Original Article

Combined statistical physics models and DFT theory to study the adsorption process of paprika dye on TiO₂ for dye sensitized solar cells

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A B S T R A C T

This study reported the combination of advanced statistical physics modeling and density functional theory (DFT) investigation for the interpretation of the adsorption of Paprika dye on TiO₂ surface for dye sensitized solar cells. By using a statistical physics modeling method, an adequate monolayer model with four energies was successfully used to interpret the adsorption process at a macroscopic level. The DFT simulation has been used to study the interaction of the Paprika dye on TiO₂ surface to understand some of the atomistic details that are crucial to the dye/semiconductor interaction. We pay particular attention to the adsorption modes, geometries and energies between the paprika dye and TiO₂. The DFT simulation determined different binding modes which participated in the adsorption of Paprika dye on TiO₂ surface: monodentate coordination via hydrogen atom bond, monodentate coordination via oxygen atom bond and bidentate coordination via two oxygen atoms bond. In particular, calculations showed that the interaction between the paprika dye and TiO₂ is strengthened with the bidentate coordination mode via the two hydroxyl and ether functionalities groups involved in the adsorption process.

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1. Introduction

Since their invention in 1991, the dye-sensitized solar cells (DSSCs) have been extensively studied as an alternative to the silicon-based solar cells, owing to their simple structure, transparency, flexibility, low production cost, and wide range of applications. However, the low efficiency of DSSCs compared to that of silicon-based cells has limited their commercial implementation [1]. Consequently, there is a critical need to improve the efficiency of state-of-the-art DSSCs in order to realize next generation solar cells. DSSCs consist of a TiO₂ electrode adsorbed dye, an electrolyte solution, and a platinum counter electrode. In this kind of cells, the TiO₂ electrode plays a main role in relation to the loading dyes and in separating and transporting electrons [2,3]. In the assembly of DSSCs, the dye plays a key role in absorbing sunlight and converting solar energy to electrical energy with the aid of a semiconductor photoanode [4,5]. In DSSCs cells, the dye adsorbed on TiO₂ nanoparticles is excited by photons of the solar light, transferring electrons to the conduction band of the TiO₂. In order to ensure a high cohesion between the dye and the TiO₂ mesoporous of such hybrid devices, a relatively strong electronic coupling between the excited dye and the semiconductor is needed, which is achieved if the dye is attached directly to the semiconductor surface and

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chemical anchoring groups should be used to link the two sub-units [6]. These groups should chemically bind the molecules and the metal oxide surface to obtain robust devices for further improving the device performance. That makes more stability and increases the performance of the dye sensitized solar cells. Recently, a great deal of attention has been directed towards the titanium dioxide (TiO₂) for useful applications such as photocatalytic behavior [7–9] because of the powerful oxidation and reduction properties that arose as a result of the absorption of photon energy. Moreover, the photocatalytic oxidation of organic contaminants by titanium dioxide (TiO₂) has drawn attention as a promising chemical procedure for environmental removal and particularly the TiO₂ nanoparticles are efficient for the photocatalytic degradation of various organic pollutants in water [7]. In addition, in the catalytic activity, the magnetically recoverable graphene-based nanocomposite material has been found as an efficient heterogeneous composite nanocatalyst [10]. Moreover, the cell performance is mainly dependent on the type of dyes used as a sensitizer [11]. Numerous metal complexes and organic dyes [4,5] have been synthesized and used as sensitizers. Ruthenium-based complexes are considered as good sensitizers for DSSCs because of their intense charge transfer absorption over the entire visible range and highly efficient metal to ligand charge transfer [12,13]. However, the organic dyes have often presented problems, such as complicated synthetic routes and low yields. Nonetheless, the natural dyes have several advantages over rare metal complexes (ruthenium-based complexes) because they can be extracted by simple procedures, they have large absorption coefficients, a very low, a non-toxicity. They are environmentally friendly, easily biodegradable and widely available [14,15]. Among them, the Paprika oleoresin dye (Capsicum annuum L) extracted and produced from the fruits of the genus Capsicum is widely consumed as a vegetable, spice, or food colorant. The species Capsicum annuum L. is used to manufacture a paprika extract for food coloration. Carotenoids, such as capsanthin and capsorubin, are the capsanthin and capsorubin, are the main compounds responsible for the red color. Furthermore, numerical modeling studies of adsorption of the dye are of practical importance in the performance of the dye sensitized solar cells. In addition, using a computational simulations rooted in density functional theory (DFT) and time-dependent DFT (TDDFT) have become a crucial tool to understand the detailed atomistic of different adsorption dyes on TiO₂ for dye sensitized solar cells [16–18]. Getting the appropriate information about the adsorption equilibrium of different organic and inorganic dyes for dye sensitized solar cells is essential to understand the adsorption mechanism for further improving the device performance. Several papers have proposed conventional models (e.g. Langmuir, Freundlich, Henry, Temkin, Dubinin–Astakhov, etc.) for the description of adsorption process of the conventional N3 and N719 dyes onto TiO₂ and ZnO materials [19–21]. However, these models are not enabling to describe and to interpret accurately the adsorption phenomena because of the lack of quantitative discussions about physico-chemical parameters. In this context, the group of Ben Lamine et al. [22] have developed a statistical physics treatment which is useful to interpret the most known adsorption processes. This approach has been used to interpret various adsorbent-adsorbate system [23,24]. It permitted to develop different models containing physicochemical parameters that can characterize, microscopically and macroscopically the adsorption process. Marwa et al. [25–27] have improved this theory and developed new statistical physics models for modeling adsorption isotherms of dyes for DSSCs applications. At the best of our knowledge, there are no studies related to the interpretation of adsorption process of paprika dye on TiO₂ material and in general in organic or inorganic dyes for dye sensitized solar cells application that combines the interpretations of statistical physics modeling and DFT simulation. Indeed, in this work the combination of both approaches has been used for the first time to interpret the adsorption process of Paprika dye on TiO₂ for dye sensitized solar cells.

In this work, the main objective is to combine these both approaches to interpret the different adsorption isotherms of Paprika oleoresin dye (Capsicum annuum L) into TiO₂ mesoporous at three temperatures: 288 K, 298 K, and 308 K. In one hand, the interpretations and discussions are reinforced by the use of statistical physics formalism in the modeling of these adsorption isotherms by developing a statistical physics model to give physical meaning to all involved parameters and to be able to better interpret and to deduce information about adsorption process at a molecular level. In another hand, we completed this study by using DFT simulations in order to study the interaction of the Paprika dye on TiO₂ surface to understand some of the atomistic details that are crucial to the dye/ semiconductor interaction for dye sensitized solar cells applications. We pay particular attention to the adsorption modes, geometries and energies between the paprika dye and TiO₂.

2. Material and methods

2.1. Adsorbate

The adsorbate is a Paprika oleoresin dye (Capsicum annuum L.). Paprika oleoresin (also known as paprika extract) is an oil-soluble extract from the fruits of Capsicum annuum and is primarily used as a dye. It is composed of capsain, the main flavoring compound giving pungency in higher concentrations, and capsanthin and capsorubin, the main coloring compounds among other carotenoids [28]. The chemical structure of the Paprika oleoresin red dye is illustrated in Fig.1.

2.2. Adsorbent

The adsorbent is a TiO₂ mesoporous which was synthesized by the group Kim et al. by using a TiO₂ paste (DSL18NR-T, Dyesoil) [29]. They applied a conventional method to prepare mesoporous TiO₂ films for dye sensitized solar cells. The TiO₂ paste was placed in the mask opening using the squeeze printing technique, followed by annealing at 723 K for 30 min [29]. The Thickness of TiO₂ film is approximately 10 μ with a size of 4 cm² and it was deposited on the FTO glass substrate (Pilkington, TEC-8, 80% transmittance in the visible region) [29].
2.3. Carrying out of adsorption isotherms

The experimental adsorption isotherms of Paprika oleoresin dye on TiO$_2$ film at three different temperatures have been investigated by Kim et al. [29]. Paprika oleoresin solution was dissolved in acetonitrile in required concentrations (10, 25, 50, 100, 200 mg/L). For the adsorption equilibrium experiments, TiO$_2$ thin film and the dye solutions (20 cm$^3$) were placed in a 50 cm$^3$ flask and shaken for 1 day in a shaking incubator at different temperatures (288, 298, 308 K). After reaching the equilibrium state, the samples were filtered through a Whatman glass microfilter. The amount of adsorption at equilibrium has been determined by measuring the concentration of the separated solutions using UV-VIS spectrophotometry (UV-1601, Shimadzu) at 415 nm. The evaluated weight of the TiO$_2$ thin film has been measured before and after the deposition of the TiO$_2$ thin film on each photoelectrode before starting the dye adsorption experiment [29].

Fig. 2 illustrates the adsorption isotherms of Paprika oleoresin dye on TiO$_2$ film at three different temperatures [29].

3. Statistical physics formalism of the adsorption isotherms model

The study with statistical physics cannot be realized without using the grand canonical ensemble to take account of the particle number variation through the introduction of the chemical potential variable in the adsorption process [30,31]. The modeling of the adsorption isotherms in gas or liquid phase based on statistical physics development is a powerful technique used for surface characterization. One of the advantages of applying this theory is to give a physicochemical meaning to the parameters involved in the model and then to provide more interpretations of the adsorption process at molecular level. In order to treat the adsorption process by using the statistical physics methods, some hypotheses were considered to facilitate the interpretations of the adsorption process. The first approximation is, the interaction between the dye molecules was neglected. Second, the internal degrees of freedom of the studied molecules are neglected but only the translation freedom degrees. Indeed, electronic degrees of freedom cannot be thermally excited, the rotational freedom degrees are frozen into the solution and the vibrational contribution is very weak relatively to the translational ones.

Based on these assumptions, in the liquid phase, the adsorption reaction of dye molecule (D) onto receptor sites (S) should include a stoichiometric coefficient $n$ in the following equation:

$$nD + R \rightleftharpoons D_nR$$

(1)

Where $n$ represents the fraction of a molecule if $n$ is less than unity or the number of adsorbed dye molecules per site $D$ if $n$ is greater than the unity and $D_nR$ is the formed dye-TiO$_2$ complex.

In this treatment, firstly, we apply the grand canonical ensemble to describe the microscopic details adsorption process.

Then, the grand canonical partition function of one receptor site can be expressed as:

$$Z_{gC} = \sum_{N_i} e^{-\beta(-\epsilon + \mu)N_i}$$

(2)

where ($\beta$) is the receptor site absorption energy, $\mu$ is the chemical potential, $N_i$ is the receptor site occupation state, and $\beta$ is defined as $1/k_BT$, where $k_B$ is the Boltzmann constant and $T$ is the absolute temperature.

The total grand canonical partition function related to $N_m$ receptor sites per unit mass is written as follows:

$$Z_T = (Z_{gC})^{N_m}$$

(3)
Table 1 – Partition functions of the five tested models.

<table>
<thead>
<tr>
<th>Name of tested models</th>
<th>Partition function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( z_p(T, \mu) = \sum_{N=1}^{N_0} e^{-\beta(N-\mu)} = 1 + e^{\beta(x)} )</td>
</tr>
<tr>
<td>Monolayer model with one energy (Model 1)</td>
<td>( z_p(T, \mu) = \sum_{N=1}^{N_0} e^{-\beta(N-\mu)} = 1 + e^{\beta(x)} )</td>
</tr>
<tr>
<td>Monolayer model with two energies (Model 2)</td>
<td>( z_p(T, \mu) = \sum_{N=1}^{N_0} e^{-\beta(N-\mu)} = 1 + e^{\beta(x)} )</td>
</tr>
<tr>
<td>Monolayer model with three energies (Model 3)</td>
<td>( z_p(T, \mu) = \sum_{N=1}^{N_0} e^{-\beta(N-\mu)} = 1 + e^{\beta(x)} )</td>
</tr>
<tr>
<td>Monolayer model with four energies (Model 4)</td>
<td>( z_p(T, \mu) = \sum_{N=1}^{N_0} e^{-\beta(N-\mu)} = 1 + e^{\beta(x)} )</td>
</tr>
</tbody>
</table>

The average site occupation number \( N_0 \) calculated from the total grand canonical partition function [26,17]:

\[
N_0 = \frac{1}{\beta} \ln Z_T = N_m \cdot K_b \cdot T \cdot \ln z_p
\]

(4)

For \( n \) molecules anchored per site the total number of adsorbed molecules \( Q \) is given by:

\[
Q = nN_0
\]

(5)

The experimental adsorption isotherms which represent the adsorbed quantity versus the dye concentration \( C \) have been fitted with five model analytical expressions: the known conventional model Langmuir and four other statistical physics models that we respectively call: monolayer model with one energy (Model 1), monolayer model with two energies (Model 2), monolayer model with three energies (Model 3) and monolayer model with four energies (Model 4). In the next section, we will present the development of the adequate model that we will use for the interpretations and discussions of the adsorption process. In Table 1, we resumed all the partition functions of all tested models.

For each partition function we developed as indicated the analytical expression of the adsorbed quantity \( Q \). We will choose the best fitting model expression.

3.1. Fitting of the adsorption isotherms: best fitting model for experimental isotherms

The Microlab Origin Lab software (Origin Lab, Northampton, MA) has been used to fit the different adsorption isotherms of Paprika oleoresin dye on TiO2 by the cited five models.

In order to select the adequate model, two main criteria have been used in the present work: 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 \( R^2 \) was calculated using the equation given by Ref. [32]:

\[
R^2 = 1 - \left( \frac{\sum_{j=1}^{m} (Q_{j,\text{exp}} - \hat{Q}_{j,\text{exp}})^2 - \sum_{j=1}^{m} (Q_{j,\text{EXP}} - \hat{Q}_{j,\text{model}})^2}{\sum_{j=1}^{m} (Q_{j,\text{EXP}} - \hat{Q}_{j,\text{exp}})^2} \right) \times \left( \frac{n_p - 1}{n_p - p} \right)^2
\]

(6)

Table 2 – Adjustment coefficient \( R^2 \) and RMSE for each model.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Langmuir</th>
<th>Model 1</th>
<th>Model 2</th>
<th>Model 3</th>
<th>Model 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>0.95</td>
<td>0.987</td>
<td>0.977</td>
<td>0.890</td>
<td>0.999</td>
</tr>
<tr>
<td>298</td>
<td>0.97</td>
<td>0.898</td>
<td>0.978</td>
<td>0.795</td>
<td>0.998</td>
</tr>
<tr>
<td>308</td>
<td>0.96</td>
<td>0.856</td>
<td>0.988</td>
<td>0.784</td>
<td>0.999</td>
</tr>
</tbody>
</table>

RMSE

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Langmuir</th>
<th>Model 1</th>
<th>Model 2</th>
<th>Model 3</th>
<th>Model 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>0.4</td>
<td>0.001</td>
<td>0.01</td>
<td>0.2</td>
<td>0.002</td>
</tr>
<tr>
<td>298</td>
<td>0.7</td>
<td>0.6</td>
<td>0.06</td>
<td>0.05</td>
<td>0.001</td>
</tr>
<tr>
<td>308</td>
<td>0.6</td>
<td>0.7</td>
<td>0.05</td>
<td>0.6</td>
<td>0.003</td>
</tr>
</tbody>
</table>

where, \( Q_{j,\text{exp}} \) is each value of \( Q \) measured experimentally, \( Q_{j,\text{model}} \) is each value of \( Q \) estimated by the fitted model, \( Q_{j,\text{exp}} \) is the average of \( Q \) experimentally measured, \( n_p \) is the number of performed experiments and \( p \) is the number of parameters of the fitted model.

For a number \( p \) of adjustable parameters, the estimated standard error is given by the following relation [32]:

\[
\text{RMSE} = \sqrt{\frac{\sum_{j=1}^{m} (Q_{j,\text{cal}} - Q_{j,\text{exp}})^2}{m' - p}}
\]

(7)

The RSS parameter is the residual sum of squares and given by:

\[
\text{RSS} = \sum_{j=1}^{m'} (Q_{j,\text{cal}} - Q_{j,\text{exp}})
\]

(8)

With \( Q_{j,\text{cal}} \) is the calculated adsorption quantity, \( Q_{j,\text{exp}} \) is the experimental adsorption quantity and \( m' \) is the number of experimental data.

The Table 2 illustrates the adjustment coefficients \( R^2 \) and RMSE of the five treated models at three temperatures.
This model is an extended Hill model with four types of receptor sites which are established in terms of the grand canonical ensemble in statistical physics. To develop this model, we supposed that the adsorption occurs onto four types of sites characterized by four adsorption energies ($\epsilon_1, \epsilon_2, \epsilon_3,$ and $\epsilon_4$). The value of energy is characteristic of the receptor site with a density of receptor sites noticed Nmi. The receptor site is supposed to be empty or occupied by one or more dye molecules. The first step to establish this model is to express the grand canonical partition function of one receptor site describing the microscopic states of the adsorbing system. Therefore, the grand canonical partition function of one site of the four types has the following forms:

$$Z_T = (z_{1gc})^{N_{m1}} (z_{2gc})^{N_{m2}} (z_{3gc})^{N_{m3}} (z_{4gc})^{N_{m4}}$$ (9)

$$Z_{1gc} = \sum_{N_i=0}^{N_{m1}} e^{-\beta(\epsilon_1-\mu)N_i} = 1 + e^{\beta(\epsilon_1+\mu)}$$ (10)

$$Z_{2gc} = \sum_{N_i=0}^{N_{m2}} e^{-\beta(\epsilon_2-\mu)N_i} = 1 + e^{\beta(\epsilon_2+\mu)}$$ (11)

$$Z_{3gc} = \sum_{N_i=0}^{N_{m3}} e^{-\beta(\epsilon_3-\mu)N_i} = 1 + e^{\beta(\epsilon_3+\mu)}$$ (12)

$$Z_{4gc} = \sum_{N_i=0}^{N_{m4}} e^{-\beta(\epsilon_4-\mu)N_i} = 1 + e^{\beta(\epsilon_4+\mu)}$$ (13)

With $z_{1gc}, z_{2gc}, z_{3gc}$ and $z_{4gc}$ being the partition functions of the four types of sites.

$\mu$ is the chemical potential and $N_i$ is the number of occupation.

Therefore, the total partition function of the monolayer model of four receptor sites is:

$$Z_t = (z_{1gc})^{N_{m1}} (z_{2gc})^{N_{m2}} (z_{3gc})^{N_{m3}} (z_{4gc})^{N_{m4}}$$ (14)

Using the previous definition of occupation number, the average numbers of occupied sites is:

$$N_{O1} = \frac{N_{m1}}{1 + (\frac{C_1}{C})^{\beta_1}}$$,  
$$N_{O2} = \frac{N_{m2}}{1 + (\frac{C_2}{C})^{\beta_2}}$$,

$$N_{O3} = \frac{N_{m3}}{1 + (\frac{C_3}{C})^{\beta_3}}$$,  
$$N_{O4} = \frac{N_{m4}}{1 + (\frac{C_4}{C})^{\beta_4}}$$

With $C_1$, $C_2$, $C_3$ and $C_4$ being the concentrations at half saturation for the four types of receptor sites respectively.

Finally, the total number of adsorbed molecules of dye versus the concentration C is:

$$Q = n_1N_{O1} + n_2N_{O2} + n_3N_{O3} + n_4N_{O4}$$

Finally, the expression of Q can be written as:

$$Q = \frac{n_1N_{m1}}{1 + (\frac{C_1}{C})^{\beta_1}} + \frac{n_2N_{m2}}{1 + (\frac{C_2}{C})^{\beta_2}} + \frac{n_3N_{m3}}{1 + (\frac{C_3}{C})^{\beta_3}} + \frac{n_4N_{m4}}{1 + (\frac{C_4}{C})^{\beta_4}}$$

Model 4

This expression will be used used for fitting of all the adsorption isotherms.

The adjusting parameters of the adequate model are reported in Table 3.

From the Table 3, we classified these parameters into two categories: steric parameters such as the numbers of dye molecules adsorbed per site $n_1$, $n_2$, $n_3$ and $n_4$, the densities of receptor sites $N_{m1}$, $N_{m2}$, $N_{m3}$ and $N_{m4}$ and the adsorbed quantities at saturation $Q_{sat1}$, $Q_{sat2}$, $Q_{sat3}$ and $Q_{sat4}$. The second category of parameters is energetic such as the halves-saturation concentrations $C_1$, $C_2$, $C_3$ and $C_4$ which reflect the adsorption energies of the paprika dye molecules.
on the four types of receptor sites of the mesoporous TiO₂. In the next section, we will interpret the adsorption isotherms by the two cited categories of the adequate model parameters. The usefulness of the parameters meaning plays, an important role to understand the adsorption process. We studied the behavior of each of these parameters as function of temperature in order to enrich understanding of the adsorption process at a microscopic scale.

4. Stereographic parameters

4.1. The parameters n₁, n₂, n₃ and n₄

The reaction Eq. (1) can be replaced, using model 4, by four reactions Eqs. (15), (16), (17) and (18). The parameters n₁, n₂, n₃ and n₄ in the adsorption reaction Eqs. (15), (16), (17) and (18) represent the stoichiometric coefficients for each type of receptor sites and also the number of adsorbed dye molecules per site is given in the expression of the Model4.

The reaction in the first site is written as:

\[ n₁D + R \rightleftharpoons RDn₁ \]  \hspace{1cm} (15)

The reaction in the second site is written as:

\[ n₂D + R \rightleftharpoons Dn₂R \]  \hspace{1cm} (16)

The reaction in the third site is written as:

\[ n₃D + R \rightleftharpoons Dn₃R \]  \hspace{1cm} (17)

The reaction in the four site is written as:

\[ n₄D + R \rightleftharpoons Dn₄R \]  \hspace{1cm} (18)

The Eq. (1) could be considered as an average equation of all the four equations. A steric parameters nᵢ have two main meanings: In one hand, they can describe the geometric adsorption position of dye molecule on the adsorbent surface as function of their values determined by numerical simulation. In another hand, nᵢ can describe the aggregation phenomenon of dye molecules in solution that proceeds the anchorage of this aggregate on the receptor sites [33]. In term of adsorption position of dye, we distinguished two configurations relative to the surface: In the first case, when the value of nᵢ is superior to 1, it represents the number of docked molecules which interact with one receptor site describing called a multi-molecular process. This case describes the dye molecules when it is adsorbed on the adsorbent surface with a non-parallel position or an inclined position. This case is illustrated in Fig.4.

**Fig. 4 – Example of multi-anchorage of Paprika dye molecules into a pore of TiO₂ with a non-parallel position (n < 1).**

In the second case, when this value is inferior to 1, it would represent “the fraction of the dye molecule per site”, since all the fractions of the molecule are anchored it leads to a horizontal docking on the adsorbent surface and showing that the adsorption process is called a multi-docking process or a parallel anchorage [33]. In that case we take n' = 1/n which is superior to the unity. It represents the anchorage number of one dye molecule on an average number of receptor sites [31].

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**Table 3 – Adjustment parameters value corresponding to the best fitting model4**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>n₁</th>
<th>n₂</th>
<th>n₃</th>
<th>n₄</th>
<th>Nm₁ (mg/g)</th>
<th>Nm₂ (mg/g)</th>
<th>Nm₃ (mg/g)</th>
<th>Nm₄ (mg/g)</th>
<th>Qₛₐ₄₁ (mg/g)</th>
<th>Qₛₐ₄₂ (mg/g)</th>
<th>Qₛₐ₄₃ (mg/g)</th>
<th>Qₛₐ₄₄ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>0.8</td>
<td>1.8</td>
<td>3.5</td>
<td>4</td>
<td>1.4</td>
<td>0.8</td>
<td>0.5</td>
<td>0.4</td>
<td>1.12</td>
<td>1.44</td>
<td>1.75</td>
<td>1.6</td>
</tr>
<tr>
<td>298</td>
<td>0.9</td>
<td>2.2</td>
<td>3.8</td>
<td>5.8</td>
<td>1.9</td>
<td>1.2</td>
<td>0.9</td>
<td>0.6</td>
<td>1.71</td>
<td>2.64</td>
<td>3.42</td>
<td>3.48</td>
</tr>
<tr>
<td>308</td>
<td>1.5</td>
<td>3.1</td>
<td>4</td>
<td>6.2</td>
<td>2.5</td>
<td>1.4</td>
<td>1.2</td>
<td>0.8</td>
<td>3.75</td>
<td>4.34</td>
<td>4.8</td>
<td>4.96</td>
</tr>
</tbody>
</table>
Fig. 5 – Example of anchorage of one Paprika dye molecule into a pore of TiO₂ with a parallel position (n < 1).

Now with these considerations and referring to the values of those parameters (Table 3), we noticed that there are values superior and others inferior to the unity when varying temperature. Based on these considerations and information, we can say that there are two possible anchorage positions of the adsorbed dye molecule: parallel position when the dye molecules interact with a multi-anchorage and non-parallel position when the adsorbed dye on the surface of TiO₂ is multi-molecular. To make a simple analysis, we give an example of n₁ = 0.8 which is a value between 1/2 and 1; therefore, this value 0.8 is an average between two anchorage one with n₁ = 0.5 and the second with n₁ = 1, so, we can write this relation: 0.8 = x×1+(1-x)×1/2 which allow to calculate the percentage value of a single docked molecule with n₁ = 1 (x = 20%) and with double docked one with n₁ = 0.5 (1-x = 80%). We illustrated this case in Fig. 5.

Another example when n₁ = 1.5, which is an average of 1 and 2, we can represent it by this relation 1.5 = 1’x+ (1-x)’2. Indeed, a rate of 50% receptor sites are docked by one molecule and 50% of receptor sites are docked by two molecules with a non-parallel position. It is interesting to see the effect of the temperature on the evolution of the various parameters n₁.

Fig. 6 depicts the evolution of the number of adsorbed dye molecule(s) per site as a function of the temperature.

The first remark is that from the first type of receptor sites to the fourth and last type, the parameter n₁ is growing and the aggregation phenomenon is accentuated from the first to the last. This behavior is due to an energetic effect since as we will see in the next paragraph the first type is the less energetic for the adsorption. So, the more energetic with gather more molecules. The anchorage type is changing from multi-anchorage to the multi molecule one from the first type to the last type of receptor sites.

It addition, we remark that these numbers n₁ of adsorbed dye molecules increase slightly as a function of the temperature. This behavior is probably due to an endothermic adsorption process (Table 3). Therefore, the thermal agitation allows to go over the activation energy.

4.2. Densities of receptor sites Nmᵢ

These densities represent the receptor sites numbers per unit mass available to be occupied during the adsorption process by the dye molecules. The evolution of this parameter is illustrated in Fig. 7. This figure exhibits, that the increase in temperature leads to the increase of Nmᵢ parameter. The one explanation of this increase is that the increase of temperature and of thermal agitation may allow some molecules to attain more receptor sites with higher energy. This can facilitate the contribution of more dye molecules in the adsorption process. We can also notice that inversely to the parameters nᵢ, the parameters Nmᵢ are decreased from the first type to the last type. This indicated that the size of all aggregate is high (nᵢ is high), the density is weak (Nmᵢ is weak). This is due to the stereographic hindrance effect.
4.3. The adsorbed quantities at saturation

The parameters $Q_{sat_i}$ represent the partial saturation adsorption quantities of the studied system. It depends on the number of molecules per site and the densities of receptor sites.

$$Q_{sat_i} = Q_{sat_1} + Q_{sat_2} + Q_{sat_3} + Q_{sat_4} = \sum_{i=1}^{4} Q_{sat_i} = n_iN_{m_i}$$

The evolution of this parameter as a function of the temperature is reported in Fig. 8. Fig. 8 exhibits that the adsorbed quantities at saturation increase with the increase of temperature. This behavior is attributed to the both increases of the two steric parameters ($n_i$ and $N_{m_i}$) presented in Figs. 6 and 7. Therefore, the stero- graphic effect is preponderant. In addition, this increase is also in a good agreement with the experimental data presented in Fig. 2.

5. Energetic interpretation: adsorption energies

In order to investigate whether functional groups have an impact on how dye molecules interact with the TiO$_2$ mesoporous, we used the four energetic parameters $C_1$, $C_2$, $C_3$ and $C_4$ to calculate the adsorption energies ($\varepsilon_1$), ($\varepsilon_2$), ($\varepsilon_3$) and ($\varepsilon_4$) by using the following expressions:

$$\varepsilon_1 = R T \ln \left( \frac{C_1}{C_4} \right)$$  \hspace{1cm} (19)

$$\varepsilon_2 = R T \ln \left( \frac{C_2}{C_4} \right)$$  \hspace{1cm} (20)

$$\varepsilon_3 = R T \ln \left( \frac{C_3}{C_4} \right)$$  \hspace{1cm} (21)

$$\varepsilon_4 = R T \ln \left( \frac{C_4}{C_4} \right)$$  \hspace{1cm} (22)

$$\ln(C_1) = \ln \left( C_1 - \frac{\varepsilon_1}{RT} \right)$$  \hspace{1cm} (23)

$$\ln(C_2) = \ln \left( C_2 - \frac{\varepsilon_2}{RT} \right)$$  \hspace{1cm} (24)

$$\ln(C_3) = \ln \left( C_3 - \frac{\varepsilon_3}{RT} \right)$$  \hspace{1cm} (25)

$$\ln(C_4) = \ln \left( C_4 - \frac{\varepsilon_4}{RT} \right)$$  \hspace{1cm} (26)

Where $R$ is the ideal gas constant, $R = 8.314 J/(mol \cdot K)$ and $C_4$ is the saturated concentration of dye.

We determined the value of adsorption energies by the slopes of the plots $\ln C_1$, $\ln C_2$, $\ln C_3$ and $\ln C_4$ versus $1/T$ in Fig. 9 and the values of the adsorptions energies are illustrated in the Table 4.

From the slopes of Fig. 9, we deduced that the all values of adsorption energies ($\varepsilon_1$), ($\varepsilon_2$), ($\varepsilon_3$) and ($\varepsilon_4$) have been

Table 4 – Values corresponding to the adsorption energies of the four adsorption sites in TiO$_2$ surface.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$C_1$ mg/L</th>
<th>$C_2$ mg/L</th>
<th>$C_3$ mg/L</th>
<th>$C_4$ mg/L</th>
<th>$-\varepsilon_1$ kJ/mol</th>
<th>$-\varepsilon_2$ kJ/mol</th>
<th>$-\varepsilon_3$ kJ/mol</th>
<th>$-\varepsilon_4$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>54</td>
<td>80</td>
<td>100</td>
<td>150</td>
<td>4.38</td>
<td>29</td>
<td>123.85</td>
<td>168</td>
</tr>
<tr>
<td>298</td>
<td>60</td>
<td>89.7</td>
<td>121.6</td>
<td>165.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>75</td>
<td>90</td>
<td>140</td>
<td>198.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
calculated respectively \(-e_2\) = 4.38 kJ mol\(^{-1}\), \(-e_3\) = 29 kJ/mol, \(-e_3\) = 123.85 kJ/mol and \(-e_4\) = 168 kJ mol\(^{-1}\)

The adsorption energy value of the first receptor site \((-e_1\) and the second receptor sites indicate that the anchorage between paprika dye and the TiO\(_2\) surface takes place via a physical adsorption such as hydrogen binding. In general, the physisorption phenomenon shows values lower than 40 KJ/mol [34]. However, the energy bonding forces in the chemical adsorption process are mostly higher than 80 kJ/mol [34]. Indeed, in this work, a chemisorption appears in the third and the four receptor sites.

According to these all estimated values, we notice that there is a coexistence of the two adsorption phenomenon chemisorption and physisorption during the adsorption process of the paprika dye on the TiO\(_2\) surface.

### 6. Pore size distribution PSD determined by the Kelvin’s equation

The mesoporous structure of nanocrystalline TiO\(_2\) anode is a key factor in enhancing dye diffusion and adsorption in incident light transportation and in illumination as well as in electron transmission efficiency [35,36]. This is due to the high porosity since the size of mesoporous and small pores present a high adsorption energy which allows to bind molecules chemically. Therefore, the mesoporous TiO\(_2\) has been widely used in the photocatalysis application because of its good photodegradation properties and of its high porosity. Its porosity can facilitate pollutant access, their adsorption and their decomposition [37]. Indeed, the adsorbates can be adsorbed in large quantities onto the surface. Hence, it is important to estimate the pore size distribution of its pores as accurately as possible when developing a TiO\(_2\) mesoporous material in the field of adsorption and catalysis. Since the adsorption process is governed by stereographic considerations, it is useful to calculate the pore size distribution (PSD) in order to investigate the adequation of the adsorbate molecule size and the pore size. So, the stacking of number of layers into a pore will be an information about the adsorption process. In this work, the PSD of the adsorbent surface will be estimated in order to describe the morphology and the geometric heterogeneity of the mesoporous TiO\(_2\) during the adsorption process of the paprika oleoresin dye. This pore size distribution (PSD) will give also information on the interaction energy between the adsorbate and the adsorbent. The PSD is estimated by using the Kelvin’s law relating the pore radius \(r\) to the dye concentration \(C\) and the concentration at saturation \(C_s\) [24,25].

The Kelvin’s law is given by the following equation:

\[
\ln\left(\frac{C}{C_s}\right) = \frac{-2\gamma V_m}{rRT}
\]  
\(27\)

So, we can write this relation as following:

\[
\frac{C}{C_s} = e^{-\frac{-2\gamma V_m}{rRT}} = e^{\frac{k_b}{T}}
\]  
\(28\)

Where \(C_s\) is the paprika oleoresin dye solubility or its concentration in a solvent at saturation, \(k_b = 2\gamma V_m\) is the constant of Kelvin, \(V_m\) is the molar volume of the solution, \(\gamma\) is the surface tension of the Wall with contact angle \(\theta\), \(T\) is the temperature, \(R = 8.314\) is the ideal gas constant and \(r\) is the cylindrical pore radius of TiO\(_2\).

The pore size distribution of the TiO\(_2\) mesoporous will be obtained by the derivative of the adsorbed amount \(Q\) relative to the radius [26,27]:

\[
\text{PSD} = \frac{dQ}{dr}
\]  
\(29\)

The pore size distribution of the adsorbent TiO\(_2\) is illustrated in the Fig. 10.

The Fig. 10 shows that the pore size distribution of the TiO\(_2\) surface confirmed essentially that the adsorbent is a mesoporous material with pore radius varying between 2 nm and 25 nm. Based on this result, we notice that, these estimated values are already close to the PSD of the same adsorbent mesoporous TiO\(_2\) varying between 2 and 20 nm but determined using another molecule probe which was natural Gardenia Yellow dye molecule already carried out by the same method in our previous work [27]. Therefore, we deduced that this a little variation of PSD of the TiO\(_2\) mesoporous between this present work and our recently published work could be attributed to the variation of the probe adsorbate. This proved that the variation of the adsorbate has an effect of the determination of the pore size distribution. Moreover, the Fig. 10 shows that the pore size distribution is multimodal and more precisely four-modal corresponding to the four types of different kinds of receptor sites. Lastly, we notice that the PSD is translated toward high values of radius when the temperature is increased. A various synthetic methods have been used to synthesize porous titanium dioxide. Among them a method used: a soft template method or a sol-gel synthesis method which is the most widely used due to its simple film preparation or a chemically induced self-transformation (CIST) or an evaporation-induced self-assembly and application of ionic liquids [38,39]. In many cases, the titanium precursors or templates have been used for preparing porous TiO\(_2\). [40]
We presented in Table 5 the Barrett-Joyner-Halenda (BJH) measurement of PSD mesoporous TiO$_2$ prepared by different methods.

The Table 5 shows that the PSDs of mesoporous TiO$_2$ determined by BJH analysis, are very close to our results obtained with the Kelvin method. The variation of the PSD of these different synthesized materials could be attributed to the calcinations temperatures which has a significant effect on the variation of the pore size distributions. Recently, [45] it has been demonstrated that increasing in calcination temperature of mesoporous TiO$_2$ in dye sensitized solar cells leads to increase the crystal size, to decrease the surface area and to increase the pore size. This means that the increase of calcination temperature has a good effect on the mesoporous TiO$_2$ as photocatalytic activity for organic dyes [46].

In the next section, we will complete our study of the adsorption process of paprika dye on TiO$_2$ surface by using DFT simulations and the result will be compared with the statistical physics results.

### Table 5 – BHJ measurement of PSD of mesoporous TiO$_2$ prepared by different methods.

<table>
<thead>
<tr>
<th>Method of preparation of mesoporous TiO$_2$</th>
<th>Techniques of characterization</th>
<th>PSD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft Template method</td>
<td>BJH</td>
<td>5–10</td>
</tr>
<tr>
<td>Sol-gel method</td>
<td>BJH</td>
<td>2–23</td>
</tr>
<tr>
<td>Chemically induced self-transformation (CIST)</td>
<td>BJH</td>
<td>2–10</td>
</tr>
<tr>
<td>Evaporation-Induced Self-Assembly</td>
<td>BJH</td>
<td>8–15</td>
</tr>
<tr>
<td>TiO$_2$ paste (DSL 18 NR-T, Dyesol)</td>
<td>Kelvin method</td>
<td>2–25</td>
</tr>
</tbody>
</table>

### 7. Study of paprika dye/TiO$_2$ interface in DSSCs by DFT simulation

In this part, we present a DFT study of the interaction of the Paprika sensitizer on TiO$_2$ mesoporous to understand some of the atomistic details that are crucial to the dye/semiconductor interaction. We pay particular attention to the adsorption mode of the sensitizer and to the effect of the complexation on the electronic structure of the dye.

#### 7.1. DFT protocol data

The quantum chemical calculations are done to compute the molecular geometry like bond length and bond angle values and energy value of intermolecular interactions with Guassian-09W [xx] program using the DFT/B3LYP/6-311++G(d,p) basis set. The B3LYP functional has been broadly used for calculations of various organic compounds, which justifies its use for the given system. This functional takes into account weak interactions between components of the calculated system (including electrostatic interactions), which in turn also justifies its use for the calculations on the system under investigation. The computational results showed the formation of hydrogen bonding and electrostatic interactions that suggest the increased reactivity and potential adsorption activity of these complexes.

#### 7.2. Molecular electrostatic potential analysis

The molecular electrostatic potential V(r), at a given point r(x, y, z) in the vicinity of a molecule, is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and a positive test charge (a proton) located at r. It is related to the electronic density (ED) and is a very useful to predict reactive sites for electrophilic attack and nucleophilic reactions as well as hydrogen-bonding interactions [47–49].

The Molecular electrostatic potential (MEP) of paprika dye and TiO$_2$ structures are plotted in Fig.11.

From the MEP it is evident that the negative charge (red) of paprika dye covers the ether oxygen atom (O2) with a minimum value of −0.06019 a.u hydroxyl oxygen atom (O1) and amide oxygen atom (O1) and the maximum positive region (blue) on phenol hydrogen atom (H34) with a maximum value of 0.05019 a.u, amine hydrogen atom (H 28). Therefore, this result confirms the existence of four reactive sites and an intermolecular O–H...O interaction.

#### 7.3. Molecular geometries optimization of paprika dye adsorbed on the TiO$_2$ surface

The anchoring modes of the dye to the TiO$_2$ surface are of crucial importance. The bonding type and the extent of electronic coupling between the dye-excited state and the semiconductor unoccupied states is directly influencing the DSSCs performance [50,51].

In this work, and in order to analyze the interatomic interactions between the paprika dye and the TiO$_2$ mesoporous and to determine the different possible modes contributing on the adsorption of Paprika dye on TiO$_2$ surface, a proposed structure of adsorbent surface and the adsorbate were optimized by DFT calculations. The molecular geometry optimization and all quantum chemical calculations have been performed by using the hybrid B3LYP/6-311++G (d,p) method with the Gaussian 09 software package and the GaussView molecular visualization program [52–54].

Four possible optimized modes for adsorption paprika dye on TiO$_2$ surface were selected to understand the molecular interaction during the adsorption process: 1) monodentate coordination mode via Hydrogen atom H 34 of the pheno- nal functional group, 2) monodentate coordination mode via hydrogen atom H 28 of amine functional group, 3) mon- odentate coordination mode via oxygen atom O1 of amide functional group, 4) bidentate coordination mode via two oxygen atoms O2 and O3 of the ether and hydroxyl functionalities groups respectively. DFT simulations were performed also to estimate the bond length involved in the paprika dye adsorp-
Fig. 11 – The molecular electrostatic potential (MEP) map of (a) paprika dye and (b) TiO$_2$.

Fig. 12 – Possible binding modes for paprika dye on surface TiO$_2$: a) optimized TiO$_2$ used in DFT simulation. b) monodentate hydrogen bond H 34 (Mode 1) c) monodentate hydrogen bond H28 (Mode 2) d) monodentate oxygen bond O1 (Mode 3) e) bidentate oxygen atoms bond O2 and O3 (Mode 4).

The different optimized geometries structures of the adsorption paprika dye on TiO$_2$ surface are illustrated in Fig. 12 and the results of DFT simulations are given in Table 6.

From Table 6, it seems that the interaction energies are ranged from –4.73 kJ/mol to –215.26 kJ/mol. While, the bond length are ranged from 1.72986 to 2.12Å. Moreover, we notice that these values of interaction energies –4.73 kJ/mol and –28.14 kJ/mol of the interaction of Mode 1 O52…H34 and interaction of Mode 2 Ti50…H23 are lower than –126.05 kJ/mol and –160.35 kJ/mol which one obtained by for the monodentate oxygen atom bond of mode 3 and bidentate oxygen atom bond of mode 4. However, it is observed that the values of interaction energies of bidentate oxygen atoms O2 of the ether functional group and O3 of hydroxyl functional group are higher than that obtained by the monodentate oxygen bond of mode 3 and by monodentate hydrogen bond of mode 1 and mode 2. This can be attributed to the participation of the more oxygen atoms in the interaction. On the other hand, the binding energies for the interaction by the combination of both ether and hydroxyl functionalities groups are the strongest indicating their better thermodynamic stability for the adsorption paprika dye in comparison to the phenol, amine, amide functionalities groups. This result is in agreement with results previously published in the literature which proved that the binding energies of the conventional N719 and N3 dyes on the TiO$_2$ surface via the bidentate chelate linkage of the carboxylic functional group is higher than that of the monodentate linkage which makes more stability and increases the performance of dye sensitized solar cells. They are considered as preferred adsorption mode, while the monodentate is usually predicted to be less stable [55,56]. Therefore, in this work, the calculations showed that the preferred adsorption mode is the bidentate anchoring with involving both ether and hydroxyl functionalities groups of the paprika dye. Indeed, they appeared to be good candidates as anchoring groups for the performance of dye sensitized solar cells.

Now, it is very important if we compare all these DFT modes with the values of energies fitted by statistical physics modeling, we can notice that all these obtained values of interaction energies of all modes are in a good agreement with the four values of the adsorption energies calculated by the statistical physics model. Indeed, the DFT simulations have confirmed that the paprika dye is adsorbed physically and chemically on the TiO$_2$ surface via monodentate hydrogen atom bond, monodentate oxygen atom bond and bidentate oxygen atoms bond. Therefore, basis on these results of DFT simulations we illustrated in Fig. 13 two probable anchoring models in a chemisorption and two probable anchoring models in a physisorption

According to the obtained values of the number of adsorbed dye per site (Table 3) which determined by the statistical physical modeling and proved that the paprika dye can anchor on the TiO$_2$ surface with parallel and perpendicular position and according also to the result obtained by the DFT simulations, (Fig. 12, Table 6), we deduced that the paprika dye is adsorbed chemically with perpendicular position via phenol functional group and two ether and hydroxyl functionalities groups. This case could be associated to the two configurations (a–d), and in the case of physisorption the paprika dye adsorbed with parallel position via amine and amide functionalities groups. They can be only these two possible configurations (b–c).
Table 6 – Results of DFT simulations for the adsorption paprika dye on TiO$_2$ surface

<table>
<thead>
<tr>
<th>Interaction of the different Modes</th>
<th>Bond length (Å)</th>
<th>$E_{int}$ (kJ/mol)</th>
<th>Average value of the interaction energy $E_{avg}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interaction of Mode 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O51…H33</td>
<td>2.46602</td>
<td>−7.16</td>
<td></td>
</tr>
<tr>
<td>O52…H33</td>
<td>2.70624</td>
<td>−5.73</td>
<td></td>
</tr>
<tr>
<td>O52…H34</td>
<td>1.72986</td>
<td>−4.73</td>
<td></td>
</tr>
<tr>
<td>Interaction of Mode 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O51…H31</td>
<td>2.49407</td>
<td>−6.96</td>
<td></td>
</tr>
<tr>
<td>O51…H28</td>
<td>1.90083</td>
<td>−28.94</td>
<td></td>
</tr>
<tr>
<td>O52…H40</td>
<td>2.84749</td>
<td>−347.05</td>
<td></td>
</tr>
<tr>
<td>Ti50…H23</td>
<td>2.12730</td>
<td>−28.14</td>
<td>70.01</td>
</tr>
<tr>
<td>Ti50…H47</td>
<td>2.18659</td>
<td>−24.98</td>
<td></td>
</tr>
<tr>
<td>Ti50…C6</td>
<td>2.62214</td>
<td>−25.49</td>
<td></td>
</tr>
<tr>
<td>Ti50…C5</td>
<td>2.57970</td>
<td>−28.49</td>
<td></td>
</tr>
<tr>
<td>Interaction of Mode 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O51…H22</td>
<td>2.28683</td>
<td>−10.61</td>
<td></td>
</tr>
<tr>
<td>O52…H29</td>
<td>2.32578</td>
<td>−1.30</td>
<td>37.14</td>
</tr>
<tr>
<td>Ti50…O1</td>
<td>2.05514</td>
<td>−126.05</td>
<td></td>
</tr>
<tr>
<td>O51…H32</td>
<td>2.28683</td>
<td>−10.61</td>
<td></td>
</tr>
<tr>
<td>Interaction of Mode 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti50…O2</td>
<td>2.10959</td>
<td>−105.44</td>
<td>160.35</td>
</tr>
<tr>
<td>Ti50…O3</td>
<td>1.93404</td>
<td>−215.26</td>
<td></td>
</tr>
</tbody>
</table>

The DFT simulation has been carried out in order to complete this statistical physics investigation by studying the interaction of the Paprika dye on TiO$_2$ surface to understand some of the atomistic details that are crucial to the dye/semiconductor interaction. The DFT simulation has determined different binding modes which participate in the adsorption of Paprika dye on TiO$_2$ surface. In particular, the interaction between the paprika dye and TiO$_2$ is strengthened with the bidentate coordination mode via the two hydroxyl and ether functionalities groups involving in the adsorption process.

8. Conclusions

The adsorption process of paprika dye on TiO$_2$ surface has been investigated by using a combination between the statistical physics modeling and a DFT simulation. The statistical physics treatment and the results of fitting showed that the developed monolayer model with four energies is able to predict the microscopic topography and the geometry of the adsorbed dye molecules on TiO$_2$. The stenographic and energetic parameters which deduced by this best fitting model have allowed physical interpretations and discussions describing the adsorption process of the paprika oleoresin dye on the TiO$_2$ surface at the three different temperatures. The adsorption geometry was described by the number of molecules per site and showed that the dye molecules can be anchored on the TiO$_2$ mesoporous with the two parallel and nonparallel configurations. From the energetic viewpoint, the calculated adsorption energies values revealed that the dye is adsorbed physically and chemically on the TiO$_2$ surface.

Conflict of Interest

The authors declare that they have no conflict of Interest.

Appendix A

Nomenclature

$C_s$ The solubility concentration of dye
$C_i$ The initial concentration
$C_e$ The equilibrium concentration
$C$ The concentration of dye molecules
$C_{1/2}$ The concentration at half saturation
h Planck’s constant.
$K_B$ Boltzmann constant
$n_1$ Number of molecules per site for the first receptor site
$n_2$ Number of molecules per site for the second receptor site
$n_3$ Number of molecules per site for the third receptor site
$n_4$ Number of molecules per site for the four receptor site
$N_a$ The total number of adsorbed molecules.
$N_{m_1}$ The density of receptor sites for the one receptor site
$N_{m_2}$ The density of receptor sites for the second receptor site

Fig. 13 – Two Probable models for the physisorption of the paprika dye (a-b) which illustrate the monodentate hydrogen bond of phenol functional group and the monodentate hydrogen bond of amine functional group respectively. Two probable models for the chemisorptions (c-d) which illustrate the monodentate oxygen bond of the amine functional group and bidentate oxygen bond of the ether and hydroxyl functionalities groups respectively.
N\textsubscript{r3} The density of receptor sites for the third receptor site
N\textsubscript{r4} The density of receptor sites for the fourth receptor site
N\textsubscript{T} The state of occupation number receptor
N\textsubscript{g} The average number of occupied sites
Q The amount of adsorbed dye molecules
R The ideal gas constant
T Temperature in K
\(Z_{\text{GC}}\) The grand canonical partition function of one site
\(Z_{\text{TR}}\) The grand canonical partition function of N\textsubscript{m} sites
\(\epsilon_{1}\) The adsorption energy of the first receptor site
\(\epsilon_{2}\) The adsorption energy of the second receptor site.
\(\epsilon_{3}\) The adsorption energy of the third receptor site.
\(\epsilon_{4}\) The adsorption energy of the fourth receptor site.
\(\epsilon_{m}\) The energy of an adsorbed molecule
\(\mu\) The chemical potential of the adsorbate state.
\(\beta\) Boltzmann factor

REFERENCES


