

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

**Experimental and theoretical studies of adsorption of ibuprofen
on a raw and two chemically modified activated carbons: new
physicochemical interpretations**

Lotfi Sellaoui¹, Hanen Guedidi², SarraWjihi¹, Laurence Reinert², Salah Knani¹,
Laurent Duclaux², Abdelmottaleb Ben Lamine^{1*}

(1) Unité de Recherche de Physique Quantique, UR 11 ES 54, Faculté des Sciences de
Monastir, Tunisie.

(2) Univ. Savoie Mont Blanc, LCME, F-73000 Chambéry, France.

* Correspondence to be sent to: Ben Lamine Abdelmottaleb, Faculty of Sciences of Monastir, 5019
Monastir, TUNISIA. Email: abdelmottaleb.benlamine@gmail.com

Abstract

The knowledge of the ibuprofen (IBP) adsorption isotherms is important to understand and to improve its depollution process. In this work, the double layer model with two energies was applied to simulate the adsorption isotherms of ibuprofen on a raw activated and two chemically modified granular activated carbons, obtained experimentally at pH=7 and at different temperatures (298, 313 and 323 K). The chemically modified samples were obtained by treatment at 700 °C under nitrogen flow and ultrasonic treatment in H₂O₂ solution of the raw granulated activated carbon. The establishment of the model is based on statistical physics approach, and especially on the grand canonical ensemble. The double layer model with two energies for each layer was found to be the best model to describe the adsorption process of ibuprofen. Using this model, the different adsorption isotherms of ibuprofen were described sterically and energetically through these parameters. The different parameters were interpreted as function of temperature. In addition to this, the entropy, free enthalpy and the internal energy governing the adsorption process were calculated and interpreted.

Key words: Adsorption, ibuprofen, activated carbon, Adsorption energy, thermodynamic functions.

1- Introduction

Concern and awareness of the problems related to water pollution due to emerging contaminants are of growing interest in the industrial societies [1,2] and in the scientific community. Pharmaceuticals represent an overgrowing fraction of trace emerging contaminants in urban aquatic environments due to their worldwide consumption. Although concentrations are usually much lower (less than $\mu\text{g/L}$) than that of the therapeutic doses, they are continually discharged into the environment. So the levels remain quite constant, raising considerable toxicological concerns to human health and aquatic ecosystems, particularly when present as components of complex mixtures [3,4].

Most of them are only poorly removed and/or degraded by conventional biological treatment, used in wastewater treatment plants [5-9]. One of the possibilities for removing these molecules is the adsorption on activated carbon. Recently, several works have studied the removal of ibuprofen (IBP) by using activated carbons [10,11]. The determination of adsorption isotherms plays an important role to understand the adsorption process of IBP on activated carbons. According to the profiles of the different adsorption isotherms, the equilibrium studies are normally analyzed and interpreted by the Langmuir, Freundlich and Redlich-Peterson models. These models are adequate to obtain the adsorption energy with an empirical manner [23]. However, most of these models do not provide any indication about the adsorption mechanism and their isotherm equations have no physical significance or relationship with the physico-chemical parameters involved in the adsorption process.

In the present work, a statistical physics approach was employed to study the adsorption of IBP on a raw and two chemically modified activated carbons, in order to obtain new physicochemical interpretations at a molecular level. The main objective of this work was to simulate and interpret the different adsorption isotherms of IBP using the statistical physics approach. Steric and energetic parameters were deduced such as the numbers of molecules per

site, the receptor sites density, and the adsorption layer energies. The different parameters were determined by fitting the experimental data and interpreted at different temperatures. By application of this statistical physics model, three thermodynamic functions were calculated and interpreted; i.e. entropy, free enthalpy and internal energy, to characterize macroscopically the adsorption process.

2-Experimental methods

2-1 Ibuprofen properties

2-[4-(2-Methylpropyl) phenyl]propanoic acid, also named ibuprofen (IBP), was purchased from Sigma–Aldrich (>98% purity). The atomic positions of IBP were determined by molecular modelling using chemsketch 3D viewer. The dimensions of IBP included in a parallelepiped were obtained by adding the Van der Waals radius value (0.1 nm) to the hydrogen atoms at extreme distance. Important physicochemical properties of the IBP molecule are reported in Table 1.

2-2 Adsorption isotherms

The adsorption isotherms are defined by the relation between the concentration of adsorbate and its degree of accumulation on the adsorbent surface. In this work, the different adsorption isotherms of IBP were determined on three activated carbons. They were a raw granular activated carbon (Sigma-Aldrich, ref.292591, 4-14 mesh) referred by AC, an AC sample oxidized by ultrasonic irradiation in 35 % H_2O_2 named AC[H_2O_2]US and an activated carbon sample heat-treated at 973 K under a nitrogen flow (for 1 hour) named AC(700N₂). The characterization of their surface chemistries and porosities, and the preparation of AC[H_2O_2]US and AC(700N₂), were described in details in reference [12]. For the investigation of the different adsorption isotherms, the IBP solutions were prepared from UHQ water (Ultra High Quality, 18.2 M Ω purity) containing 10 vol % of methanol in order to increase the solubility. The IBP adsorption isotherms on the three activated carbons were

determined at three different temperatures: 298, 313 and 323 K and at pH 7. Activated carbons (10 mg) were added to the IBP solutions (30 mL) of varying concentrations (5–100 mg L⁻¹) and stirred for 5 days. The IBP concentrations were determined by UV–visible spectrometry (Varian, Cary50) at the maximum absorbance observed at 220 nm. The adsorbed amount of the IBP on activated carbon was calculated using the following mass balance equation:

$$Q_a = \frac{(C_i - C) * V}{m_{AC}} \quad (1)$$

Where V is the solution volume (L), C_i and C are respectively the initial and equilibrium concentrations of IBP (mg/L) and m_{AC} is the mass of the activated carbon (mg).

3- Different models and partition functions

To understand the adsorption process, the adsorption isotherms should be well fitted with an appropriate model chosen among many possible models. Four statistical physics models were selected and discussed: the homogenous monolayer with one single energy (Model 1), the homogenous double layer model with two layer energies (Model 2), the homogenous multilayer model with saturation having two layer energies (Model 3) and the Langmuir model (Model 4). All these models were established using the grand canonical ensemble in statistical physics and assuming different working hypotheses. The expressions of the partition functions of one receptor site are summarized for each studied model in Table 2.

For the monolayer model with one constant (independent of surface coverage) adsorption energy, it was assumed that the IBP molecules are adsorbed with one energy and that a single layer is formed. This model represents the general case of the Hill model and the Langmuir model. Indeed, for the Langmuir model, it is known that a receptor site may be empty or occupied by one molecule, but for the monolayer model with single energy, the receptor site

can be empty or occupied by one or more molecules (Hill model). The double layer model with two energies was selected to fit the different adsorption isotherms as the molecules adsorbed on activated carbon can form two layers.

The assumptions of this model are the same as the general assumptions of the other models; namely, the number of molecules per site are taken to be noticed by n (but which is repeated at the second layer, so it will be $2n$ adsorbed molecules per surface site) and the density of sites are also noticed N_M .

The multilayer model with saturation was also selected assuming that many layers were formed on the activated carbon. For this model, it was supposed that the molecules of the first layer were adsorbed with $(-\varepsilon_1)$ energy and the molecules of the next layers (N_2 layers) were adsorbed with $(-\varepsilon_2)$ energy. We should mention here that for the previous model N_2 took the value unity.

4- Formulation of the adequate model and simulation

The Microcal Origin Lab software (OriginLab, Northampton, MA) was used to fit the different adsorption isotherms of IBP on AC, AC[H₂O₂]US and AC(700N₂) by the three described models. The mathematical fitting method was based on the Levenberg-Marquardt iterating algorithm using a multivariable non-linear regression. The fitting criterion in the present work was the well-known correlation coefficient R^2 and the residual root mean square error (*RMSE*) also called the estimated standard error of the regression. The correlation coefficient R^2 is given by [20]:

$$R^2 = 1 - \left[\frac{\sum_i^m (Q_{i,\text{exp}} - \bar{Q}_{i,\text{exp}})^2 - \sum_i^m (Q_{i,\text{exp}} - Q_{i,\text{model}})^2}{\sum_i^m (Q_{i,\text{exp}} - \bar{Q}_{i,\text{exp}})^2} \right] \times \left[\frac{n_p - 1}{n_p - p} \right] \quad (2)$$

where $Q_{i,\text{model}}$ is the i -th value of Q by the model fitted, $Q_{i,\text{exp}}$ is the i -th value of Q measured experimentally, \bar{Q}_{exp} is the average value of Q experimentally measured, n_p is the number of experiments performed and p is the number of parameters.

For a p number of adjustable parameters, the estimated standard error is given as:

$$RMSE = \sqrt{\frac{RSS}{m' - p}}$$

where RSS is the residual sum of squares ($RSS = \sum_{j=1}^m (Q_{j,\text{cal}} - Q_{j,\text{exp}})^2$, $Q_{j,\text{cal}}$ and $Q_{j,\text{exp}}$ are the calculated and experimental values of the adsorbed uptake respectively) and m' is the number of experimental data. The different values of these coefficients are reported in Table 3.

According to this table, the double layer model with two energies presents the highest R^2 values (from 0.978 to 0.996) and the lowest $RMSE$ values. So this model would provide the best description of the adsorption process of IBP on the activated carbons. The fitting of the adsorption isotherms using this model are reported in Figure 1.

In Table 4, the different values of the adjusted parameters are reported.

The double layer model with two energies was established using a statistical physics approach. As an approximation, the mutual interactions between the adsorbate molecules were neglected, and the adsorbate was considered as an ideal gas [16]. The model was established using the grand canonical partition function describing the microscopic states of a system in which this system is placed [17].

It was assumed that the first adsorbed layer had an adsorption energy ($-\varepsilon_1$) and the second one had a different adsorption energy ($-\varepsilon_2$) lower than the first one as the molecules were supposed to be firstly adsorbed directly on the activated carbon having a higher adsorption energy. The partition function in this case of one receptor site was written [14]:

$$z_{gc} = \sum_{N_i} e^{-\beta(-\varepsilon_i - \mu)N_i} = 1 + e^{\beta(\varepsilon_1 + \mu)} + e^{\beta(\varepsilon_1 + \varepsilon_2 + 2\mu)} \quad (3)$$

where ($-\varepsilon_i$) is the receptor site adsorption energy, μ is the chemical potential of the formed complex, N_i is the receptor site occupation state and β is defined as $1/k_B T$ where k_B is the Boltzmann's constant and T the absolute temperature.

A variable number of IBP molecules were considered to be adsorbed on N_M receptor sites located on a unit mass of the adsorbent.

The total grand canonical partition function related to N_M receptor sites per surface unit mass, assumed to be identical and independent, is written then:

$$Z_{gc} = (z_{gc})^{N_M} = (1 + e^{\beta(\varepsilon_1 + \mu)} + e^{\beta(\varepsilon_1 + \varepsilon_2 + 2\mu)})^{N_M} \quad (4)$$

The average site occupation number can be written as:

$$N_o = k_B T \frac{\partial \ln Z_{gc}}{\partial \mu} = N_M k_B T \frac{\partial \ln z_{gc}}{\partial \mu} \quad (5)$$

The total number of the adsorbed molecules is [14]:

$$Q_a = nmN_o = nmN_M \frac{\left(\frac{c}{c_1}\right)^n + 2\left(\frac{c}{c_2}\right)^{2n}}{1 + \left(\frac{c}{c_1}\right)^n + \left(\frac{c}{c_2}\right)^{2n}} \quad (6)$$

The analytical expression of this model contains four physicochemical parameters that can be deduced by fitting the experimental data with the analytical expression (Eq 6): the number of molecules per site n , the density of receptor sites N_M and the c_1 and c_2 concentrations at half saturation for the first and the second layer respectively. m is the adsorbed molecule mass.

5- Results and discussion

The adsorption of IBP on AC, AC[H₂O₂]US and AC(700N₂) at different temperatures was interpreted through the fitted values of the different parameters in terms of steric and energetic points of view. The steric parameters were n , N_M , $Q_{asat}=nN_MN_i$, and N_i in Q_{asat} (Table 3).

5-1 Number of molecules per site

The n parameter, as a stoichiometric coefficient, represents the number of adsorbate molecules of IBP per site. It can be smaller or greater than 1. A n value greater than 1, represents the number of docked molecules per site, according to a multimolecular adsorption mechanism [15]. A n value smaller than 1, represents the fraction of molecule per site if a multi-docking adsorption mechanism may be assumed [15]. In Figure 2, a schematic illustration of the assumed docking arrangement of IBP is given.

The n parameter is in principle a natural number or a fractional number for one molecule but for the whole system it can be any number while it is an average number which can be greater or smaller than the unity. $1/n$ would represent the docking number of one molecule on several different receptor sites [15]. Figure 3 shows the variation of the number of molecules per site versus temperature for the three studied systems: IBP-AC, IBP-AC[H₂O₂]US and IBP-AC(700N₂).

Two cases of IBP adsorption occur: multimolecular adsorption and multi-docking adsorption (Figures 2a, 2b and 2c).

For IBP adsorbed on AC(700N₂) at 298 K, $n=1.25$. The percentage of molecules which are either docked by one site (x) or two sites ($1-x$) is between 1 and 2 and satisfies the following equation: $x.1+(1-x).2=1.25$. This gives 75% of the adsorbed molecules singly docked to one site (Figure 2a), and 25 % doubly docked (Figure 2b) on one site. For AC(700N₂) the number of molecules per site varies from 1.25 to 2.12. The n values might suggest that the IBP molecules would be in a form of monomer ($n=1$), or dimer ($n=2$) or even a polymer but not multi-docked in the adsorbate solution before and during the adsorption on the receptor sites of the AC(700N₂). The number of molecules per site for the adsorption on AC and AC[H₂O₂]US does not exceed 1.5 but it can be also smaller than 1. In this case the IBP molecules can be either multimolecular or multi-docked. Thus the IBP molecule would be multi-docked and parallel to the carbon surface of AC or AC[H₂O₂]US at low temperature. The number of molecules per site follows the trend: n (IBP-AC(700N₂)) > n (IBP- (AC)) > n (IBP-AC[H₂O₂]US) at different temperatures. This can be related to the higher affinity of the functionalized receptor sites in AC(700N₂) than in AC and AC[H₂O₂]US. The thermal treatment under nitrogen would cause this difference by increasing the hydrophobicity of the surface through removal of the oxygenated group.

Moreover, the basic content groups in AC(700N₂) is equal to 1.14 meq/g [12] and higher than in AC (0.99 meq/g) [12] or AC[H₂O₂]US (0.62 meq/g) [12].

For the three studied systems, the number of molecules per site was found to increase together with the temperature. The aggregation of the ibuprofen in solution could be an endothermic reaction since it is thermally activated in agreement with the evolution of the n values with temperature.

5-2 Density of receptor sites

Figure 4 shows the evolution of the effectively occupied receptorsites (N_M) as a function of the temperature. The increase in temperature has led to the decrease in the receptor sites

density for the three studied systems and this is probably due to athermal effect. The N_M values varies as follows: $N_M(\text{IBP-AC}[\text{H}_2\text{O}_2]\text{US}) > N_M(\text{IBP-AC}) > N_M(\text{IBP-AC}(700\text{N}_2))$. The N_M parameter for the IBP-AC(700N₂) is lower than for the two other systems. This is related to the increase in the number of molecules per sites together with temperature and the tendency to aggregate (dimerisation and trimerisation: 1.25 to 2.12). This aggregation could hinder the accessibility of the other aggregates to some adsorption sites.

5-3 Adsorbed quantity at saturation

According to its analytical expression, the adsorbed quantity at saturation, $Q_{\text{asat}} = 2nN_M$ is a steric parameter which depends on the number of molecules per site and the density of receptor sites and represents the ability of the surface of activated carbon to retain the IBP molecules. Figure 5 shows a decrease in Q_{asat} together with temperature.

The increase in temperature could cause the rise of the thermal collisions and then the molecules would not be easily fixed on the activated carbon as already observed by the N_M decrease at high temperature.

5-4 Adsorption energies

The expressions of the adsorption energies are given by [15]:

$$-\varepsilon_1 = -k_B T \ln\left(\frac{c_s}{c_1}\right) \quad (7)$$

$$-\varepsilon_2 = -k_B T \ln\left(\frac{c_s}{c_2}\right) \quad (8)$$

where c_1 and c_2 represent the concentration at half saturation of the first and the second layer respectively, c_s is the solubility of the adsorbate in aqueous solution. The first adsorption energy ($-\varepsilon_1$) is related to the interaction between the IBP molecule and the adsorbent surface whereas the second adsorption energy ($-\varepsilon_2$) represents the IBP-IBP interaction. For physical

adsorption such as hydrogen bonding energies values are lower than 30 kJ/mol [21]. The physical adsorption energies due to the van der Waals forces are usually in the range 4-10 kJ/mol, hydrophobic bond forces energies about 5 kJ /mol, coordination exchange energies about 40 kJ/mol and dipole bond forces energies 2–29 kJ /mol [22]. On the other hand, the chemical bond forces energies are usually >80 kJ /mol [22]. In our work, the different values of the adsorption energies were below to 20 kJ /mol which is consistent with both the hydrogen bond and hydrophobic interaction. According to the Figure 6, the first energy was found higher than the second because the adsorbate-adsorbate interactions were lower than the adsorbate-adsorbent interaction. The adsorption energy was found to decrease together with the temperature. This evolution is probably related to the decrease in the adsorbed quantity as heating in agreement with the exothermic adsorption of IBP at this pH.

6-Thermodynamic functions

The grand canonical ensemble in statistical physics correspond allows to calculate the potential thermodynamic functions characterizing the adsorption process of IBP and giving a macroscopic description of it. The entropy, free enthalpy and internal energy were calculated.

6-1 Entropy

The entropy gives information about the order and disorder at the adsorbent surface during the adsorption. The expression of the entropy was established from the definition of the grand potential J using the grand canonical partition function Z_{gc} [18]:

$$J = -k_B T \ln Z_{gc} = E_a - \mu_a Q_a - TS_a \quad (9)$$

$$J = -\frac{\partial}{\partial \beta} \ln Z_{gc} - T.S_a \quad (10)$$

By equalizing these two expressions, it can be obtained:

$$TS_a = -\frac{\partial}{\partial \beta} \ln Z_{gc} + k_B T \ln Z_{gc} \quad (11)$$

From which the expression of the entropy can be derived:

$$S_a / k_B = -\frac{\partial}{\partial \beta} \ln Z_{gc} + \ln Z_{gc} \quad (12)$$

Finally, the expression of the entropy is given by:

$$\frac{S_a}{k_B} = N_M \left[\ln \left(1 + \left(\frac{c}{c_1} \right)^n + \left(\frac{c}{c_2} \right)^{2n} \right) - \frac{\left(\frac{c}{c_1} \right)^n \ln \left(\frac{c}{c_1} \right)^n + \left(\frac{c}{c_2} \right)^{2n} \ln \left(\frac{c}{c_2} \right)^{2n}}{1 + \left(\frac{c}{c_1} \right)^n + \left(\frac{c}{c_2} \right)^{2n}} \right] \quad (13)$$

From Figure 7, the entropy presents two maxima at two particular concentrations. Indeed, the entropy increases with concentration at low concentrations. This means that the disorder at the adsorbent surface increases, which could be understood by the fact that the adsorbed molecule of IBP has many possibilities to be docked on the empty sites at low concentrations. The entropy reaches its first maximum value at half saturation of the first adsorbed layer since the IBP molecule has the maximum possibilities to be docked on the empty receptor sites of the first type. After that, the entropy decreases since the possibilities of finding an empty first type site decreases more and more when the saturation of the first adsorbed layer is almost reached. The observed minimum value of the entropy does not reach zero, because before the first type is totally saturated, the second one starts to be filled and the disorder increases again. When the second type reaches saturation, the entropy decreases and goes towards zero. All the evolutions of the entropy for the three studied systems were found similar since the mobility of IBP molecules is not influenced on the adsorbent surface by the different

treatments. The decreases in entropy can be also explained by the free space reduction in the cavities and the limitation of the freedom degree of molecules as reported by Zhou et al [24]. It suggests that the model that is used induces a theoretical filling of the pores that is likely to be homogeneous [24].

6-2 Free enthalpy

The free enthalpy defines if an adsorption process of a given system is spontaneous or not [16,24]. The evolution of this potential function was investigated by calculating its expression according to the double layer model with two energies. The free enthalpy is given by [19]:

$$G = \mu_a Q_a \quad (14)$$

Where μ_a is the chemical potential of the receptor site, and Q_a is the adsorbed amount. The chemical potential is given by [12]:

$$\mu_a = k_B T \ln\left(\frac{c}{z_v}\right) \quad (15)$$

where z_v represents the translation partition function per unit volume.

The free enthalpy has the following expression:

$$G = k_B T \ln\left(\frac{c}{z_v}\right) \left[n N_M \frac{\left(\frac{c}{c_1}\right)^n + 2\left(\frac{c}{c_2}\right)^{2n}}{1 + \left(\frac{c}{c_1}\right)^n + \left(\frac{c}{c_2}\right)^{2n}} \right] \quad (16)$$

Figure 8 depicts the evolution of the free enthalpy against the free adsorbate concentration in solution for the different studied systems. All the values of the Gibbs free adsorption enthalpy are negative, as the adsorption reaction is spontaneous. The decreasing in the free enthalpy with increasing temperature shows a decrease in feasibility of adsorption at higher temperature. The adsorbed uptakes of the IBP on the three activated carbons are quite close. Thus, the values of Gibbs energies have quite the same magnitude whatever the activated carbon type.

6-3 Internal energy

The evolution of the internal energy was calculated from the following equation [19]:

$$\frac{E_{\text{int}}}{k_B} = -\frac{\partial \ln(Z_{gc})}{\partial \beta} + \frac{\mu}{\beta} \left(\frac{\partial \ln(Z_{gc})}{\partial \mu} \right) \quad (17)$$

Finally, the expression of the internal energy is given by:

$$E_{\text{int}} = -N_M \left\{ \frac{\left[\left(\frac{1}{\beta} \right) \left(\frac{c}{c_1} \right)^n \ln \left(\frac{c}{c_1} \right)^n + 2 \left(\frac{c}{c_2} \right)^{2n} \ln \left(\frac{c}{c_2} \right)^{2n} \right]}{1 + \left(\frac{C}{C_1} \right)^n + \left(\frac{c}{c_2} \right)^{2n}} + \mu \frac{\left[\left(\frac{c}{c_1} \right)^n + 2 \left(\frac{c}{c_2} \right)^{2n} \right]}{1 + \left(\frac{C}{C_1} \right)^n + \left(\frac{c}{c_2} \right)^{2n}} \right\} \quad (18)$$

The evolution of this parameter is depicted in Figure 9. The internal energy is negative confirming that the system evolves spontaneously since it releases energy. The internal energy increases in module as the temperature increases and this can be probably related to the increase in thermal collision.

Conclusion

The double layer model with two successive energies established from the grand canonical partition function better reproduces the experimental isotherms, among the proposed models.

According to this model, the different adsorption isotherms of IBP on the three activated carbons were analyzed and interpreted at different temperatures. The study of the effect of the temperature on the number of molecules per site for the IBP- AC(700N₂) system showed that the IBP molecules could be in the form of monomer ($n=1$), or dimer ($n=2$) in the adsorbate solution before and during the adsorption on the receptor sites. The increase in temperature has led to the decrease in the receptor sites density for the three studied systems upon thermal agitation. The temperature dependence of the adsorbed uptake at saturation shows that the low temperature is the best condition to obtain an efficient removal of IBP. The values of the different adsorption energies demonstrate that IBP is physically adsorbed. To characterize the adsorption process, the entropy was calculated according to the chosen model. The molecules of IBP have various possibilities to interact with a receptor site as they are adsorbed in the first layer and therefore the disorder increases at the surface as increasing the concentration. The disorder decreases when the first layer tends towards saturation. Similar behavior was observed for the adsorption in the second layer. The evolutions of the free energy and internal energy show that the adsorption is spontaneous until the saturation is attained.

Nomenclature

IBP: Ibuprofen.

AC: The raw activated carbon.

AC[H₂O₂]US and AC(700N₂): The two chemically modified samples.

n : The number of molecules per site.

N_M : The receptor site density (mg/g).

Q_{asat} : The adsorbed quantity at saturation (mg/g).

$-\varepsilon_1, -\varepsilon_2$: The adsorption energies (kJ).

V : The solution volume (L).

C_i : The initial concentration of IBP (mg/L).

C : The equilibrium concentration of IBP (mg/L).

Q_a : The adsorbed amount of IBP (mg/g).

m_{AC} : The mass of the activated carbon (g).

m : The mass of the adsorbed molecule (mg).

N_2 : Layers number of the multilayer model with saturation.

BET: Brunauer–Emmett–Teller.

$RMSE$: The residual root mean square error.

R^2 : The correlation coefficient.

$Q_{i, model}$: The i -th value of Q by the model fitted.

$Q_{i, exp}$: The i -th value of Q measured experimentally.

Q_{exp} : The average of Q experimentally measured.

n_p : The number of experiments performed.

p : The number of parameters of the fitted model.

RSS : The residual sum of squares.

Q_{jcal} and Q_{jexp} : The calculated and experimental values of adsorbed quantity.

m^{\cdot} : The number of experimental data.

$-\varepsilon_i$: The receptors site adsorption energy (kJ).

μ : The chemical potential of the formed complex (kJ).

μ_a : The chemical potential of the receptor site (kJ).

N_i : The receptor site occupation state.

β : The Boltzmann's factor.

k_B : The Boltzmann's constant ($1.3806488 \cdot 10^{23} J K^{-1}$).

T : The absolute temperature (K).

z_{gc} : The partition function of one receptor site.

Z_{gc} : The total grand canonical partition function.

N_0 : The average site occupation number.

c_1 and c_2 : The concentrations at half saturation for the first and the second layer respectively (mg/L).

c_s : The solubility of IBP in aqueous solution.

S_a : The entropy.

G : The free enthalpy.

z_v : The translation partition function per unit volume.

E_{int} : The internal energy.

References

- [1] M.J. Gómez, M. Petrović, A.R. Fernández-Alba, D. Barceló, Journal of Chromatography A, 2006, 1114, 224–233.

- [2] J. Nriagu, T.A. Ternes, A. Joss, Human Pharmaceuticals, Hormones and Fragrances: The , IWA Publishing, London, 2006.
- [3] A.P. Carvalho, A.S. Mestre, M.A. Andrade, C.O. Ania, Nova Publisher, 2013, 1–60.
- [4] S. M.Richards, C. J.Wilson, D. J.Johnson, D. M.Castle, M.Lam, S. A.Mabury, P. K.Sibley, K.R.Solomon, Journal of Environmental Toxicology and Chemistry , 2004,23 1035–1042.
- [5] A.J. Watkinson, E.J. Murby, S.D. Costanzo, Water Research, 2007, 41, 4164–76.
- [6] M. Clara, B. Strenn, O. Gans, E. Martinez, N. Kreuzinger, H. Kroiss, Water Research, 39 2005, 4797–807.
- [7] T.A. Ternes, M. Meisenheimer, D.Mcdowell, F. Sacher, H.J. Brauch, B. Haist-Gulde, G. Preuss, U. Wilme, N. Zulei-Seibert, Environmental Science and Technology, 36, 2002, 3855–3863.
- [8] B. Kasprzyk. Hordern, R.M. Dinsdale, A.J. Guwy, Water Research, 43 2009, 363–80.
- [9] P.C. Rúa-Gómez, W. Püttmann, , Environmental. Science and Pollution Research, 192012, 689–99.
- [10] A.S. Mestre, J. Pires, J.M.F. Nogueira, A.P. Carvalho, Carbon 45, 2007, 1979–1988.
- [11] S.P. Dubey, A.D. Dwivedi, M. Sillanpää, K. Gopal, Chemical Engineering journal, 165 2010, 537-544.
- [12] H. Guedidi, L. Reinert, J.M. Lévêque, Y. Soneda, N. Bellakhal, L. Duclaux, Carbon, 54 2013, 432-443.
- [13] S. Knani, M. Mathlouthi, A. Ben Lamine, Food Bioprocess, 2007, 183-192.

- [14] M. Khalfaoui, A. Nakhli, Ch. Aguir, A. Omri, M. F. M'henni, A. Ben Lamine. *Environ Science Pollution Research*, **21**, 2014, 3134-3144.
- [15] L. Sellaoui, H. Guedidi, S. Knani, L. Reinert, L. Duclaux, Abdelmottaleb Ben Lamine, *Fluid phase equilibria journal*, 387, 2015, 103-110.
- [16] M. Khalfaoui, A. El Ghali, C. Aguir, Z. Mohamed, M. Hassen, V. Baouab, A. Ben Lamine, *Industrial Crops and Products* 67, 2015, 169-178.
- [17] A. Nakhli, M. Khalfaoui, C. Aguir, M. Bergaoui, Mohamed F. M'henni, A. Ben Lamine. *Separation Science and Technology*, 49, 2014, 2525-2533.
- [18] F. Aouaini, S. Knani, M. Ben Yahia, N. Bahloul, N. Kechaou, A. Ben Lamine, *Drying Technology*, 32, 2014, 1905-1922.
- [19] B. Diu, C. Guthmann, D. Lederer, B. Roulet, (1989).
- [20] D.W. Marquardt, *Journal of the Society for industrial and applied mathematics*, 11, 1963, 431-441.
- [21] M.T. Ward, P.R. Upchurch, *Journal of Agricultural and Food Chemistry*, 13, 1965, 334-338.
- [22] B. von Oepen, W. Kördel, W. Klein, *Chemosphere* 22, 1991, 285-304.
- [23] G.L. Dotto, L.A.A. Pinto, M.A. Hachicha, S. Knani, *Food Chemistry* 171, 2015, 1-7
- [24] X. Zhou, Yi, Honghong, X. Tang, Hua Deng, Haiyan Liu. *Chemical Engineering Journal* 200-202, 2012, 399-404.

Figure 1: Experimental data fitted with the statistical physics model.

Figure 2: Schematic illustration of the assumed docking arrangement of IBP on activated carbon.

Figure 3: Evolution of the number of molecules per site at different temperatures.

Figure 4: Evolution of the density of receptor sites at different temperatures.

Figure 5: Evolution of adsorbed quantity at saturation at different temperatures.

Figure 6: Evolution of the adsorption energies at different temperatures.

Figure 7: Evolution of the entropy versus concentration for the three studied systems.

Figure 8: Evolution of the free enthalpy versus concentration for the three studied systems at three different temperatures.

Figure 9: Evolution of internal energy versus concentration for the three studied systems.

Figure 1

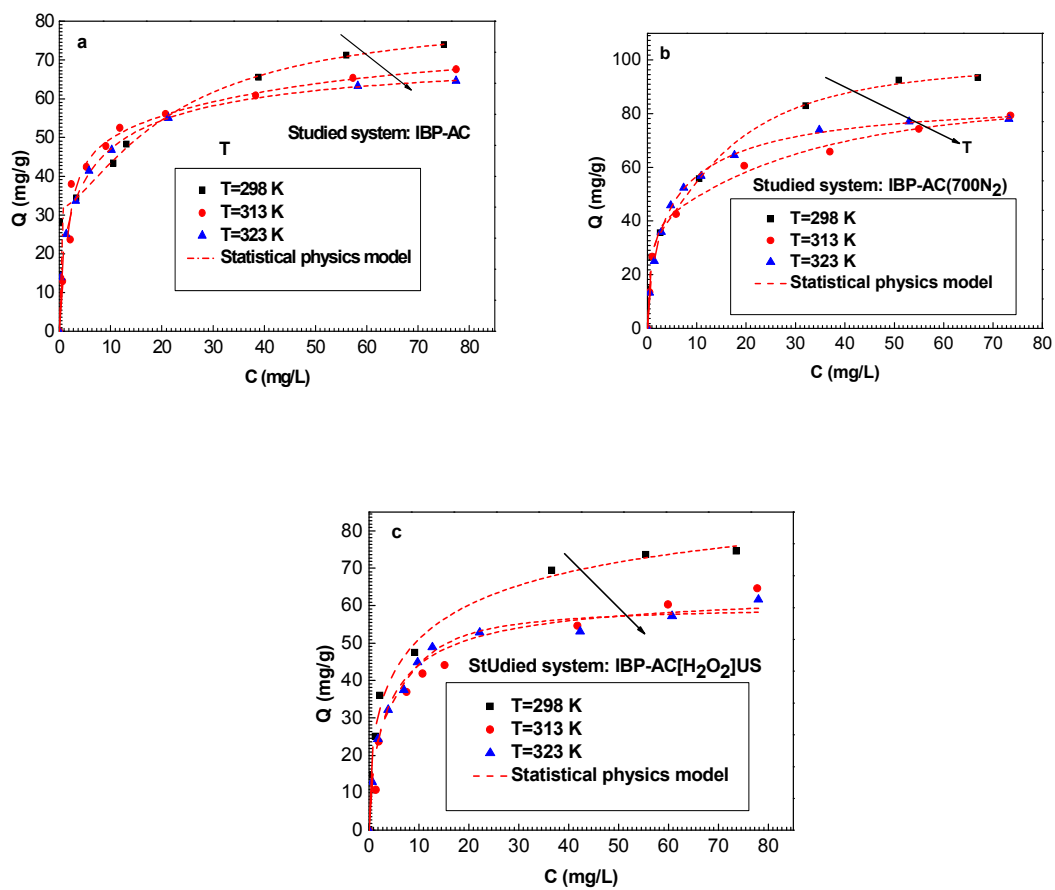


Figure 2

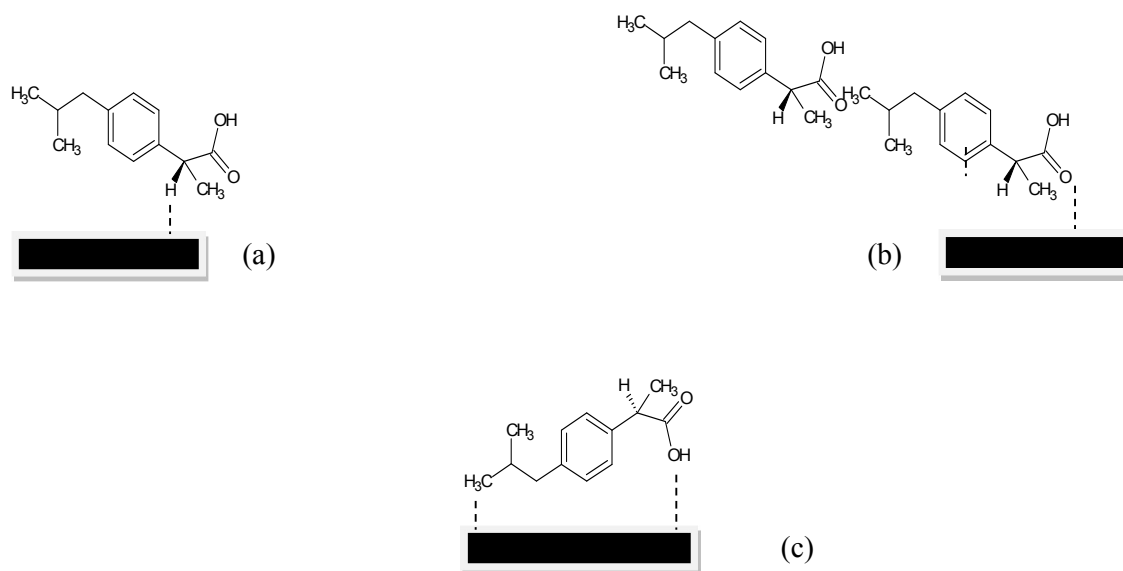


Figure 3

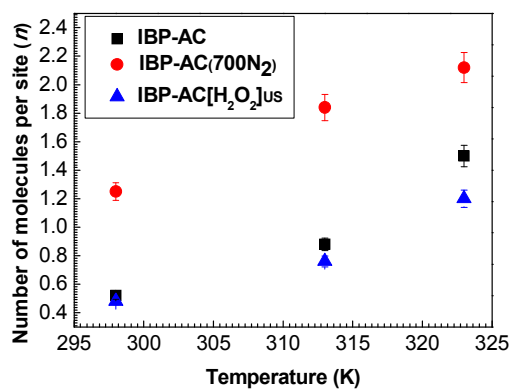


Figure 4

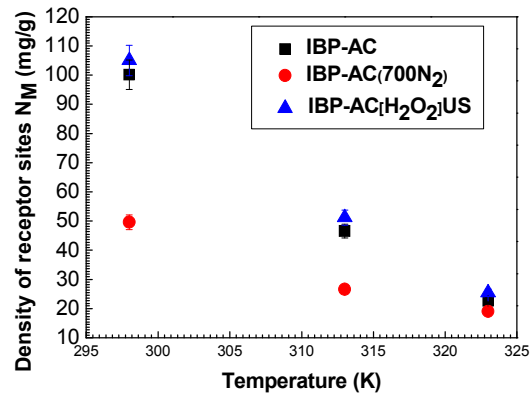


Figure 5

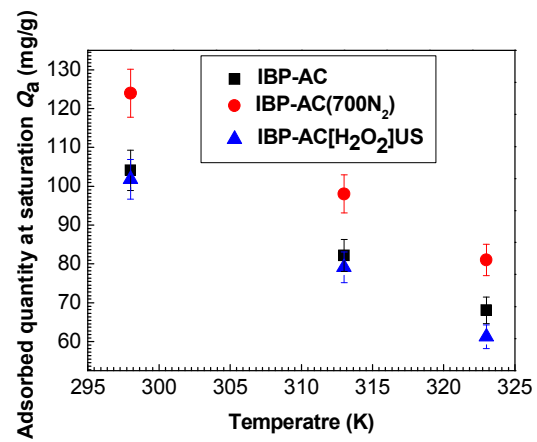


Figure 6

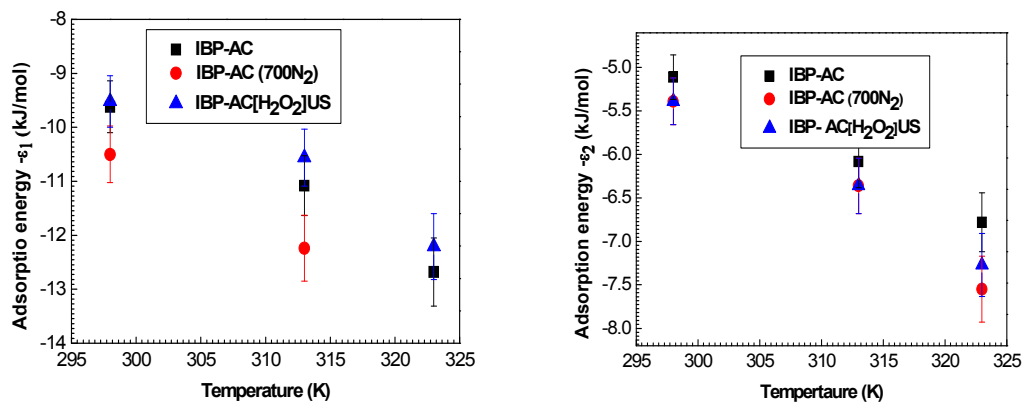


Figure 7

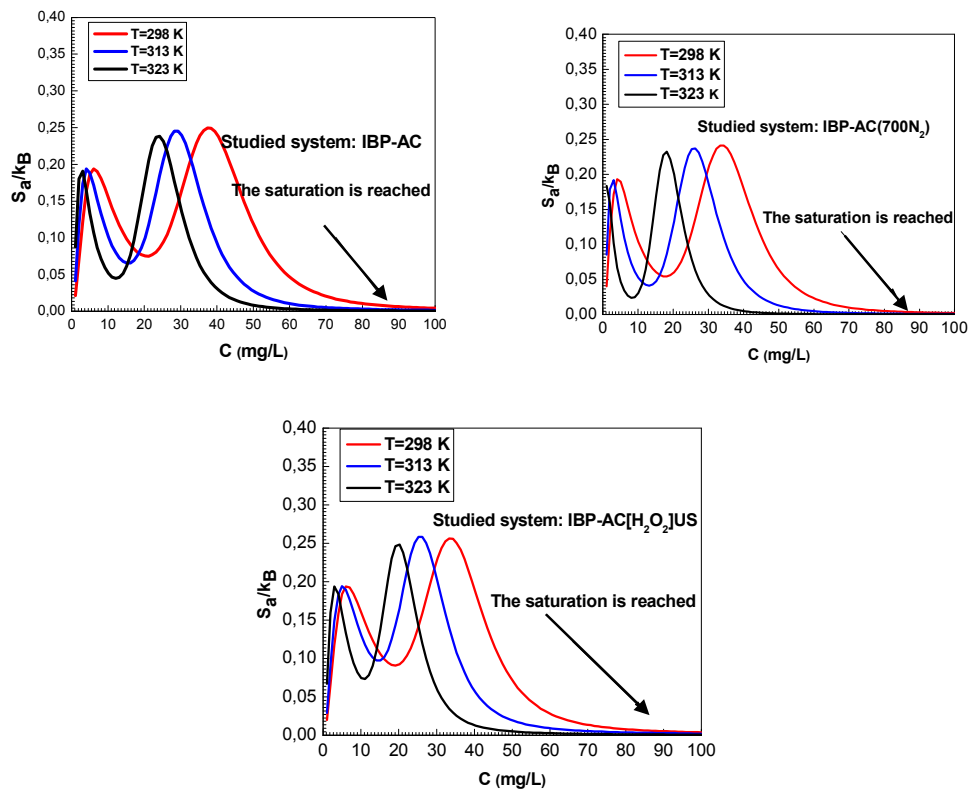


Figure 8

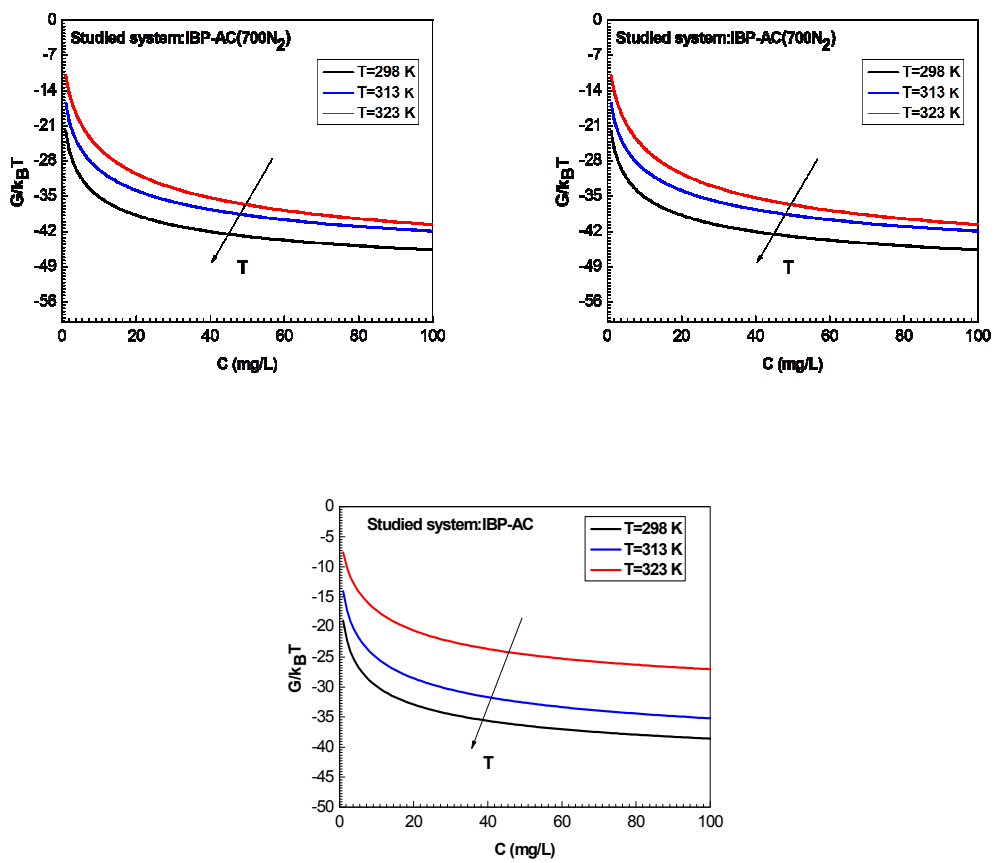


Figure 9

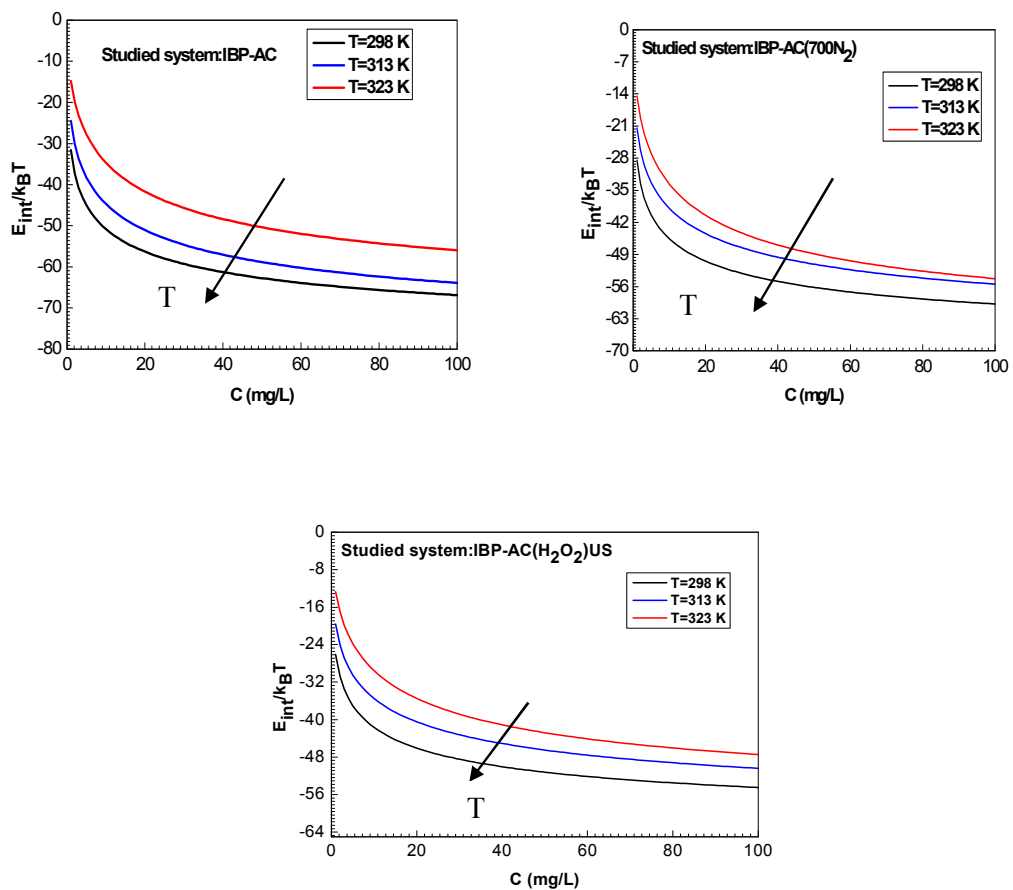


Table 1: Physicochemical properties of IBP molecule.

Table 2: Partition functions of each discussed model.

Table 3: Values of coefficient of determination R^2 and $RMSE$ of each model.

Table 4: Values of the different adjusted parameters according to the double layer model with two layer energies.

Table 1

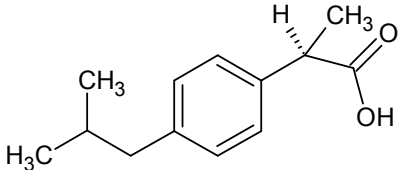
Compound (IBP)	Molecular formula	Molecular weight (g/mol)	pKa	dimensions
	C ₁₃ H ₁₈ O ₂	206.28	4.91	length: 1.36 nm width: 0.74 nm thickness: 0.52 nm

Table 2

Model number	Model names	Partition functions	References
Model 1	monolayer model with one homogenous energy	$z_{gc} = 1 + e^{\beta(\varepsilon + \mu)}$	[13]
Model 2	homogenous double layer model with two layer energies	$z_{gc} = 1 + e^{\beta(\varepsilon_1 + \mu)} + e^{\beta(\varepsilon_1 + \varepsilon_2 + 2\mu)}$	[14]
Model 3	homogenous multilayer model with two layer energies with saturation	$z_{gc} = 1 + e^{\beta(\varepsilon_1 + \mu)} + e^{\beta(\varepsilon_1 + \varepsilon_2 + 2\mu)} \frac{1 - (e^{\beta(\varepsilon_2 + \mu)})^{N_2}}{1 - e^{\beta(\varepsilon_2 + \mu)}}$	[15]
Model 4	Langmuir model	$z_{gc} = 1 + e^{\beta(\varepsilon + \mu)}$	[13]

Table 3

	IBP-AC			IBP-AC[H ₂ O ₂]US			IBP- AC(700N ₂)		
	<i>R</i> ²								
T (K)	286	313	323	286	313	323	286	313	323
M ₁	0.972	0.969	0.971	0.962	0.981	0.977	0.975	0.975	0.970
M ₂	0.978	0.979	0.988	0.984	0.990	0.996	0.988	0.986	0.981
M ₃	0.974	0.979	0.981	0.982	0.984	0.981	0.979	0.985	0.980
M ₄	0.970	0.964	0.970	0.961	0.977	0.973	0.971	0.973	0.969
	<i>RMSE</i>								
M ₁	2.56	2.71	2.55	2.73	2.18	2.55	2.51	2.51	2.48
M ₂	2.10	2.04	1.78	1.98	1.57	1.24	1.75	1.95	1.99
M ₃	2.62	2.22	2.10	2.22	2.17	2.11	2.57	2.59	2.38
M ₄	2.86	2.79	2.58	2.79	2.25	2.88	2.59	2.57	2.94

M: model

Table 4

Studied system	T(K)	n	N_M	$Q_{asat}=nN_MN_i(\text{mg/g})$	$-\varepsilon_1$ (kJ/mol)	$-\varepsilon_2$ (kJ/mol)
IBP-AC	298	0.52	100.11	104.12	-9.62	-5.11
	313	0.88	46.59	82.18	-11.08	-6.08
	323	1.50	22.66	68.05	-12.68	-6.78
IBP- AC(700N ₂)	298	1.25	49.6	124	-10.50	-5.39
	313	1.84	26.63	98	-12.24	-6.36
	323	2.12	19.10	81	-14.65	-7.55
IBP- AC[H ₂ O ₂]US	298	0.48	105.02	101.79	-9.52	-5.39
	313	0.76	51.22	79.11	-10.56	-6.36
	323	1.20	25.41	61.22	-12.21	-7.27

Graphical abstract

