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Adsorption thermodynamics in the framework of the statistical physics formalism: basic blue 41 adsorption onto Posidonia biomass

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ABSTRACT

Adsorption isotherms have important practical applications, including in interface chemistry where they have been used to model adsorbate/adsorbent interactions. Basing on the grand canonical formalism in statistical physics, a finite multilayer model with multisite occupancy was established. The main purpose of that work was to predict some adsorption thermodynamic parameters. Here, the model is developed further to obtain expressions for the configurational entropy, *S*, the Gibbs free enthalpy, *G* and the Helmholtz free energy, *F*. These calculated thermodynamic parameters are used to interpret the adsorption process and the interactions of adsorbate with each other, as well as, with the adsorbent surface. In this paper, we show how the grand canonical formalism will be emphasized for treating more advanced adsorption model with thermodynamic study.

Keywords: Thermodynamic parameters; Theoretical modelling; Grand canonical ensemble; Surface disorder; Finite multilayer adsorption

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1. Introduction

Interfacial processes are central to understand many processes in environmental sciences and technologies, chemical engineering, earth sciences, ocean sciences and atmospheric sciences. Thermodynamics has been used as a classical method to describe interfacial equilibrium properties over the last century [1–5]. Experimentally measurable macroscopic parameters of adsorption capacity are widely used as the basic parameters in many equations/models to describe the equilibrium characteristics of adsorption reactions at solid–water interfaces. For instance, methods of equilibrium adsorption constants or adsorption isotherms are commonly used to describe the equilibrium relationship between concentration in solution and adsorption capacity on solid surfaces.

Adsorption is a natural process and may be characterized on the basis of different adsorption models [6–15] such as Langmuir, Toth and Dubinin equations. Multilayer adsorbed model is a topic of increasing attention in different fields as food, ethylene, water, argon and lead ions [16–20]. Among the various theories and models that have been proposed to describe multilayer adsorption in equilibrium, the ones of Brunauer–Emmet–Teller (BET) [21] are the

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most widely used and practically applicable. Anderson [22] modified BET theory by assuming that adsorption heat from the second to about the ninth layer differs from the heat of condensation by a constant amount, while for the layers following these, the heats of adsorption and condensation are the same. Anderson's equation, better known in the literature as the GAB isotherm [23] is a significant improvement on the BET theory, and has been widely used in the literature for many food materials [24,25]. Other multilayer adsorption isotherms have been presented in the pertinent literature so, more recently, Sun and Chakraborty [26] developed a formalism of adsorption isotherm from the rigour of partition function of each adsorptive site and the isosteric heat of adsorption at zero surface coverage for the calculation of adsorbate uptakes on various adsorbent materials. Those authors assumed that s numbers of adsorbate molecules are adsorbed on each adsorbent site of an adsorbent–adsorbate system, where s varies from 0 to its maximum value m. Furthermore, as mentioned by Sun and Chakraborty [26] that empirical or semi-empirical isotherms including [7]: Toth, Sips, Unilan, Javanovich equations, etc., correlate experimental data with empirical parameters with little or no physical meanings. Recently, we developed theoretical approach based on statistical physics models [27]. The aim of the analytical and theoretical development was to give physical meaning to the model parameters and therefore to promote a better understanding of the adsorption process at the molecular level. This new finite multilayer model describes the physisorption when the number of adsorbed layers is greater than the unit but not infinite like in BET model. This finite multilayer model with multisite occupancy is analytically treated by statistical physics and it shows five adsorption parameters such as the number or the fraction of the adsorbed molecule(s), n, the receptor sites density, N_m, the number of adsorbed layers, N_ℓ and the two characteristic concentrations C_1 and C_2.

On the other hand, adsorption is considered an effective process for the removal of impurities from the environment [28–31]. The adsorption study of dye on natural adsorbents is of vital importance for finding cheap adsorbents [32–35]. *Posidonia* biomass is one of the most abundantly available cheap adsorbents that can be considered as a natural filter for water purification [36–39]. Different adsorption mechanisms may be found by studying the dependence of adsorption on various variables (pH, concentration of solutes, ionic strengths, and the type and topology of surfaces), and by interpreting the parameters of the determined adsorption isotherms. Also, thermodynamic parameters of adsorption from solutions provide a great deal of information concerning the type and mechanism of the adsorption process [5,40]. The knowledge of thermodynamic parameters is of fundamental importance for learning about the spontaneous occurrence of a given process at a given temperature. Adsorption is a spontaneous process that occurs with the evolution of the heat of adsorption [8]. The spontaneity of the adsorption process may be found on the basis of the sign of Gibbs free energy. If adsorption occurs spontaneously, with the rate of adsorption being higher than desorption, Gibbs free energy will always be a negative quantity. In fact, the adsorption process is useful only if it occurs spontaneously. The spontaneity of the adsorption process is also affected by the thermodynamic parameters, heat of adsorption and entropy change. Thus, knowledge of the signs of various thermodynamic parameters is highly important in determining the spontaneity of a given process.

In the present study, the grand canonical partition function was further exploited to evaluate some thermodynamic functions related to adsorption process such as the configurational entropy, Helmholtz free energy and Gibbs free enthalpy. These parameters have been widely used in the literature and their usefulness have focused attention for any theoretical developed model, since they are contributed to reinforce the interpretations of the adsorption systems and they were determined with a classical manner [41–47]. Furthermore, thermodynamic parameters in multilayer adsorption have been commonly used in several literature works [4,5,40]. However, using our method, the thermodynamic parameters are directly derived from the partition function of the adequate model. Furthermore, our model leads us to calculate these thermodynamic functions as a function of the adsorbate concentration and not a mean value as can be obtained with a classical manner. Thus, the aim of the present work was to give physical meaning to the model parameters basing an statistical physics approach on the one hand, and to evaluate thermodynamic functions related to adsorption process directly from the grand canonical partition function, on the other hand. Consequently, to better understand the experimental adsorption data of BB41 on *Posidonia* biomass at molecular level, our statistical physics model is applied and new interpretations in thermodynamic point of view are derived.

2. Theoretical background of studies

2.1. Equations for calculating the adsorption isotherm

The analytical expression of the finite multilayer adsorption model with multisite occupancy will be established using statistical physics approach. For that, it is assumed that the dye molecules are treated as an ideal gas [48–51], since their concentration will be relatively low. The grand canonical formalism will be used since the adsorption process involves an exchange of molecules between the solution and the adsorbed state. The adsorption energy level of each adsorbed layer is given by $-\varepsilon_{N_\ell} = -[\varepsilon_1 + (N_\ell - 1)\varepsilon_2]$. Where $(-\varepsilon_1)$ is the monolayer adsorption energy due to the adsorbent–adsorbate interaction and $(-\varepsilon_2)$ is an adsorption energy related to the adsorbate–adsorbate interaction. Moreover, it is assumed that any given receptor site can be empty $(N_i = 0)$, occupied by one layer $(N_i = 1)$ and so on till N_ℓ layers are adsorbed $(N_i = N_\ell)$.

The grand canonical partition function for one receptor site is [48,52,53]:

$$z_{gc} = \sum_{N_i=0}^{N_\ell} e^{-\beta\left(-\varepsilon_{N_\ell}-\mu\right)N_i} = 1 + e^{\beta(\varepsilon_1+\mu)}\left[\frac{1-e^{N_\ell\beta(\varepsilon_2+\mu)}}{1-e^{\beta(\varepsilon_2+\mu)}}\right] \tag{1}$$

where μ is the chemical potential of the adsorbed phase, T being the experimental temperature, k_B represents the Boltzmann constant, N_i is the occupation number and $N_\ell$is the average number of the adsorbed layers.

The grand canonical partition function has the following form for N_m identical receptor sites per unit mass:

$$\begin{aligned} Z_{gc} &= \prod_{i=1}^{N_m} z_{gc} \\ &= \left[\frac{1-e^{\beta(\varepsilon_2+\mu)} + e^{\beta(\varepsilon_1+\mu)} - e^{\beta(\varepsilon_1+N_\ell\varepsilon_2+(N_\ell+1)\mu)}}{1-e^{\beta(\varepsilon_2+\mu)}}\right]^{N_m} \end{aligned} \tag{2}$$

The occupation number of identical N_M receptor sites is therefore given as follows [49,53,54]:

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

In general, the adsorption reaction of dye molecule (D) onto receptor site (S) should include a stoichiometric coefficient, n, according to the following equation [50]:

$$nD + R \rightleftarrows D_nR \tag{4}$$

where n is the number or the fraction of the adsorbed molecule(s) anchored per site which can help us about topography of adsorption, and then we can understand the conformation of any molecule. The molecule is multimolecularly adsorbed onto the solid surface with a vertical position when n is greater than unity $(n > 1)$ and in the case where the value of this parameter is lower than the unit $(n < 1)$, the molecule is multianchored onto the solid surface with a horizontal position.

According to the equilibrium conditions written above and the mass action law, we can write [54]:

$\varepsilon = n_a$ and $\mu = n\mu_a$

With ε and μ as the adsorption energy and the chemical potential of a receptor site, respectively. The subscript a conveys the adsorbate molecule.

According our previous published works [55], the total number of adsorbed molecules is given as:

$$Q_a = nN_o \tag{5}$$

Then, to express the adsorbed amount as a function of concentration of the adsorbate, we need to use relationship between the fugacity and the concentration which written as [49]:

$$e^{\beta\mu} = \frac{N}{Z_{gtr}} = \frac{C}{z_{gtr}} \tag{6}$$

where N is the number of adsorbate molecules, C is the concentration of adsorbed molecules at equilibrium, μ is the chemical potential of a molecule assimilated for an ideal gas and z_{gtr} is the partition function of translation per unit volume that can be written as follows [48,53]:

$$z_{gtr} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \tag{7}$$

With m is the mass of an adsorbed molecule, h is Planck's constant and k_B is the Boltzmann constant.

Finally, the adsorbed quantity is written as a function of the dye concentration as:

$$Q_a = nN_m \frac{\left(\frac{C}{C_1}\right)^n \left[1-(N_\ell+1)\left(\frac{C}{C_2}\right)^{nN_\ell} + N_\ell\left(\frac{C}{C_2}\right)^{n(N_\ell+1)}\right]}{\left[1-\left(\frac{C}{C_2}\right)^n\right]\left[1-\left(\frac{C}{C_2}\right)^n + \left(\frac{C}{C_1}\right)^n - \left(\frac{C}{C_1}\right)^n\left(\frac{C}{C_2}\right)^{nN_\ell}\right]} \tag{8}$$

where

$$C_1 = C_s e^{-\Delta E_1^a/RT} \tag{9}$$

$$C_2 = C_s e^{-\Delta E_2^a/RT} \tag{10}$$

where C_1 is the half-saturation concentration of a monolayer coverage, C_2 is the half-saturation concentration of global isotherm, C_s is the solubility of adsorbate in aqueous solution, R is the ideal gas constant and T is the isotherm temperature [5,27,48–56].

The model used in this study contains physicochemical parameters, namely the number or fraction of adsorbed molecule(s), n, the receptor sites density per mass unit, N_m, the average number of the adsorbed layers, N_ℓ, and the adsorption energies, $\left(-\Delta E_1^a\right)$ and $\left(-\Delta E_2^a\right)$ at the first layer and the next ones, respectively. These parameters are determined by numerical fitting.

2.2. Thermodynamic functions

According to the statistical physics treatment, thermodynamic properties can be evaluated to reinforce the interpretations of the adsorption systems. These thermodynamic functions are configurational entropy, Gibbs free adsorption enthalpy and Helmholtz free energy.

The grand potential is given by [5,52,53]:

$$J = -k_B T \ \ln\left(z_{gc}\right) = -\frac{\partial \ln\left(z_{gc}\right)}{\partial \beta} - TS \tag{11}$$

where J is the grand potential, z_{gc} is the grand canonical partition function for one receptor site and S is the configurational entropy.

Then, the expression of configurational entropy is expressed as follows:

$$\frac{S}{k_B} = \ln \ z_{gc} - \beta \frac{\partial \ln \ z_{gc}}{\partial \beta} \tag{12}$$

According Eq. (1), giving the grand canonical partition function for one receptor site, the quantity $\frac{S}{k_B}$ can be evaluated.

The Gibbs free adsorption enthalpy is given as follows [51,52,56]:

$$G = \mu N_o \tag{13}$$

Using Eq. (6), the chemical potential can be written as:

$$\mu = \ln\left(\frac{C}{z_{gtr}}\right) \tag{14}$$

Combining Eqs. (1), (3) and (14), the Gibbs free adsorption enthalpy can be expressed as a function of the adsorbate concentration.

The Helmholtz free energy is expressed as [51,52,56]:

$$F = -\frac{\partial \ln \ z_{gc}}{\partial \beta} + \frac{\mu}{\beta}\left(\frac{\partial \ln \ z_{gc}}{\partial \mu}\right) = -\frac{\partial \ln \ z_{gc}}{\partial \beta} + G \tag{15}$$

Then, this last equation can be evaluated regarding Eq. (13).

It is noticed that all thermodynamic functions that derived above can be expressed as a function of the adsorbate concentration, and then they can be evaluated at each equilibrium state. Their investigation during the adsorption process will be discussed.

3. Materials and methods

The supports used for the immobilization of basic dye are the raw *Posidonia* biomass (P_0) and carboxymethylated one (MP). Details for these adsorbents and experimental isotherms plotting are given elsewhere [39].

The dye used as adsorbate is basic blue 41 referred to as BB41. Its chemical structure and characteristic have been given previously [39].

The experimental isotherms of the dye onto raw and modified *Posidonia* were presented in form of adsorbed quantity vs. concentration, at equilibrium. These isotherms show that the adsorption quantity increases with concentration to reach a saturation level (Fig. 1).

The finite multilayer model was applied to the experimental isotherms. Iteration method was used to obtain the model parameters for all experimental data. The model parameters obtained by matching experimental data are summarized in Table 1.

The fitting criterion in the present investigation is the well-known correlation coefficient R. We used Microcal OriginLab software (OriginLab, Northampton, MA). The ideal fitting is obtained when the value of R is close to the unit. It is clear that finite multilayer adsorption model with multisite occupancy describes well the adsorption process of BB41 dye onto *Posidonia* biomass.

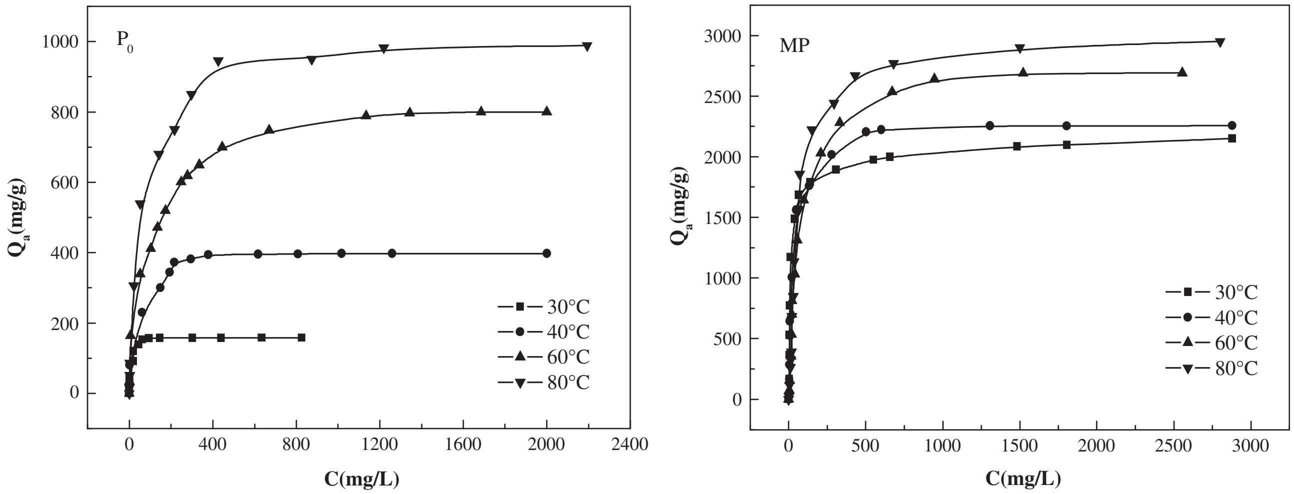

Fig. 1. Adsorption isotherm of the BB41 on raw (P_0) and modified *Posidonia* (MP) at different temperatures.

Table 1
The results of fitting parameters according the finite multilayer with multisite occupancy model

Samples	T (°C)	R^2	n	N_m (mg/g)	N_ℓ	C_1 (mg/L)	C_2 (mg/L)	n^*N_m (mg/g)
P_0	30	0.992	1.481	30.535	3.512	0.381	18.620	45.251
	40	0.995	1.290	102.368	3.079	0.770	92.124	132.054
	60	0.999	1.408	217.564	2.659	4.809	211.560	306,539
	80	0.995	1.073	419.136	2.282	13.397	149.578	449,905
MP	30	0.994	2.374	668.831	1.320	7.537	225.725	1,588.233
	40	0.994	1.702	844.143	1.591	10.729	151.310	1,437.129
	60	0.997	1.728	864.228	1.826	24.956	227.701	1,493.706
	80	0.995	1.815	1,183.381	1.389	35.775	327.684	2,148.688

4. Results and discussion

In order to fully understand the nature of adsorption, the thermodynamic parameters such as entropy, S, Gibbs free adsorption enthalpy, G and Helmholtz free energy, F, could be calculated.

In general, these parameters indicate that the adsorption process is spontaneous or not and exothermic or endothermic. The Helmholtz free energy for the adsorption process could be either (i) positive value indicates that the process is endothermic in nature or (ii) negative value indicates that the process is exothermic in nature and a given amount of heat is evolved during the binding dye molecule on the surface of adsorbent. The positive value of entropy indicates an increase in the degree of freedom (or disorder) of the adsorbed species at the solid surface.

4.1. Statistical thermodynamic properties of our advanced model

In this section, we want to express the theoretical evolution of the thermodynamic parameters such as entropy, S, Gibbs free enthalpy, G and Helmholtz free energy, F, according to the finite multilayer model.

Fig. 2 depicts the theoretical evolution of the entropy as a function of adsorbate concentration of various physicochemical adsorption parameters (n, N_ℓ, C_2 and C_1) according to the finite multilayer model. The effect of the steric parameter n on the entropy evolution is shown on Fig. 2(a). It can be noted that the smaller the n value is, the more important the width of peaks is. Furthermore, only one peak is observed for small value of n and two peaks appear for high value of n. Thus, the first entropy peak corresponds to the monolayer filling. The second one conveys the filling of the next layers as demonstrated in Fig. 2. Indeed, in the case of multianchorage adsorption ($n < 1$), it is probably that the filling of the next layers starts before the monolayer is saturated. When the adsorption is multimolecular ($n > 1$), a partial saturation level appears where a multilayer adsorption already occurs while the first layer is still incomplete.

Fig. 2(b) shows the effect of the number of adsorbed layers on the evolution of the entropy. It is

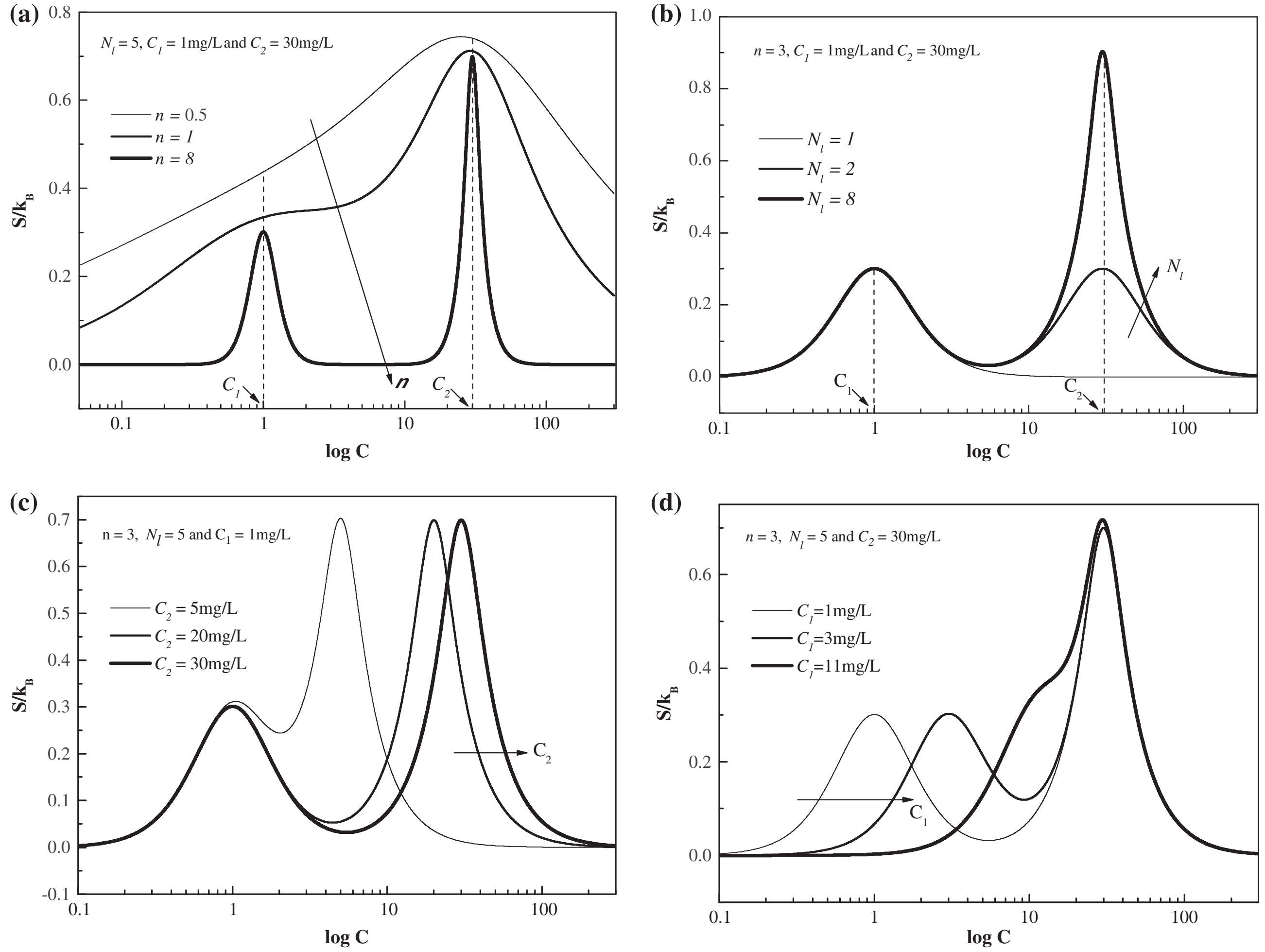

Fig. 2. Theoretical evolution of the entropy as a function of adsorbate concentration according to the finite multilayer model: (a) effect of the n parameter; (b) effect of the N_ℓ parameter; (c) effect of the C_2 parameter; (d) effect of the C_1 parameter.

obviously that the parameter ε_{N_ℓ} affected only the second peak. This confirms the result found when studying the effect of parameter n on the entropy. Indeed, when the number of adsorbed layers increases, the number of possible complexation also increases.

Fig. 2(d) and (e) represents the effect of the two energetic parameters C_1 and C_2 on the entropy evolution. From the obtained data, it can be noted that the first peak is affected by C_1 while the second one is influenced by C_2. Indeed, the C_1 parameter is related to the monolayer adsorption energy. The C_2 parameter is related to the next layers adsorption energy. Therefore, the two peaks are merged when C_1 and C_2 are close to each other. This means that there is no difference between the fittings of the layers.

Fig. 3(a) represents the evolution of the Helmholtz free energy, F, vs. concentration with different values of n. At low concentrations, the smaller the n value is, the greater F is. Consequently, the adsorbate–adsorbent interaction increases when the molecules are anchored with several receptor sites to the surface. Beyond C_1, the reserve phenomenon is observed, i.e. the adsorbed quantity increases with increasing the number of adsorbed molecules per site. Then, at high concentrations and high values of n, the Helmholtz free energy is greater in modulus. Indeed, when an important number of molecules are adsorbed per site at high concentrations, the energy of the system is important. In the contrary, when the adsorption is parallel to the solid surface (low value of n) the adsorbed quantity is relatively low and so the energy of the system is low.

Based on the obtained results (Fig. 3(b)), two regions are distinguished: (i) When $C < C_2$, the all observed data are superimposable, the Helmholtz free energy of the first monolayer is independent of; and

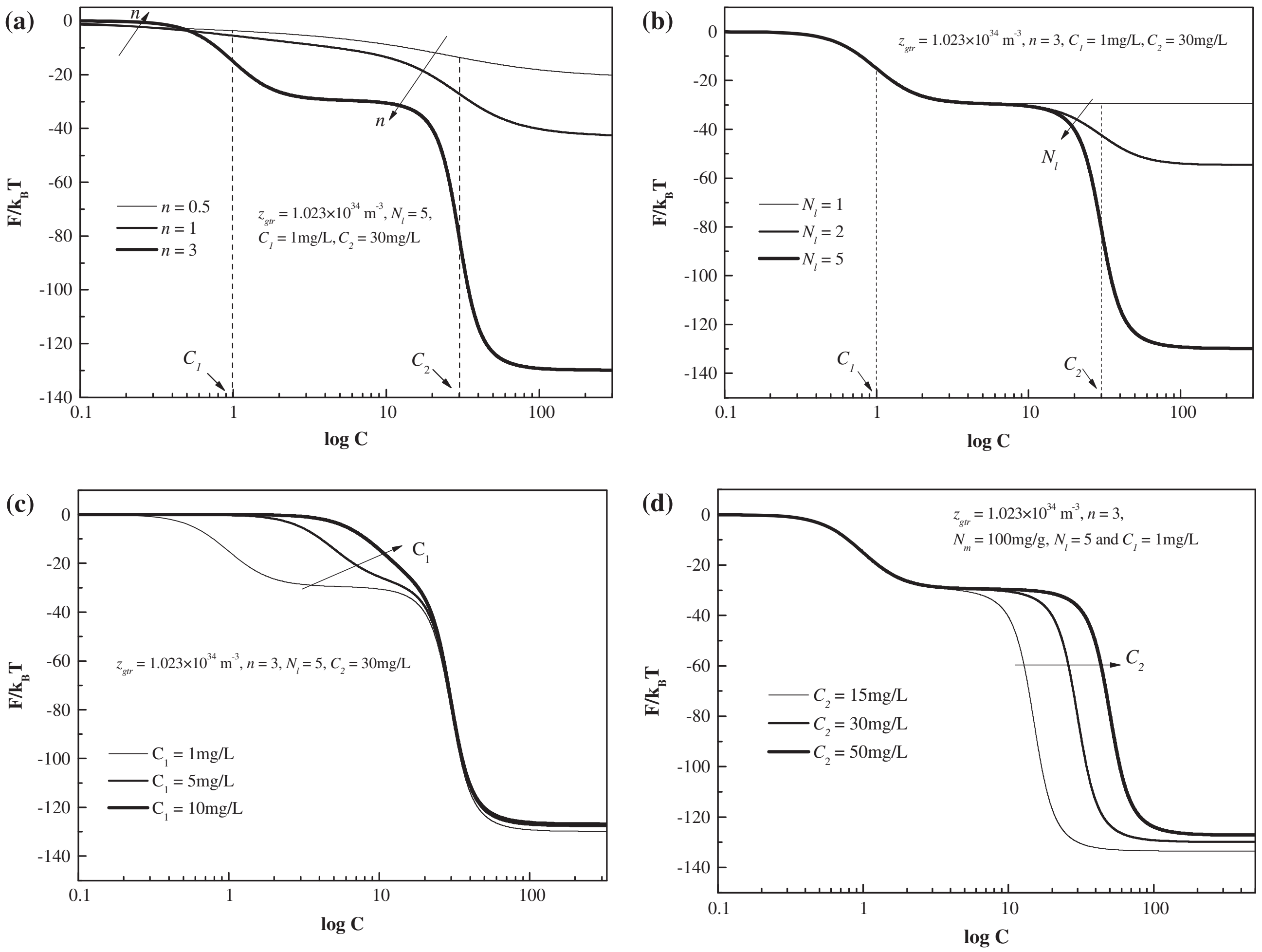

Fig. 3. Theoretical evolution of the Helmholtz free energy as a function of adsorbate concentration according to the finite multilayer model: (a) effect of the n parameter; (b) effect of the N_ℓ parameter; (c) effect of the C_1 parameter; (d) effect of the C_2 parameter.

(ii) when $C > C_2$, the increase in Helmholtz free energy, F, is obviously proportional to the number of adsorbed layers N_ℓ

The effect of the parameter C_1 appears only in the region of the first layer (Fig. 3(c)). Indeed, this parameter informs us about the adsorbent–adsorbate interaction for the monolayer. The C_2 parameter affects the evolution of the Helmholtz free energy at high concentrations (Fig. 3(d)). Furthermore, at a fixed adsorbate concentration, the higher the adsorbate–adsorbate interaction is (respectively the smaller the value of C_2 is) the higher the Helmholtz free energy is.

Fig. 4(a) represents the evolution of Gibbs free enthalpy against the concentration for four different n values. At low concentrations, the adsorbed amount is higher when the adsorbate molecule is multianchored onto the adsorbent surface ($n < 1$). The opposite phenomenon occurs just after the half-saturation of the monolayer. As the monolayer will serve as receptor sites for the following layers, a similar phenomenon occurs before and after C_2, since the probability to find neighbour empty sites becomes low near the saturation of the first layer and the last ones.

It is clear from Fig. 4(b) that the N_ℓ parameter affects the Gibbs free enthalpy after the monolayer filling. Especially, in the case of monolayer adsorption ($N_\ell = 1$), there is no additional decrease in the Gibbs free enthalpy. It can be also deduced that the higher the number of adsorbed layers is, the more spontaneous the adsorption process is.

Fig. 4(d) and (e) indicates that the first parameter C_1 affects the adsorption at the first layer. While the parameter C_2 affects the adsorption at the next layers. This observation can be attributed to the fact that the two parameters C_1 and C_2 are related to the

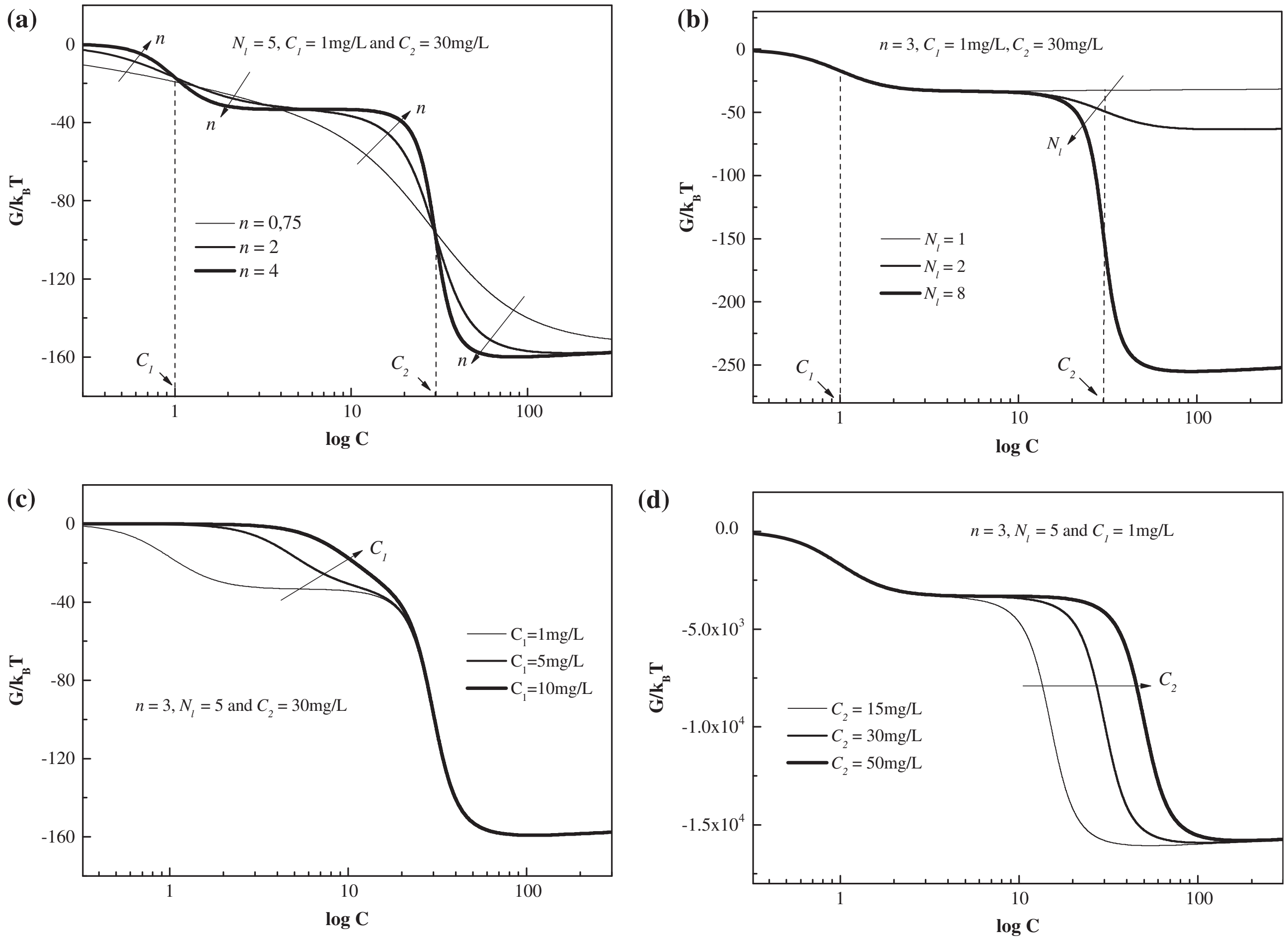

Fig. 4. Theoretical evolution of the free Gibbs enthalpy as a function of adsorbate concentration according to the finite multilayer model: (a) effect of the n parameter; (b) effect of the N_ℓ parameter; (c) effect of the C_1 parameter; (d) effect of the C_2 parameter.

adsorption energies for the first layer and the second one, respectively.

4.2. Model applications to experimental data

Simplicity and accuracy are desired in solving the thermodynamic relations derived in calculating the entropy, Gibbs free enthalpy and Helmholtz free energy of adsorption from experimental data.

As an example, using the fitting parameters and Eq. (12) the evolution of the entropy of BB41 dye onto untreated, P_0, and modified, MP, *Posidonia* is illustrated in Fig. 5. The general shapes of the entropy curves are remarkably similar. The positive entropy change suggests that some structural changes occur on the adsorbent, and the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process [51]. However, the negative change shows a greater order of reaction during the adsorption on the surface that could be due to fixation of BB41 to the adsorbent sites resulting in a decrease in the degree of freedom of the systems.

From the obtained data (Fig. 5), two peaks are distinguished with an exception for 80°C. Indeed, at low concentrations, the entropy increases to reach a maximum at half-saturation of the monolayer. This could be possible because the mobility of adsorbate molecules in the solution decreases with the increase in concentration and that the affinity of adsorbate on the adsorbent is higher at low concentration. Furthermore, when $C < C_1$, the receptor sites are almost empties and the molecule has several possibilities to choose an unoccupied receptor site. Thus, the disorder at the surface increases with the increase in the adsorbed quantity until reaching a maximum at a concentration equal to C_1. Then the entropy decreases till reaching a minimum value different from zero. This observation could be attributed to the already occurring multilayer

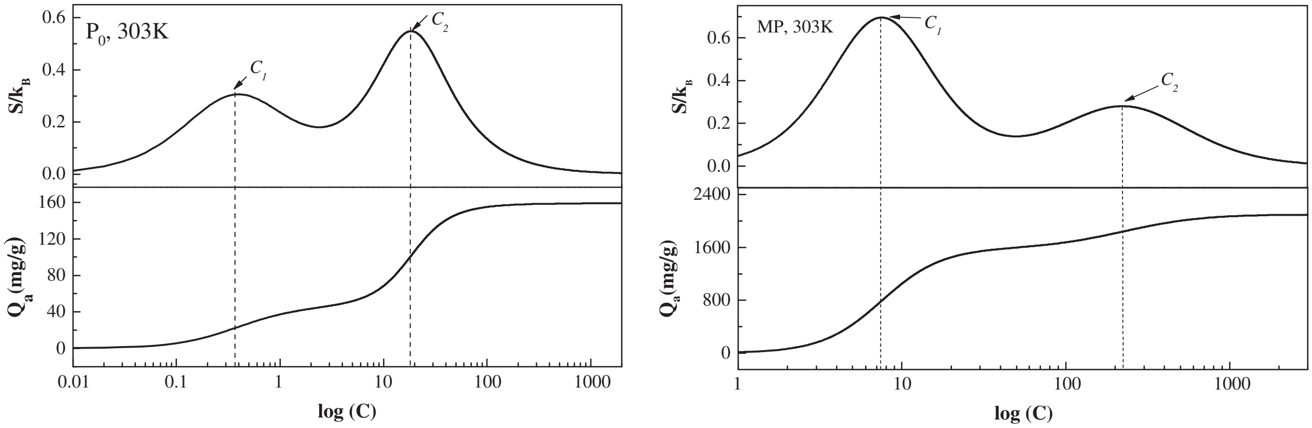

Fig. 5. Illustration of the behaviour of the entropy adsorbed quantity.

adsorption while the first layer is still incomplete. After this minimum, a new disorder appears when the other layers begin to be filled. This disorder decreases (for $C > C_2$) to reach a value toward zero when the saturation is reached.

It can also be seen that, the adsorption entropy of the first monolayer is small compared to the one into the second layer (Fig. 5(a)). However, the entropy of the first layer is higher compared to the one of the second layer, which was the case of the MP (Fig. 5(b)). These behaviours of entropy could be explained by the fact that the adsorption process occurs according two different mechanisms. Indeed, adsorption takes place by the van der Waals or hydrogen bonding in the case of P_0, while adsorption of BB41 onto MP is mainly based on ion exchange mechanism. In addition, it was found that the number of adsorbed layers in the case of P_0 is situated between 2 and 3. This explains what the disorder is high in the next layers than the first one. In the contrary, for MP, is situated between 1 and 2 indicating that the disorder is more important at the first layer.

Temperature and entropy are closely connected. While entropy is a measurement of the amount of atomic disorder contained in a body, temperature describes how strong the atomic agitation that means the intensity of random particle motion is. Fig. 6 depicts the evolution of entropy vs. the dye concentration at different temperatures. It can be noted that in the case of the raw *Posidoni*a, P_0, the entropy of the process is slightly decreased with the temperature. However, the entropy of the adsorption of BB41 on MP was increased with the rise in temperature. This contrast entropy behaviour between the two forms of *Posidonia* could be explained from the different microscopic structures between P_0 and MP, as well as the linkage modes of adsorbed dye on P_0 and MP. It means that with the temperature the ion exchange has taken place resulted in creation of the steric hindrances [57] which is reflected in the increased values for entropy of the system.

It can also be noted that in the case of the raw and modified *Posidoni*a, at 353 K, the curves have one envelope (Fig. 6). This means that the first and the next layers are filled simultaneously at high temperature unlike the filling at low temperature and this is probably due to the thermal collisions.

The evolution of the Helmholtz free energy of BB41 dye onto P_0 and MP is presented in Fig. 7. The negative values of the free energy are indicative of an exothermic process. From Fig. 7, carboxymethylated *Posidonia* shows a higher energy for all temperatures than raw *Posidonia*, which implies that modified *Posidonia* has a stronger affinity for molecules dye in aqueous solution than P_0. This is in agreement with the result of adsorbing capacity. This result is also in accordance with the proposed mechanism. Indeed, adsorption takes place by the van der Waals or hydrogen bonding in the case of P_0, while adsorption of BB41 onto MP is mainly based on ion exchange mechanism in addition to van der Waals and hydrogen bonding.

As shown in Fig. 7 Helmholtz free energy of adsorption steadily increased with an increase in the temperature expected at 80℃, suggesting the occurrence of lateral interactions between adsorbate molecules on the adsorbent surface [58]. Furthermore, the Helmholtz free energy is very high at low coverage and decreases sharply with an increase in surface coverage. It has been suggested that the high (F) values at low surface coverage are due to the existence of highly active sites on the adsorbent surface. In addition, at low concentration, adsorbate and adsorbent display mainly their direct interaction. Therefore, the

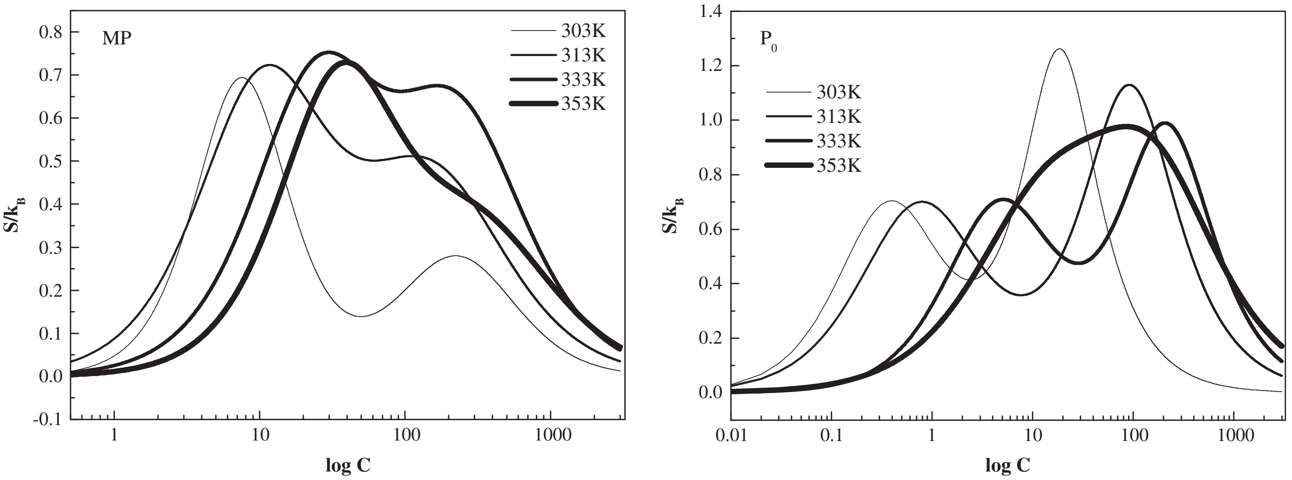

Fig. 6. Evolution of entropy of BB41 dye onto P_0 and MP at different temperatures.

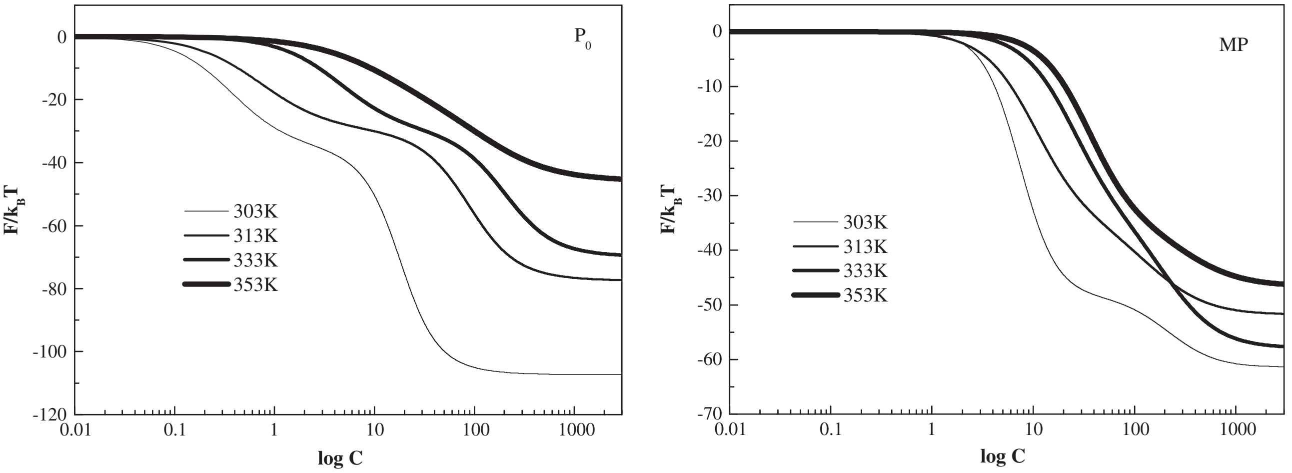

Fig. 7. Evolution of the Helmholtz free energy of BB41 dye onto P_0 and MP at different temperatures.

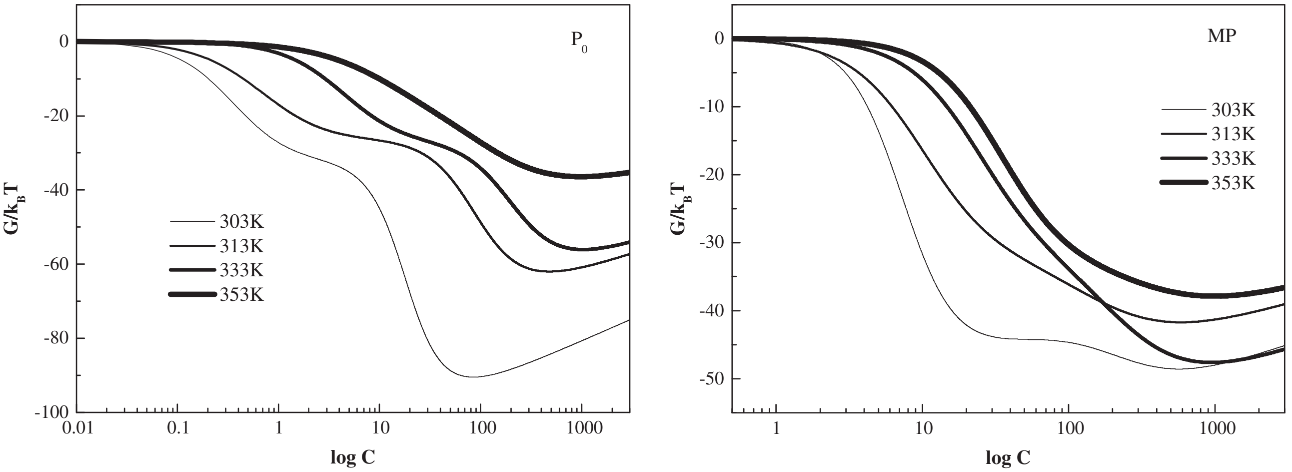

Fig. 8. Evolution of the Gibbs free enthalpy of BB41 dye onto P_0 and MP at different.

adsorbent–adsorbate interaction takes place initially at lower surface coverage resulting in high heats of adsorption. Then, increasing in the surface coverage gives rise to lower heats of the adsorption [59]. Continuous variations of the heat of adsorption with coverage have been reported by several workers as due to the heterogeneous nature of surfaces [60].

In order to describe the thermodynamic behaviour of BB41 sorption onto P_0 and MP from aqueous solution, Gibbs free enthalpy is evaluated. The Gibbs free enthalpy of adsorption indicates a favourable adsorption process for the adsorbent/adsorbate system. As can be seen from Fig. 8, variations of the adsorption free enthalpy with temperature as well as with concentration are always small. This confirms the physical character of the adsorption process and also verifies a compensation effect of the entropic contribution at low adsorption levels. The negative Gibbs free enthalpy values are as expected because the solute tends to be more concentrated on the adsorbent than in bulk solution. The increasing in g values with the rise in temperature shows an increase in feasibility of sorption at higher temperature. The adsorption free enthalpy for MP is always lower than that P_0, which manifests that dye undergo preferential adsorption on MP. This result confirms well with those obtained with configurational entropy and Helmholtz free energy.

5. Conclusion

The present study shows a theoretical model with thermodynamic study to describe the adsorption process at the molecular level. The finite multilayer with multisite occupancy model was established using the grand canonical partition function in statistical physics that can be adapted for successful dye adsorption modelling. Then, this simpler model is developed further to obtain thermodynamic expressions of configurational entropy, Gibbs free enthalpy and Helmholtz free energy and therefore to reinforce the interpretations of the adsorption systems.

Based on the thermodynamic data, it can be concluded that the various behaviours of thermodynamic parameters is due to the different microscopic structures of adsorbents and the different adsorption mechanisms. Indeed, adsorption takes place by van der Waals or hydrogen bonding in the case of raw material, P_0, while adsorption of BB41 onto modified one, MP, is mainly based on ion exchange mechanism.

We showed that the many of the same conclusion regarding the evolution of the various thermodynamics parameters can be summarized as follows: (1) The evolution of the entropy during the adsorption process informs us about randomness at the solid surface. Indeed, the positive change in the entropy indicates the increase in disorder while the negative change conveys the reduction of degrees for freedom for adsorbed dye. (2) The negative values of Helmholtz free energy are indicative of exothermic process. In addition, modified *Posidonia* shows a higher Helmholtz free energy than raw *Posidonia* indicating that carboxmethylated *Posidonia* has a strong affinity regarding BB41 dye. (3) Negative values of Gibbs free enthalpy indicate the spontaneous nature of adsorption and it becomes more or less difficult near the saturation. It was also deduced that the adsorption of BB41 onto modified *Posidonia* is more spontaneous that on the raw *Posidonia.*

Nomenclature

C — concentration of adsorbed molecules at equilibrium (mg/L)
C_1 — half-saturation concentration of a monolayer (mg/L)
C_2 — half-saturation concentration of global isotherm (mg/L)
C_s — concentration of solubility (mg/L)
D — adsorbed molecule (s)
F — energy of Helmholtz (kJ/mol)
G — enthalpy of Gibbs (kJ/mol)
J — grand potential (kJ/mol)
h — Planck's constant (6.626×10^{-34} m^2 kg/s)
k_B — Boltzmann's constant (1.380×10^{-23} m^2 kg/s K)
m — mass of an adsorbed molecule (mg)
N — number of adsorbate molecules
n — number of adsorbed molecule (s) per site S
N_m — receptor site densities (mg/g)
N_i — occupation number in ε_i level
N_o — average occupation number of receptor sites N_m
N_ℓ — average number of the adsorbed layers
Q_a — adsorbed quantity (mg/g)
R — ideal gas constant (8.314 J/K mol)
R^2 — correlation coefficient
S — configurational entropy
T — temperature (K)
Z_{gc} — grand canonical partition function
z_{gtr} — partition function of translation per unit volume
μ — chemical potential of a molecule assimilated for an ideal gas (kJ/mol)
ε — adsorption site energy (kJ/mol)
ε_i — adsorption energy of the receptor site i (kJ/mol)
ε_{N_ℓ} — adsorption energy level of each adsorbed layer (kJ)
ΔE_1^a — adsorption energy at the first layer (kJ/mol)
ΔE_2^a — adsorption energy at the next layers (kJ/mol)

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