{ad} = \frac{N_m\, C_{eq}}{\left[k_T + C_{eq}^m \right]^{1/m}} \tag{7}$$

where N_m, k_T, and m are the equation parameters meaning the monolayer capacity, temperature dependent parameter, and the heterogeneity parameter that is temperature independent respectively.

In all cases the corresponding parameters have been determined from the adsorption isotherms using a nonlinear least squares fitting algorithm. Figure 1 shows the experimental isotherm of phenol at 298 K. All the equations tested have been applied to this experimental isotherm.

The BET equation, in its linear form, produced a straight line with a correlation coefficient better than 0.99 as could be inferred from Figure 2. The monolayer capacity value is 0.00211 mol/g, C = 229, and the specific surface area obtained is, using 0.485 nm^2 for the cross-sectional area [14], 616 m^2/g. This value is in excellent agreement with the one derived from nitrogen isotherms on the same carbon sample (672 m^2/g). This fact also agrees with the previous finding showing that solvent effects are not important [15].

This is supported by two facts; first is that the simulated isotherms follow the same trend of the experimental ones, nevertheless the former have been calculated for the adsorption from the gas phase. The second fact is the large pKa value of phenol (pKa = 9.89 at 293.2 K), which indicates that the degree of dissociation must be negligible. Obviously, this is not true for alkaline solutions where phenol ionic species must be in higher concentrations. The BET method used with the simulated isotherm obtained for adsorption on the basal plane of graphite also produced an excellent linear correlation and the obtained surface area differed by less than 1% with respect to the area of the simulation box. We can conclude that the BET method produces valid surface areas for adsorption from solution, at least when ion adsorption is not important and solvent effects are negligible. In agreement with this, we have previously found that the heat of adsorption could be reproduced with our simulations [15].
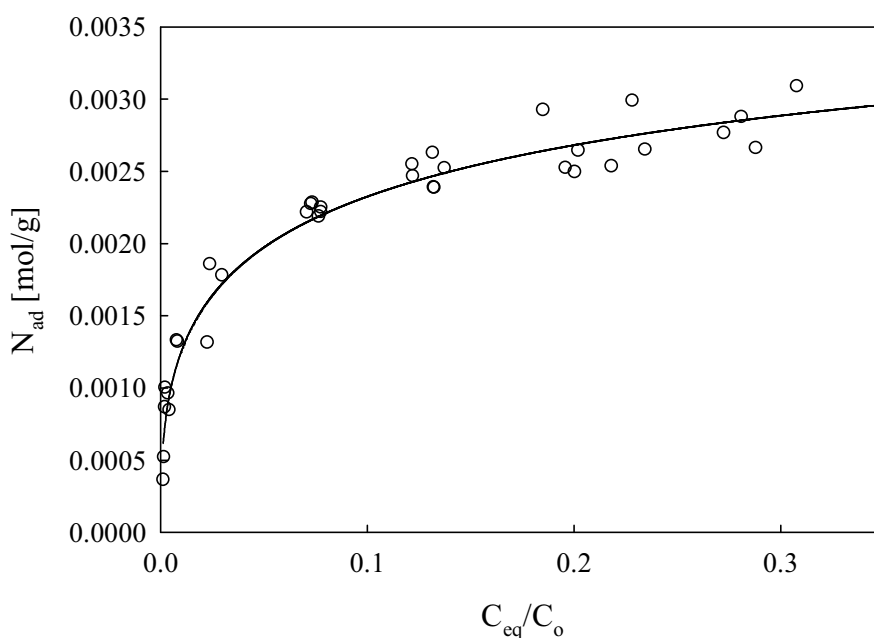

Figure 1: *Phenol adsorption isotherm on activated carbon at 298 K.*

Langmuir equation for two-site surface, equation 2, fits the experimental data quite well but the monolayer capacity determined is too large ($3.33 \ 10^{-3}$ mol/g) with respect to the BET one ($2.11 \ 10^{-3}$ mol/g). The model gives a monolayer capacity very close to the BET one for one site of the two considered. Obviously it makes nonsense to use a two-site equation to end up neglecting one of them. On the contrary, Langmuir equation including a non-specific site, equation 3, produces a reasonable monolayer capacity value ($2.0 \ 10^{-3}$ mol/g).

Redlich-Peterson equation (equation 5) representation is shown in Figure 3 for several values of the heterogeneity parameter, c, including the experimental adsorption isotherm. The value of c obtained in our case, 0.795, is within the range of other reported values for adsorption of different species on activated carbons. For example, Lucas et al

[22] have reported values ranging from 0.900 to 0.568 for the adsorption of furfural on a series of activated carbons. The fitted curve has always a high correlation coefficient as in our case. Nevertheless, the correlation between the value of c and surface heterogeneity must be reconsidered since the same equation employed with the data obtained from the adsorption of phenol on the basal plane of graphite produced c = 0.803 with a high correlation coefficient as can be seen in Figure 4. Since this surface is perfectly flat and homogeneous, the conclusion is that c cannot be taken as a measure of the surface heterogeneity. From a closer examination of Figure 3 we could conclude that since the isotherms of phenol and similar species are more or less of the same shape it is not possible to expect c values less than ca. 0.4 – 0.3.
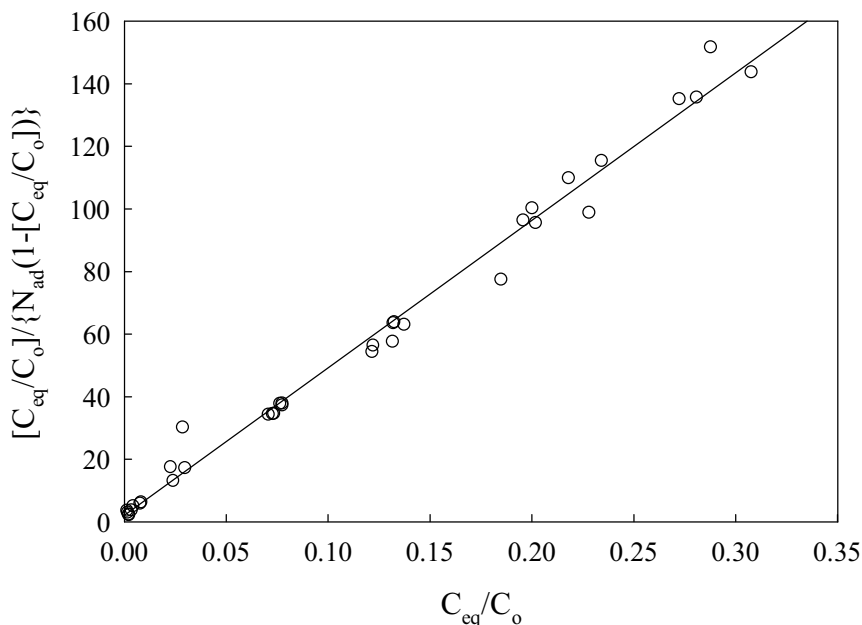

Figure 2: *BET linear representation of the adsorption isotherm showed in Figure 1.*

With respect to Freundlich's equation it can be said that the experimental data is very well fitted by the equation giving a value of the parameter n = 4.88. Finally, the last empirical equation tested is Tóth's isotherm. This equation can be successfully fitted to the experimental data but we found the same problem as with Redlich-Peterson equation. The parameters obtained for the experimental isotherm on the activated carbon are: N_m = 0.0466 mol/g; $1/k_T$ = 0.2566; and m = 0.0912. While for the simulated isotherm on the basal plane of graphite, the obtained parameters are: N_m = 0.173 molecules/$Å^2$, and m = 0.1396. It must be pointed out that besides the difference in units between both sets of parameters, neither of them reproduces the experimental values of the monolayer capacity obtained from other methods. The parameter m, related to the surface heterogeneity, is again very similar for both isotherms, the one obtained on an activated carbon and the one obtained for the basal plane of graphite.

It is very well known that the best characterization of the adsorption properties of a solid surface is obtained from the adsorption energy distribution function. The

determination of this distribution is obtained by solving the general adsorption isotherm equation given by:

$$N_{ad}(p) = N_m \int_{U_{min}}^{U_{max}} \theta^L(p, U) f(U) dU \qquad (8)$$

where N_{ad} is the amount adsorbed at pressure p, N_m is the monolayer capacity, θ^L is a function of the pressure and the adsorption potential on a patch called local isotherm, and f(U) is the adsorption energy distribution function. Equation 8 is obtained when it is assumed that a heterogeneous surface could be decomposed in regions, called patches, where the adsorption potential is constant, i.e. the patches are uniform surface portions where an adsorption isotherm equation is suitable to describe the adsorption. Unfortunately, this equation is a Fredholm integral equation that has no analytical resolution but for a few cases without interest for real cases. A numerical solution must be found to solve the equation given the experimental isotherm. A complete description of the problem can be found elsewhere [7, 8] thus we will not extend the discussion of the details here.
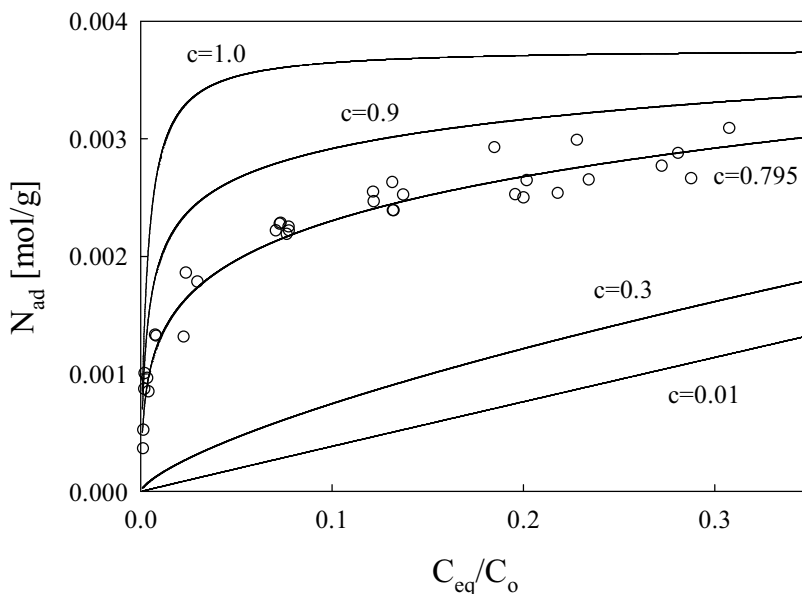

Figure 3: *Redlich-Peterson equation plotted for several c values including the experimental isotherm (T = 298 K).*

In this paper we have employed two methods to solve equation 8 starting from the experimental and simulated isotherms. The first is the numerical method known as constrained regularization method, and the second one is a least squares minimization procedure. Both methods need the assumption of a local isotherm and the least squares method also requires the mathematical form of the energy distribution. In our case and to simplify the comparison of both methods, we selected the BET equation as local isotherm and a Gaussian function as energy distribution. As was previously said, we used both methods to solve the equation for the experimental and the simulated isotherms and compared the obtained solutions with the energy map obtained for the model surface

employed in the simulations (see Figure 5). Before discussing these results we present a brief description of how the energy map of the model surface is obtained. The map is constructed by sweeping the model surface with a molecule of the adsorbate in a given orientation with respect to the surface. The entire surface is divided in a mesh (50 x 50, in our case) and the adsorption energy is calculated at each point of the mesh, the interaction energy between the molecule and the surface is minimized at each point by changing the z coordinate of the molecule, finally, the corresponding energy and z coordinate are stored. In previous studies of the adsorption of simple gases (N_2, Ar, CO_2, etc.) [23] we found that the energy distribution obtained from the surface map was reproduced by the distribution obtained from the adsorption isotherm. The obtained map must be very close to the true adsorption energy distribution function since it does not include lateral interactions effects that can alter the distribution as in real systems.
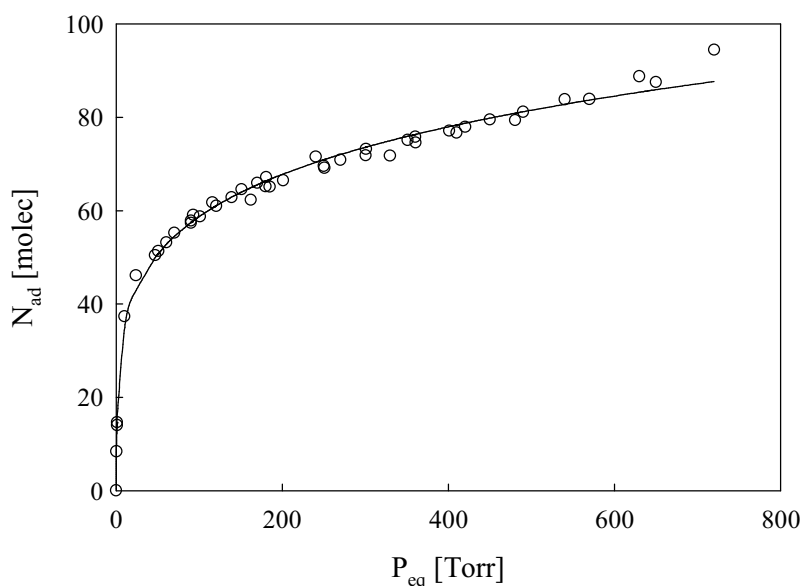

Figure 4: *Redlich-Peterson equation plotted for phenol adsorption on the basal plane of graphite (T = 298 K).*

In the present case, phenol adsorption, the surface map produces a distribution that is close to a Gaussian function with a maximum located at ca. 25 kJ/mol. Figure 5 compares all the distributions and several facts can be summarized. First, the distributions obtained with the regularization procedure are very different to the ones calculated with the least squares method. The surface map, taken as the correct distribution, is closer to the least squares solutions considering both the shape and location of the most probable adsorption energy. The regularization solutions are asymmetric and the maxima located at lower energies. An interesting point is that both methods are coincident in considering that the model and real solids are similar. The different areas of the peaks are due to the different units in which are expressed the isotherms, remember that the simulated one is obtained for vapor adsorption and the other for adsorption from solution.

The least squares method has the advantage that it uses the monolayer capacity as a criterion to select the best solution. In our case the error, with respect to the BET method, is less than 15% for the simulated isotherm and less than 10% for the real system. The regularization solutions produced monolayer capacities that are very different to the BET values (errors larger than 25%). The reason for this behavior could be in the method itself since the most important parameter, the regularization parameter, is not known a priori. This method, employed with simulated data (i.e. data generated by calculating equation 8 for a given distribution and local isotherm), is capable of reproducing the original distribution provided that the correct regularization parameter is used; otherwise the method fails to reproduce the original distribution function. This fact constitutes a serious limitation for this method to be employed as a unique source to characterize the surface. The least squares method has the extra advantage of being simpler from the mathematical point of view than the regularization method.
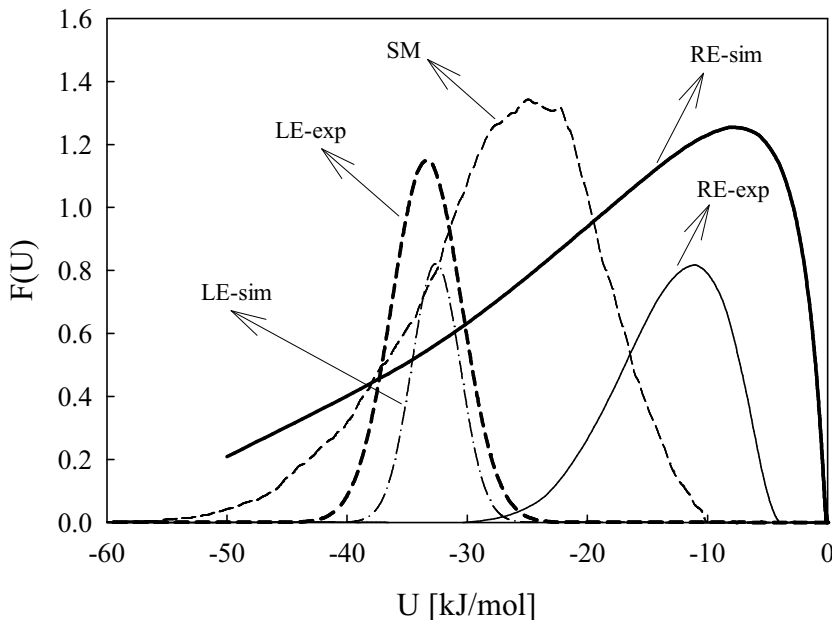

Figure 5: *Adsorption energy distribution functions obtained with the constrained regularization procedure and least squares method for the experimental and simulated isotherms. LE-sim: least squares method on simulated isotherm; LE-exp: least squares method on experimental isotherm; RE-sim: constrained regularization procedure on simulated isotherm; RE-exp: constrained regularization procedure on experimental isotherm; SM: distribution obtained from the surface energy map.*

Now, analyzing the results obtained, it could be said that our model solid exhibits the main characteristics of the real adsorbent since it reproduces quite closely the experimental distribution function. In previous studies [23] we have demonstrated that this method works very nicely for simple gases and the obtained results reproduced the monolayer capacity with errors less than 1 – 2% and that the calculated distribution agree quite well with the one derived from the energy map. The distribution obtained from the energy map could be altered if the gas – solid energy is very sensitive to the orientation

of the adsorbate. As a matter of fact, the gas – solid energy calculated for an isolated phenol molecule flat on the surface of graphite is –49 kJ/mol (at the equilibrium distance) whereas for the same molecule, standing vertical on the surface (OH group pointing toward the surface) the obtained value is –17 kJ/mol [14]. These values indicate how much the surface map could be altered if a minimization of the energy is also performed with respect to the molecular orientation. It must also be considered that those values correspond to a flat surface and that the effect will certainly be larger for an irregular surface like the one used in this work. Finally, the orientation of the adsorbate will change the surface map in both extremes (low and high energy sites). In the case of small molecules, this effect should not be very important and this is the reason why an excellent fit is achieved [23]. Whereas for larger molecules this may not be true and the map could be altered if the calculated energy is minimized allowing an orientation optimization.

Conclusions

From all the adsorption equations tested with phenol isotherms, BET and the one-site plus non-specific site Langmuir equations were the ones that produced results consistent with the information available (e.g. monolayer capacity) for the activated carbon sample employed. The empirical equations containing parameters apparently related to the surface heterogeneity give very similar values for an amorphous surface and the basal plane of graphite. Nevertheless, those equations are useful to interpolate values in an experimental isotherm since they can fit very well the data.

The adsorption energy distribution function calculated with a regularization procedure failed to reproduce the distribution obtained from the energy map of the model surface. Better results are obtained using a least squares minimization procedure. This method is capable of reproducing the monolayer capacity determined with the BET equation. The difference between the calculated distribution and the one obtained from the energy map can be explained by the dependence of the gas – solid interaction energy on the adsorbate orientation on the surface. Both methods agree in generating similar distributions for the real and model systems, which is in agreement with the fact that the simulations reproduce the experimental data quite well.

Acknowledgments

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