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On the use of the Hill's model as local isotherm in the interpretation of the behaviour of the adsorption energy distributions

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Abstract: *Activated carbons are reported to show promise for separation processes and natural gas storage, since they have a strongly heterogeneous surface. In that context, a thorough investigation of the energetic heterogeneity of activated carbon surfaces is essential for the development and improvement of materials designed for specific applications.*

We have carried out this study, to determine the Adsorption Energy Distribution (AED) corresponding to the adsorption of methane, ethane, and nitrogen on activated carbon at different temperatures by using the Hill model as local isotherm. At first, the integral equation itself is deduced by a reasoning based on the local adsorption isotherm. Then, to solve the integral equation a numerical method is proposed. The Hill isotherm was established by applying the grand canonical ensemble in a statistical physics treatment. This treatment allowed us to define the parameter n, which represents the number of molecules adsorbed per site. We have supposed as a first approach that the energy distribution function has the shape of the normal Gaussian distribution. The influence of the adsorbate type and the values of parameter n at different temperatures on the behaviour of the AED, have been studied.

***Keywords**: Adsorption energy distribution; Activated carbon; Statistical physics; Integral equation; Hill isotherm.*

I. Introduction

Ethane, methane and nitrogen are of high relevance to the natural gas and petrochemical industries [1]. Indeed, natural gas is a mixture of various hydrocarbons gases as methane and ethane, and other components such nitrogen. These composites can be separated from the gas through the natural gas processing at the gas separation plants. Each of them can be used in many sectors as transportation, agricultural and a raw material for petrochemical industry. Furthermore natural gas can be used in a cooling system. Gas separation is a process of separating various hydrocarbon components in natural gas to be used at its fullest value. Nowadays, separation and purification of gas mixtures by adsorption has become a major unit operation in chemical and petrochemical industries. Therefore, modelling of single component adsorption equilibria over a relatively wide range of experimental conditions is very useful for characterising the nature of interactions of adsorbate molecules with themselves and with different adsorbents. It is also very helpful to estimate the energetic properties of such systems and to predict the behaviour of adsorption equilibria of mixtures constituted from these components.

An energetically homogeneous surface is a surface, where every point on the surface is equivalent to the others even at a molecular level of resolution. However, on a molecular scale, most solid surfaces are characterised by different arrangements of atoms or molecules on the surface. They exhibit various chemical compositions. This geometrical disorder and chemically heterogeneous structure of real solid surfaces have a great effect on the adsorption process occurring on it, especially on the interaction between the solid surface and gas molecules which becomes more differentiated in the various sites [2]. This dispersion of the adsorption energy is commonly called the surface heterogeneity. The generally accepted quantitative measure of the energetic heterogeneity of surfaces is the adsorption energy distribution, which represents the probability density function for the adsorption energies E [2] or more precisely the distribution of the rate of different energies intervening in the adsorption process.

This trend in the theoretical studies of adsorption was introduced firstly by Roginski [3]. The adsorption was studied by applying the so-called integral equation for adsorption isotherm. The experimentally observed adsorption isotherm was assumed to be a summation (integral) of multiple adsorptions which are locally governed by a so-called local adsorption isotherm. The adsorption on receptor sites is characterized by a variable adsorption energy E, according to the adsorption energy distribution. Some years later, a variety of methods were proposed to solve the integral equation and the problem of evaluating the adsorption energy distribution of heterogeneous surface has been considered in details by many authors [4-10]. The most widely used method is the condensation approximation approach. Jaroniec and Madey [9] pointed out the importance of the condensation approximation (CA) method. Rudzinski et al. [10] suggested that simplified (CA) method is the only one which can be applied for the extraction of stable $f(E)$ by inversion. Nowadays, the integral equation can be solved by applying advanced numerical algorithms [11]. Obviously, using this integral we can obtain the known classical models in the literature, which are based on one type of energy.

Thus several continuous energy distribution functions for the adsorption on heterogeneous surfaces have been proposed based on different theoretical isotherms, as Langmuir [12], Langmuir-Freundlich [13] and Toth [14] isotherms. On the other hand, we can find models with two or several energies (E_1, $E_2,\ldots,E_i$), but the transition from a discrete model to a continuous model is not treated at our knowledge .

This study intends to explore an adsorption energy distribution by applying a statistical physics treatment. For that purpose we have developed a new methodology which leads to determine the integral equation. By establishing the integral equation using statistical physics reasoning, the description of the heterogeneity of adsorbent is significantly clarified by defining the parameter N_m'. This parameter represents the energetic density of the spatial density of the effectively occupied sites. The Hill isotherm, which is established by applying the grand canonical ensemble in a statistical physics approach [15, 16], is used as a local isotherm. The advantage to apply this model is to give a physical meaning to the parameters involved in the model and then to give new interpretations of the adsorption process at molecular level. To directly generate the energy distribution function from the integral equation, we propose in this study a numerical method. This method is determined by an adequate algorithm. The numerical method gives both the fitting of the experimental isotherm and the energy distribution function. To apply this method we have to assume mathematical expression for distribution function. In this work we have assumed that the adsorption energy distribution has the form of the normal Gaussian function.

The object of this study is to determine the site energy distribution of British Drug House (BDH)-activated carbon which is a commercial activated carbon. The experimental isotherms that we used are provided to us by Shaheen et al. [18]. Used adsorbates are nitrogen, methane and ethane. Moreover, in this paper, an investigation of the effect of the type of adsorbate and its manner of adsorption on energy distribution function behaviour is reported.

II. Methodology

2.1. Hill model

In the present study, a site energy distribution function is proposed using the Hill model. This model is established by applying grand canonical ensemble in a statistical physics approach [16]. To treat such adsorption problem with a statistical physics, some assumptions are made [16,17].

During this phase, we consider that a variable number of molecules N are adsorbed onto N_m receptor sites per mass unit of adsorbent. In our treatment, the starting point is the grand canonical partition function describing the microscopic states of the studied adsorption system. A receptor site is supposed to be empty or occupied by one or more molecules with adsorption energy ε and a chemical potential μ . For this reason, we define the state of occupation N_i and it is assumed that any given receptor site can either be empty or occupied, and consequently N_i takes the value 0 or 1. The grand canonical partition function in this case, for only one site, has the form [16]:

$$z_{gc} = 1 + \exp\left[\beta(\varepsilon + \mu)\right] \tag{1}$$

Where β is the Boltzmann factor, and for N_m identical receptor sites, the total grand canonical partition function is [16,17]:

$$Z_{gc} = \left[1 + \exp\left[\beta(\varepsilon + \mu)\right]\right]^{N_m} \tag{2}$$

The occupation number for N_m identical receptor sites is therefore given as follow [16]:

$$N_0 = k_B T \frac{\partial \ln(Z_{gc})}{\partial \mu} \tag{3}$$

The adsorbed quantity is written as a function of the gas pressure:

$$Q_a = n.N_o = \frac{n.N_m}{1 + \left(P_{1/2}/P\right)^n} = \frac{Q_{asat}}{1 + \left(P_{1/2}/P\right)^n} \tag{4}$$

Where N_m is the density of the effectively occupied sites per mass unit of adsorbent and not necessarily all the existing ones, Q_{asat} is the quantity adsorbed at saturation and n is the number or fraction of adsorbed molecule per site. The values of n may be greater or less than unity. Indeed, a molecule has several ways to be anchored onto the receptor sites. Then if n<1 the molecule is adsorbed parallelly to the surface, if n>1 the molecule is adsorbed "vertically" or not parallelly to the surface. Another parameter which is related to n is the anchorage number, n'=1/n, which represents the number of sites on which one molecule can be adsorbed.

$P_{1/2}$ is the pressure at half-saturation which is related to the adsorption energy ΔE by:

$$P_{1/2} = P_0 \exp\left(-\Delta E/RT\right) \tag{5}$$

Where P_0 is the saturated vapour pressure, R is the universal gas constant, and T is the absolute temperature.

Usually and for simplification, the Langmuir model is used as local adsorption isotherm model [12]. However, this model expresses a simple and particular adsorption process where a receptor site interacts with only one and a whole molecule of adsorbate. The corresponding reaction is as follows:

$$A + S \rightleftharpoons AS \tag{6}$$

Where A represents the adsorbate molecule and S is the receptor site. The general case of adsorption process is expressed as follows:

$$nA + S \rightleftharpoons A_nS \tag{7}$$

If n>1 many molecules are adsorbed on one receptor site. This adsorption is called multi-molecular adsorption. If n<1 a fraction of a molecule is adsorbed on one receptor site.

$$A + n'S \rightleftharpoons AS_{n'} \tag{8}$$

Then one molecule can be anchored to many receptor sites. This adsorption is called multi-anchorage adsorption.

The adequate model which can express the general case is the Hill model, which is more powerful than Langmuir model. Then, using this model to determine the adsorption energy distribution will help us to improve our understanding of the adsorption process. Indeed, adsorption treatment by statistical physics will clarify the role of some constants in the expression of the Hill model and it relates these constants to physico-chemical parameters. In this work, we present firstly the results of modelling the experimental isotherms of nitrogen, methane and ethane on BDH-activated carbon using the simple Hill model (Table 1). In the case of determination of the adsorption energy distribution this model will play the role of the local isotherm.

2.2. Integral equation

For describing adsorption on energetically heterogeneous surface we postulate that the surface of a real solid is composed of small patches of different adsorptive energies that adsorb independently one of the other [19]. Mathematically speaking, the approach provides a mean of constructing isotherm model by systematically combining hypothetical "local" isotherms. In this method we suppose that E can be varied from E_{min} to E_{max}. The local isotherm provides an explicit relationship between the adsorbed quantity on each homogeneous patch with equilibrium pressure and the adsorption energy on the patch [20,22,23,25]. To obtain the integral equation we have use the following reasoning:

It is usual to consider a model with two energies or three energies of adsorption [21]. For example for two energies E_1 and E_2 the adsorbed quantity is:

$$Q_a = Q_{a1} + Q_{a2} \tag{9}$$

$$Q_{a1} = \frac{n_1 N_{m1}}{1 + \left(\frac{P_0 \exp\left(-E_1/RT\right)}{P}\right)^{n_1}} \tag{10}$$

and

$$Q_{a2} = \frac{n_2 N_{m2}}{1 + \left(\frac{P_0 \exp\left(-E_2/RT\right)}{P}\right)^{n_2}} \tag{11}$$

We generalize this model to a model with several types of energies by supposing a discrete sum, and then we have:

$$Q_a = \sum_i Q_{ai}(E_i) = \sum_i \frac{n_i N_{mi}}{1+\left(\frac{P_0 \exp(-E_i/RT)}{P}\right)^{n_i}} \qquad (12)$$

Using Dirac delta function [28] in one type i of adsorption energy, $Q_{ai}(E_i)$ can be written as following:

$$Q_{ai}(E_i) = \int_{E_{\min}}^{E_{\max}} \frac{n_i N_{mi}}{1+\left(\frac{P_0 \exp(-E/RT)}{P}\right)^{n_i}} \delta(E-E_i)dE \qquad (13)$$

The incorporation of Eq(13) in Eq(12) will lead to:

$$Q_a = \sum_i \int_{E_{\min}}^{E_{\max}} \frac{n_i N_{mi}}{1+\left(\frac{P_0 \exp(-E/RT)}{P}\right)^{n_i}} \delta(E-E_i)dE \qquad (14)$$

As $Q_{ai}(E_i)$ is a derivable function, we can permute the integral and the sum symbols :

$$Q_a = \int_{E_{\min}}^{E_{\max}} \sum_i \frac{n_i N_{mi}}{1+\left(\frac{P_0 \exp(-E/RT)}{P}\right)^{n_i}} \delta(E-E_i)dE \qquad (15)$$

Assuming in a first approach that all n_i are identical to n, which can be considered as a mean value of all different n_i :

$$Q_a = \int_{E_{\min}}^{E_{\max}} \sum_i \frac{n}{1+\left(\frac{P_0 \exp(-E/RT)}{P}\right)^{n}} N_{mi}\delta(E-E_i)dE \cong \int_{E_{\min}}^{E_{\max}} \frac{n}{1+\left(\frac{P_0 \exp(-E/RT)}{P}\right)^{n}} dE \sum_i N_{mi}\delta(E-E_i) \qquad (16)$$

Finally we set $N_m^{'}(E) = \sum_i N_{mi}\ \delta(E-E_i)$, which will change the discrete distribution to a continuous distribution.

$$Q_a = \int_{E_{\min}}^{E_{\max}} \frac{n}{1+\left(\frac{P_0 \exp(-E/RT)}{P}\right)^{n}} N_m^{'}(E)dE \qquad (17)$$

With $N_m^{'}(E)$ is the energetic density of the spatial density of sites $N_m(E)$. It is the spatial density $N_m(E)$ per unit energy. $N_m^{'}(E)$dE = $dN_m(E)$ is the spatial density adsorbing between E and E+dE.

It is the total spatial density of all receptor sites of the adsorbent. We can then pose that $N_m^{'}(E) = N_m f(E)$.
We have necessarily after integration:

$$\int f(E)dE = 1 \qquad (18)$$

$f(E)$ is the adsorption energy distribution (AED) function.
Then we have:

$$Q_a = \int_{E_{\min}}^{E_{\max}} \frac{n}{1+\left(\frac{P_0 \exp(-E/RT)}{P}\right)^{n}} N_m f(E)dE \qquad (19)$$

Where Q_a represents the experimental adsorbed quantity measured at the temperature T and the equilibrium pressure P, E is the adsorption energy, $E_{\min}$ and $E_{\max}$ are the limits or the energy band of the energy space, $f(E)$dE is also the fraction of the surface on which the adsorption energy of the adsorbate is between E and E+dE if we adopt the model of small patches [20].
On the other hand, we can write Q_a as following:

$$Q_a = \int_{E_{\min}}^{E_{\max}} \frac{\partial Q_a}{\partial E}\, dE = \int_{E_{\min}}^{E_{\max}} q_a dE \tag{20}$$

Then

$$q_a = \frac{\partial Q_a}{\partial E} = \frac{n}{1+\left(\frac{P_0 \exp\left(-E/RT\right)}{P}\right)^n} N_m^{'}(E) \tag{21}$$

Where q_a is the density of the adsorbed amount in the space energy, i.e. the adsorbed amount per unit of energy. So $q_a dE$ is the adsorbed amount between E and E+dE. q_a is the differential adsorbed amount.
According to this result, we can affirm that the adsorption energy distribution is not equal to the derivative of the total adsorption isotherm Q_a, since $f(E)$ is different from q_a which is, however, proportional to $N_m^{'}(E)$.

We can adjust the experimental isotherm using the simple Hill model with one type of energy and one value of N_m and n (Table 1). In this case, the calculated energy ΔE represents the average of energies E situated between E_{min} and E_{max}. Using this adjustment we lose information about the AED by reducing it to a simple value of energy. Certainly this value cannot describe the pore filling whose adsorption energies are not the same.
To calculate this integral equation, an algorithm has been developed to obtain the energy distribution function from an adsorption isotherm. This method has two subjects. The first is the fitting of experimental isotherm with an integral model. The second is the calculation of the adsorption energy distribution. These two subjects are achieved at the same time.

As it is signalled, it is necessary to assume mathematical expression for the local isotherm and the energy distribution function. In this work, the Hill model is used as a local isotherm. The mean adsorption energy ΔE included in the parameter $P_{1/2}$ will be changed to a variable energy E.
This equation that we have established using a statistical physics treatment contains implicitly the approximation of Cerofolini[26] (or the theory of Polanyi [27]) which relate the adsorption energy to the pressure.

A priori, the function $f(E)$ has any complicated shape. But in a first approximation it can be approximated by a simple normal Gaussian function. It is characterized by the two parameters E_0 and σ :

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E-E_0)^2}{2\sigma^2}\right) \tag{22}$$

This function presents a maximum for $E=E_0$, and σ is the dispersion of the Gaussian distribution, which is also called the heterogeneity parameter which is related to the full width of the distribution at half maximum H [20].Then we have:

$$Q_a(P) = \int_{E_{\min}}^{E_{\max}} \frac{\mathrm{n.N_m}}{1+\left(\frac{\mathrm{P_0} \exp\left(-E/RT\right)}{P}\right)^n} . \frac{\exp\left(\frac{-(\mathrm{E}-\mathrm{E_0})^2}{2\sigma^2}\right)}{\sigma\sqrt{2\pi}} dE \tag{23}$$

The proposed program is able to determine the four parameters involved by Eq.23: n, N_m, E_0, and σ. Our objective is to obtain the correct value of these parameters. This result is based on the values of the Average Relative Error (ARE) which is given by:

$$ARE = \frac{100}{m}\sum_{i=1}^{m}\left(\frac{\left|Qa_{calc} - Qa_{\exp}\right|}{Qa_{\exp}}\right)_i \tag{24}$$

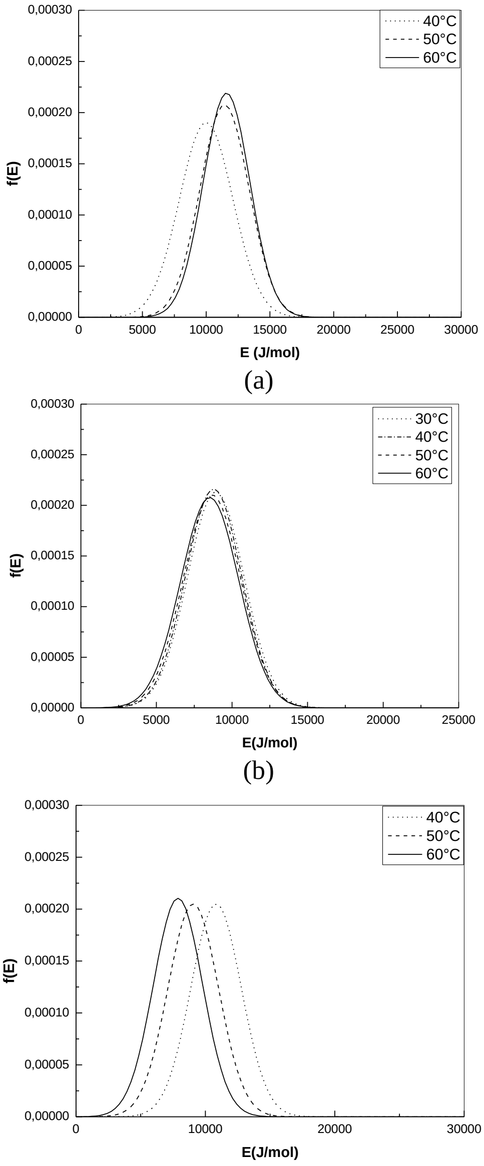
Where Qa_{calc} and Qa_{exp} are the calculated and experimental adsorbed quantity at an equilibrium pressure P, and m is the total number of points for each component. The summation is extended over all the experimental points of the isotherm.

In the integral equation only one term is known, the left side of the equation which represents the experimental isotherm. In order to obtain the correct solution, it should be necessary to identify all the value of ARE and finally choosing from among them the minimum. As consequence, the fitting process must be performed several times, always starting with a different set of parameters. In our case, we must give an initial value for all parameters introduced in Eq.23 and then a grid search is initialled to find the minimum ARE.

In the Eq. 23, it can be observed that n.N_m is a constant which can be extracted from the integral. This constant represents the quantity adsorbed at saturation Q_{asat} (Q_{asat} = n.N_m). The value of this parameter is proposed as a test of the goodness of the energy distribution function $f(E)$.

The numerical method is applied to determine the site energy distribution of a commercial activated carbon. The experimental isotherms of ethane, methane and nitrogen on BDH- activated carbon in the temperature range from 30 to 60°C for methane and from 40 to 60°C for ethane and nitrogen are selected as model adsorption systems.

III. Results



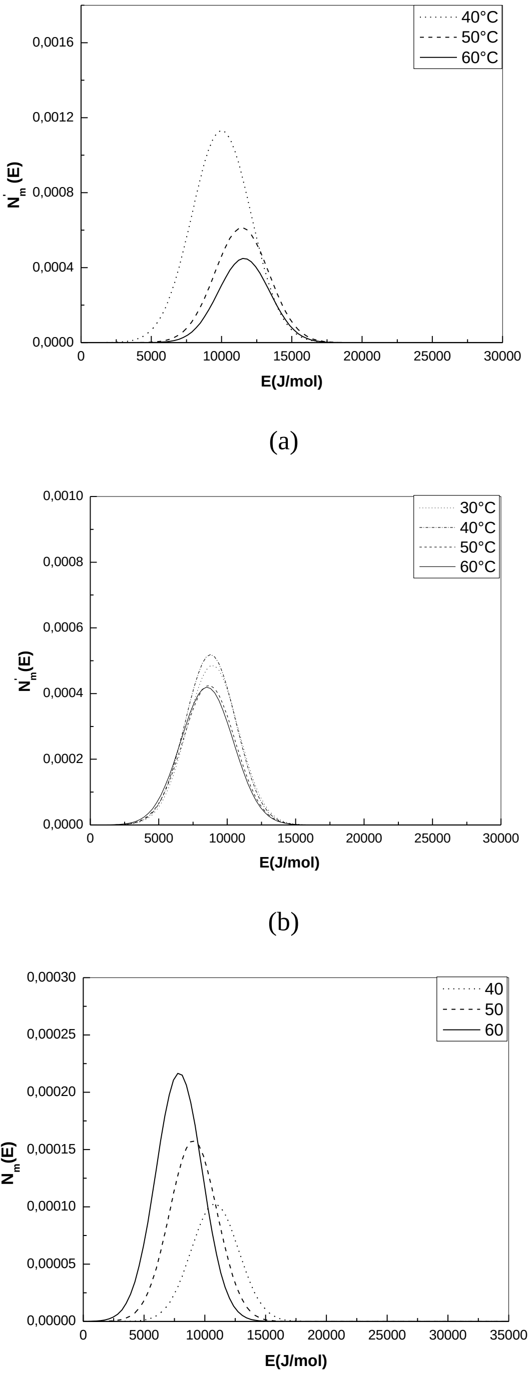
(a)

(b)

(c)

Fig. 1: The ADE by the numerical method for: (a) Ethane, (b) Methane, (c) Nitrogen

Fig. 1 illustrated the behaviour of the adsorption energy distribution for the three gases at different temperatures. Fig. 2 shows the variation of $N_m^{'}$, which represents the density of receptor sites adsorbing with the variable energy E.



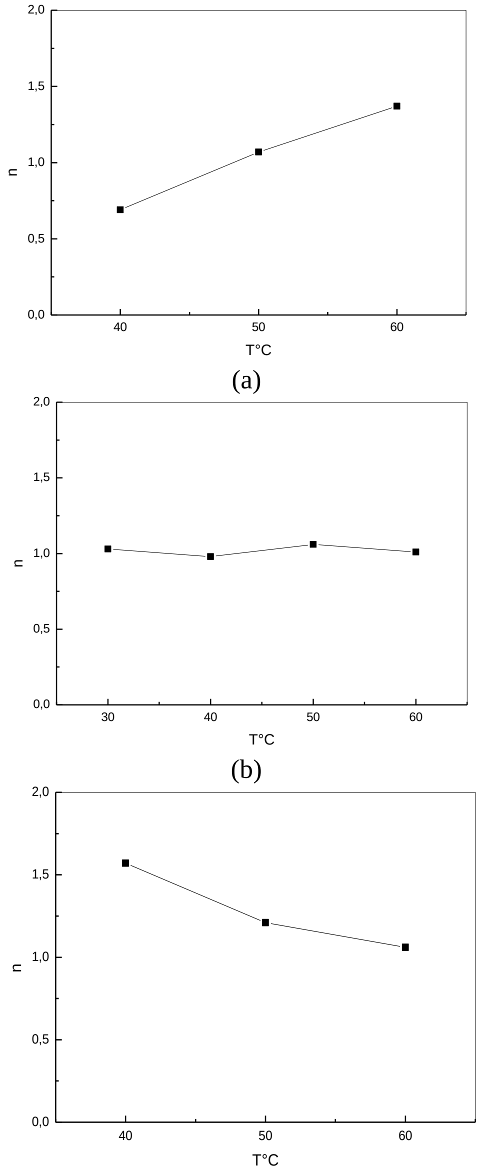
(a)

(b)

(c)

Fig. 2 : The variation of the energetic density of the spatial density of the effectively occupied sites for: (a) Ethane, (b) Methane, (c) Nitrogen

The evolution of parameter n for the three gases is illustrated in figure 3.



(a)

(b)

(c)

Fig. 3: Variation of the parameter n at various temperatures in the case of ethane (a), methane (b) and nitrogen (c).

The fitting parameters involved in Eq. 23 and the corresponding Average Relative Error (ARE) are illustrated in Tables 1,2 and 3.

Table1 : The values of parameters obtained by the numerical method in the case of ethane

Temperature(°C)	**E_0 (kJ/mol)**	**σ (kJ/mol)**	**H (J/mol)**	**N_m(mol/kg)**	**n**	**n'**	**ARE(%)**
40	10.00	2.10	4945	5.95	0.69	1.44	4.87
50	11.44	1.92	4521	2.95	1.07	0.93	0.84
60	11.60	1.82	4285	2.05	1.37	0.72	1.20

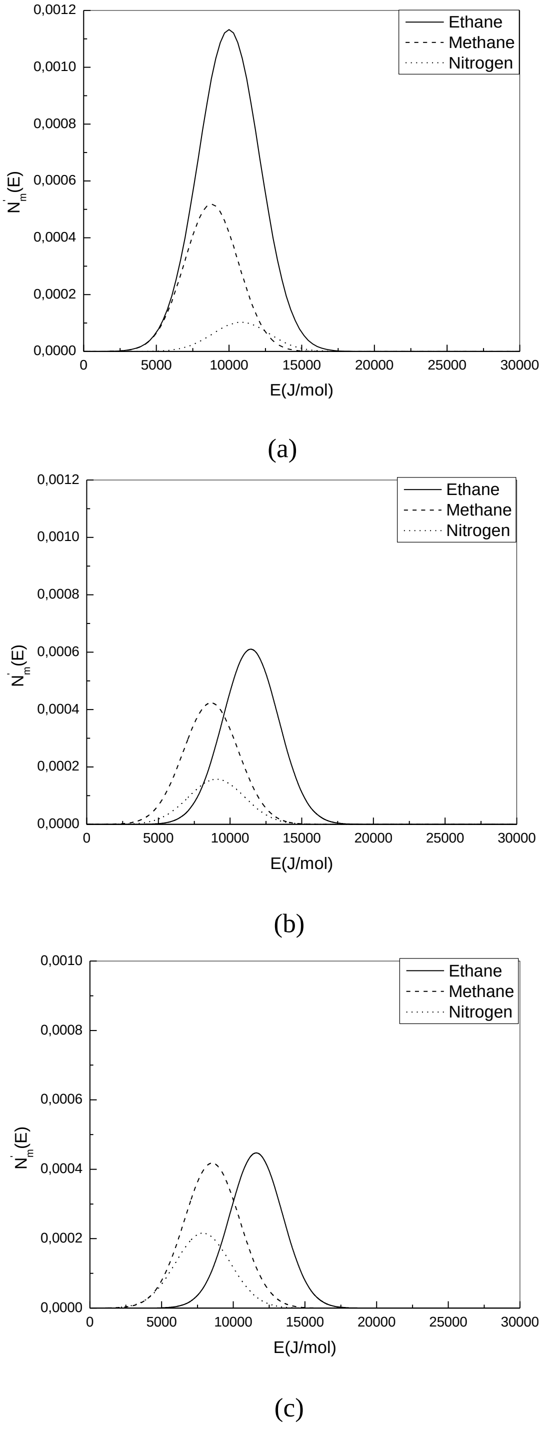
Table2 : The values of parameters obtained by the numerical method in the case of methane

Temperature(°C)	**E_0 (kJ/mol)**	**σ (kJ/mol)**	**H(J/mol)**	**N_m (mol/kg)**	**n**	**n'**	**ARE(%)**
30	8.92	1.87	4403	2.28	1.03	0.97	1.76
40	8.78	1.85	4356	2.40	0.98	1.02	1.30
50	8.67	1.90	4474	2.02	1.06	0.94	2.13
60	8.52	1.92	4521	2.02	1.01	0.99	3.47

Table3: The values of parameters obtained by the numerical method in the case of nitrogen

Temperature(°C)	**E_0 (kJ/mol)**	**σ(kJ/mol)**	**H (J/mol)**	**N_m (mol/kg)**	**n**	**n'**	**ARE (%)**
40	10.82	1.95	4591	0.50	1.57	0.63	3.27
50	9.05	1.95	4591	0.77	1.21	0.82	1.65
60	7.88	1.90	4474	1.03	1.06	0.94	2.48

The Q_{asat} determined from the program are presented in Table 4 together with those obtained by the fitting of experimental isotherms by the simple Hill model.



(a)

(b)

(c)

Fig.4: Comparison of the energetic density of the spatial density of the effectively occupied sites for the three molecules at 40°C (a), 50°C (b) and 60°C (c).

Table 4: Comparison of the Q_{asat} obtained by the fitting using the simple Hill isotherm and that obtained by using numerical method.

	Temperature	Q_{asat} (mol/kg)obtained by the fitting by using Hill model	Q_{asat} (mol/kg) obtained by the numerical method
Ethane	40	4.18	4.10
	50	3.15	3.15
	60	2.76	2.80
Methane	30	2.19	2.34
	40	2.29	2.35
	50	1.88	2.14
	60	1.81	2.04
Nitrogen	40	0.77	0.78
	50	0.89	0.93
	60	0.99	1.09

IV. Discussion

By using the Langmuir model as local isotherm, Y.Ben Torkia et al. [29] found that the values of ARE are in the interval [0.86%, 5.21%]. In this study the values of the ARE are in the interval [0.84%, 4.87%] (Tables 1,2and3). It is clear that the energy distribution function obtained by this new program, which is based on the Hill model, is the one that produces the minimum value of ARE from the simulated data and better reproduces the isotherms than the Langmuir model.

The use of the Hill model as a local isotherm in the integral equation is very helpful in the case of ethane and nitrogen, where the coefficient n is far from unity (Tables 2 and 3). Then, for nitrogen we deduce that the adsorption is a multi-molecular adsorption at different value of temperature (Table 3). This can be due to the small size of this molecule and to its attractive behaviour. In the case of the ethane molecule (Table 1), the adsorption is multi-molecular at 60°C (n=1.37). But at 40°C we notice a multi-anchorage adsorption (n=1.37). Certainly these results cannot be deduced by applying the Langmuir model. On the other side the adsorption of methane molecule is always monomolecular (n is around unity: Table 2). This is can be due to the symmetry of the molecule. The utilisation of the Langmuir model as a local isotherm in this case would suffice to describe the adsorption process.

Table 4 shows that the values of Q_{asat} obtained by the new program are closer to those obtained by fitting isotherms with the simple Hill model.

As a general remark which we can deduced from all obtained AED (Figure 1), we can see that the value of the adsorption energy does not exceed 20 kJ/mol for the high energies, which indicates that is a physisorption for all the range of energies.

Because each adsorbate gives a several possible configurations of the manner of adsorption of the molecule, the obtained AED give different information about the energy adsorption existing on the BDH-activated carbon. In this paragraph, we tried to relate the values of parameter n and n' to the behaviour of the obtained AED. As shown in Tables 1,2 and 3 , the values of n may be greater or less than unity. Indeed, a molecule has several ways to be anchored onto the receptor sites according to its geometry.

In the case of ethane, by increasing temperature the maximum of distribution E_0 translate in the direction of high energies; however the full width at half maximum, H, decreases (Fig. 1(a)). Indeed, at 40°C n is equal to 0.69 (Table 1 and Fig. 3(a)), which indicate that the molecule is adsorbed by an average of one molecule by two sites. Therefore the temperature tends to remove this double anchorage ($n \cong 0.5$) at week temperature to keep only one anchorage ($n \cong 1$) at high temperature. Otherwise, the ethane molecule is adsorbed parallely by two sites at 40°C. Whereas, the higher the temperature is the more important the thermal collisions are, which makes ethane adsorbed vertically by one site. As a consequence, N_m and Q_{asat} decreases by increasing temperature (Table 1). Clearly, the weaker anchorage disappeared, and only the strongest anchorage will be kept at high temperature. We can deduce this result from Fig. 2(a). Then it is clear that the density of sites with higher energies appeared at high temperature to the detriment of weaker energies which disappeared. For that $N_m^{'}$ has the smallest shape at 60°C.

On the other hand, when n decrease the anchorage number n' increase, hence the molecule is adsorbed by more than one site. As a result, the number of receptor sites per gram of adsorbent, $N_{m,}$ which represents the total spatial density of effectively occupied receptor sites, increases. The adsorption energy varies from one site to another. As a consequence of this, the heterogeneity of the surface is very apparent and the full width at half maximum, H, of the distribution increases by decreasing temperature (Fig. 1(a)).

Due to the electronic structure of the methane molecule, only the Van der Waals interactions contribute to the value of the adsorption energy. The energy associated with this type of interactions depends strongly on the distance between the nuclei of adsorbent and adsorbed molecules [24]. The value of n is close to the unity that is to mean that the molecule is adsorbed by an average of one molecule per site. However, by increasing temperature, the values of n stay close the unity (Figure 3(b)). Then we can deduce that the distance between nuclei of adsorbent and methane molecule doesn't have a great change by varying the temperature, which probably due the symmetry of this molecule. Therefore, the distribution keeps the same shape and also the same value of the maximum E_0 (Fig. 1(b)). We can deduce this result also from Fig. 2(b) when we can see that the energetic density of receptor sites is the same at different temperatures.

In the case of nitrogen, another phenomenon can be observed: the value of E_0 shifts toward the lower energies with increasing temperature. Table 3 and Figure 3(c) indicate that the value of n decreases but it is never lower than unity, this probably due to the small shape of nitrogen molecule. This result shows that there is a possibility that nitrogen would be adsorbed by an average of two molecules per site. Indeed, at 40°C there is 57% of nitrogen molecules adsorbed with an average of two molecules per site. By increasing temperature, the thermal agitation does not let the cohesion between gas and adsorbed nitrogen molecules. It removes this assembly and the adsorption process pass from two molecules per site to one molecule per site. Obviously the interaction energy of two separated molecules with the adsorbent surface (at high temperature) is weaker than the energy of interaction of two linked molecules (at low temperature). Indeed, this energy becomes divided in two links (two energies) which are weaker than the first. So at high temperature the weaker energies increase in the AED and the number of links increases. The number of links is expressed by $N'_m(E)$ and N_m. Then we can understand the increase of N_m and Q_{asat} at high temperature.

Fig. 1(c) shows that the density of the lower energies increases. Therefore, by increasing temperature the percentage of molecules adsorbed with an average of two molecules per site decrease to 2% at 60°C, which explain the decrease of the density of the higher energies and the increase of the lower energies. As a consequence, the density of receptor sites is greater at lower energies (at 60°C) as it is shown in Fig. 2(c).

Figure 4 show the comparison of the energetic density of the effectively occupied sites for the three molecules. Thereby we can deduce that ethane present the biggest density of receptor sites at higher energies followed by methane than by nitrogen. This result indicates strong interactions between molecules of ethane and the surface of the activated carbon as compared to methane and nitrogen.

V. Conclusion

The present study showed that the adsorption energy distribution function obtained from an improved regularisation method can be used to determine the surface heterogeneity of the commercial BDH activated carbon at different temperature in the case of the three adsorbate gases: methane, ethane and nitrogen. In this work, we have developed the integral equation using statistical physics. As a consequence, a new parameter, N'_m, appeared which represents the energetic density of the spatial density of receptor sites.

The energy distribution function is investigated by a numerical method. The advantages of this program are the simplicity in treatment and that it allows us to obtain directly the energy distribution functions from experimental isotherms. Moreover it can be used to obtain a good fitting of the experimental isotherm with an integral equation. As a local isotherm, we have used the Hill model which is obtained by applying the grand canonical ensemble in statistical physics. The adsorption energy distribution is assumed to be a Gaussian distribution. Undoubtedly, by use of this new program the description of adsorption is more complete especially by using the Hill model as a local isotherm, which allows a large interpretation of the evolution of the AED.

Analysis of the results shows that the value of the number of molecules adsorbed per site, n, has a great effect on the position of the maximum energy E_0. Then the effect of the thermal agitation on the behaviour of the AED was studied, in the purpose to describe the adsorption process at lower and higher temperatures. Moreover, the effect of the number of receptor sites per gram of adsorbent, N_m, on the full width at half maximum of the distribution is clear in the case of ethane.

As a conclusion, in the numerical method we have assumed a Gaussian distribution, which limits its shape. Then improving the expression of AED form can ameliorate the adsorption process description. On the other hand the present study is limited to the adsorption process. Then by optimizing other assumptions, the integral equation can be used to describe the desorption process.

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