Modeling of adsorption of aluminum on macrocyclic porphyrins H₂TPP and H₂TTPP:
Phenomenological investigation of aluminum (III)-porphyrin complex at the molecular level

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Abstract

This article presents a series of adsorption isotherms of aluminum chloride and aluminum sulfate on two promising adsorbents named ‘porphyrins H₂TPP and H₂TTPP’ which were carried out to prove new insights about the complexation mechanism. The adsorbed masses of aluminum (III) on the tested adsorbents were controlled at three solution temperatures using the well-known QCM protocol. The isotherms curves of each adsorption system were examined in order to check the performance of the adsorption materials for the metalloporphyrin achievement. Thus, a mono-layer process was concluded for aluminium chloride adsorption whereas; a multi-layer adsorption mechanism was discovered in the case of aluminum sulfate. The microscopic investigation of the two adsorption mechanisms was established through innovative physical modeling of the adsorption isotherms. Overall, the theoretical investigation showed that a multi-interaction mechanism occurred in the adsorption of aluminum ions onto the two tested porphyrins. The behavior of the paramount parameter density of the occupied porphyrins sites explained the endothermic feature of the studied process. The adopted models provided an excellent description of the interactions between the adsorbates and adsorbent via a calculation of the adsorption energy, indicating that aluminum particles were chemically bonded to H₂TTPP. Interestingly, the theoretical interpretations showed that AlCl₃ and H₂TTPP can be suggested for a genuine industrial application of aluminum (III)-porphyrin complex.

Keywords: Adsorption isotherms; metal-porphyrin complex; Quartz crystal microbalance; Phenomenological modeling.
1. Introduction

In recent years, porphyrins have been studied as chemical sensors materials of various metals leading to the formation of metalloporphyrins complexes [1, 2]. The metal-porphyrin complexes (metalloporphyrins) have received increased interest in several biological and environmental processes [3, 4] such as stereochemistry study and molecular recognition [5-9].

Note here that the central ion nature has significantly influenced the photophysical properties of porphyrins [10-12]. For example, these tetrapyrrolic macrocycles are involved in the chlorophyll structure (magnesium-porphyrin complex) and the hemoglobin structure (iron-porphyrin complex) so they are known as life pigments [13]. In addition, metalloporphyrins complexes were also employed as ionophores in potentiometric recognition sensors development supported with their structural variety and coordination chemistry [10-13]. In particular, the photosensitizing properties of aluminum (III)-porphyrin have promoted to its use as potential ionophore of fluoride [14, 15]. Moreover, aluminum (III)-porphyrin has been potentially used as supramolecular building blocks [19] and numerous others areas (sensing, molecular recognition, polymerisation reactions…)[16-18].

Surprisingly, it was remarked that while several papers have been devoted to metalloporphyrins complexes including the metal centers iron, zinc, rhodium, cobalt… [20], little of the attention has been paid to the aluminium-porphyrin complex (Fig. 1) despite its contribution in the interesting fields indicated above. This complex has not been thoroughly investigated because the fabrication of this ionophore is complicated and revealed practical problems (e.g. low catalyst lifetimes). In order to solve the actual problems, it was suggested in this work to use the microbalance apparatus [21] for the fabrication of this ionophore. This experimental method is a simple mass detector technique which requires the immobilization of porphyrins on solid support of quartz crystal. Then, the complexed mass of aluminum into the macromolecules cavities can be controlled through the microbalance apparatus.
In fact, adsorption isotherms of aluminum chloride and aluminum sulfate on the two tested porphyrins (H₂TPP and H₂TTPP) were carried out using the QCM strategy [21]. Other experimental approaches can be applied for the investigation of adsorption mechanism [22, 23] but, the QCM technique is selected in this work for many reasons. Firstly, the metal porphyrin complexes do not require an inert environment and they are stable in the presence of water. Secondly, the use of the QCM technique enables to plot the adsorption curves which describe the complexed amount of aluminium ions on porphyrins at different temperatures. Lastly, the microscopic characteristics of the resulting film can be followed by easily fitting the experimental isotherms with mathematical models [21].

According to the literature, the physical models were adopted by numerous authors to examine the adsorption problem. Importantly, the analytical adsorption models of the present investigation were established through the innovative statistical physics theory [24, 25] which provides a new vision about the metalloporphyrin description. Based on this idea, the fundamental aim of the modeling work of adsorption isotherms is to find the sufficient systematic model that can anticipate physical insights of porphyrins adsorption isotherms based on the physicochemical parameters of the statistical physics models [26].

2. Experimental adsorption isotherms

2.1. Materials

The Aluminium(III) chloride with the formula AlCl₃ and the Aluminium(III) sulfate Al₂(SO₄)₃ are the tested adsorbates in the paper.

The tetrakis(4-tolylphenyl)porphyrin(H₂TTPP) and the tetraphenylporphyrin (H₂TPP) are the porphyrins used in these experiments. These two porphyrins were used because all the metals could be inserted in their cavities. They were synthesized based on published method (Adler-Longo strategy) [27].
Fig. 2 showed the synthesis methods of Porphyrins H₂TPP and H₂TTPP.

H₂TPP (Fig. 2a) was synthesized through the reaction between propanoic acid (2L) and benzaldehyde (40mL). The synthesis of H₂TTPP (Fig. 2b) was performed by introducing the 4-tolualdehyde (12.5 g) with the propanoic acid (110mL). Note that the synthesis of the two tested adsorbent has been performed by following the same procedure (reflux for 30 min, allowing to cool, filtration and drying under vacuum for 3 hours). The dried solid mass of H₂TPP was 9.76 g while the obtained mass of H₂TTPP was 3 g.

The two solid compounds of porphyrins were dissolved in chloroform giving two solutions with concentration of 2.9 10⁻² M. The synthesis of porphyrins H₂TPP and H₂TTPP was directed to the detection of the cationic aluminum (III). The complexed mass of metallic aluminum into the porphyrins rings was controlled using the QCM apparatus.

2.2. Experimental adsorption measurements

The experimental adsorption data were obtained through the well-known QCM method [28-32]. First of all, a chemical functionalization of the gold electrode of the quartz crystal was performed by doping 50 µL of adsorbent (H₂TPP or H₂TTPP) using the spin coating technique [33]. Then, volumes of adsorbate were added from stock solutions of aluminium(III) chloride or aluminium(III) sulfate in the reactor (100 mL) containing the adsorption cell (functionalized quartz crystal). The QCM apparatus indicated the frequency variation after each adsorbate injection.

The adsorbed mass Qₐ of aluminum ions on the surface after each injection was determined from the frequency variation using the Sauerbrey’s equation [34-37].

The experimental adsorbed quantities of aluminum chloride and aluminum sulfate on H₂TPP and H₂TTPP are plotted in Fig. 3 at 280-320K.

2.3. Results of experimental measurements
Observing the experimental data of the four adsorption systems, it is clear that the isotherms of aluminum chloride on H$_2$TPP and H$_2$TTPP (systems (a) and (b)) show the same behaviour (a unique saturation level for all the temperatures). Whereas, the aluminum sulfate isotherms (systems (c) and (d)) present two stability states. It can be suggested that the two tested porphyrins H$_2$TPP and H$_2$TTPP adsorb only one layer of aluminium (III) for AlCl$_3$ while, many adsorbed layers are formed in the case of Al$_2$(SO$_4$)$_3$. The multilayer ionic adsorption of aluminum sulfate takes place via the layer by layer process which is based on charge neutralization between particles having opposite charge signs (anions and cations) [24, 25 and 38]. We give in Fig. 4 an approximate image describing the mono-layer and the multi-layer complexations of the two porphyrins H$_2$TPP and H$_2$TTPP.

In addition, comparing the performance of the four adsorption systems in terms of quantity, we can note the following order of adsorption performance: $Q_A$ (system (b)) > $Q_A$ (system (d)) > $Q_A$ (system (a)) > $Q_A$ (system (c)). The adsorbed quantities are the highest for AlCl$_3$-H$_2$TTPP. Then, the adsorption compounds aluminum chloride and porphyrin H$_2$TTPP can be recommended for a real application of metalloporphyrin complex. In the following section, the microscopic investigation of this experimental result is carried out through the physical modeling of the experimental isotherms.

3. Theory/calculation

3.1. Statistical physics theory

The estimated values of the physical model parameters represent the key to understand the adsorption mechanism. The first progress of this physical treatment is observed against the most known empirical equation elaborated by Langmuir et al. [39]. Langmuir model assumed that an adsorbent site can received only one particle without considering the external factors. In general, this assumption led to wrong scientific conclusions. On contrary, our statistical physics models correct this assumption by introducing a parameter defined by the number of
adsorbed particles per adsorption site; it is noted in general by ‘n’. This correction can simply provide useful interpretations regarding the adsorption mechanism.

Based on the adsorption isotherms profiles, our statistical physics models can suggest different adsorption energies that are linked to various functional groups of the adsorbent surface contrary to the traditional models like Langmuir [39] and Freundlich [40]. In the same direction, the statistical physics models are able to estimate the total number of the formed layer at all reaction temperatures [24-26]. It should be also mentioned that the multi-layer adsorption of charged ions can be only carried out via a layer by layer (LBL) process [25, 38].

A general analysis of the adsorption data led to test two models: monolayer model for AlCl₃ and LBL multilayer model for Al₂(SO₄)₃. The modeling work is then arranged as follows: (a), it is worth to mention the general methodology which allows developing the physical models expressing the adsorbed quantity as a function of concentration. (b), the statistical physics model can be applied and discussed on the experimental adsorption data, (c), the choice of the adopted model led to describe the adsorption reaction via its parameters.

**3.1.1. Advanced adsorption models**

To establish the physical models expressions, the equilibrium of the adsorption reaction can be expressed via the next equation [25, 41]:

\[
nA^+ S \leftrightarrow A_n^\text{-S}
\]

where, A represents the tested adsorbate (AlCl₃ or Al₂(SO₄)₃), S is the adsorbent receptor site of the porphyrin (H₂TPP or H₂TTPP) and Aₙ-S is the resulting complex. The variable n is a stoechiometric coefficient that represents the number of bonded ions per adsorbent site. In general, this parameter can identify the nature of the adsorption process (n≤0.5: multi-interaction process, n≥ 1 multi-ionic process) [42, 43].
The studied system is supposed in the grand-canonical situation. It is characterized by the chemical potential (μ) and the temperature (T) imposing from the outside towards the considered system. The general expression of the partition-function of the grand-canonical ensemble is written as a function of the occupation number (Nᵢ), the adsorption energy (-Eᵢ) and the Boltzmann factor (β) [41]:

\[ z_{ge} = \sum_{N_i} e^{-\beta(-E_i - \mu)N_i} \]  \hspace{1cm} (2)

Concerning the adsorption via a formation of one adsorbed layer, it can be expressed by: [43]:

\[ z_{ge} = 1 + e^{\beta(E + \mu)} \]  \hspace{1cm} (3)

For the multi-layer adsorption process (LBL adsorption), two energies can be responsible for this process. Note that the first energy (-E₁) can characterize the adsorption of the first layer; and the second energy (-E₂) is in relationship with the formation of the additional formed layers. The partition function is written as [42]:

\[ z_{ge} = 1 + e^{\beta(E_1 + \mu)} + \sum_{N_i=2}^L e^{-\beta(-E_i - (N_i-1)E_2 - N_i\mu)} \]  \hspace{1cm} (4)

We calculate the average number of occupation of Pₘ porphyrins sites for both models using the next equation [41, 44]:

\[ N_o = \frac{p_m}{\beta} \frac{\partial \ln(z_{ge})}{\partial \mu} \]  \hspace{1cm} (5)

In this modeling work, we apply the chemical potential coupled to the ideal gas approach (μ₀). In the presence of this mean potential, we can consider that one individual particle has no interaction with the rest of the system like an ideal fermions gas of electrons. It can be
written as a function of the partition-function of translation \((z_{Tr})\) and the number of adsorbates \((N)\) [40, 44 and 45]:

\[
\mu_p = \frac{1}{\beta} \ln \left( \frac{N}{z_{Tr}} \right)
\]  

(6)

Finally, the adsorbed amount expression \((Q_a)\) is determined by the next equation [41, 44]:

\[
Q_a = n^* N_0
\]  

(7)

The monolayer model of the AlCl\(_3\) adsorption with one level of energy is:

\[
Q_a = nP_m \times \left( \frac{c}{c_{1/2}} \right)^n \left( 1 + \left( \frac{c}{c_{1/2}} \right)^n \right)^{-1}
\]  

(8)

Where, \(c_{1/2}\) involves the molar adsorption energy (-\(\Delta E_{1/2}\)) and the adsorbate solubility. It has the following formula:

\[
c_{1/2} = S e^{\frac{\Delta E_{1/2}}{RT}}
\]  

(9)

The multilayer model includes two energetic coefficients \(c_1\) and \(c_2\) involving two molar adsorption energies (-\(\Delta E_1\)) and (-\(\Delta E_2\)). It has the next expression:

\[
Q_a = nP_m \times \left[ \frac{\left( \frac{c}{c_1} \right)^n + \left( \frac{c}{c_2} \right)^n \left( 1 - 2\left( \frac{c}{c_2} \right)^{nL} - L\left( \frac{c}{c_2} \right)^{nL+1} \right) + \left( \frac{c}{c_2} \right)^n \left( 1 - \left( \frac{c}{c_2} \right)^{nL} \right) \right]}{(1 - \left( \frac{c}{c_1} \right)^n)(1 - \left( \frac{c}{c_2} \right)^n) + \left( \frac{c}{c_1} \right)^n \left( 1 - \left( \frac{c}{c_2} \right)^n \right)} \right]
\]  

(10)
where:

\[
c_1 = Se^{\frac{\Delta E_1}{RT}}
\]

\[
c_2 = Se^{\frac{\Delta E_2}{RT}}
\]

3.1.2. Adjustment of statistical physics model with experimental isotherms

An adjustment of the experimental isotherms with the two physical models is performed by means of a numerical fitting program. The criterions to adopt a physical model are the RMSE coefficient (Residual-root-mean-square-error) and the determination coefficient \(R^2\) [46].

Table 1 shows the adjustment coefficients values.

Table 1 indicates that the aluminum chloride isotherms (systems (a) and (b)) can be interpreted by the mono-layer model (\(R^2 \approx 1\) and \(\text{RMSE} < 1\) for the three reaction temperatures). However, according to Table 1, the aluminum sulfate adsorption (systems (c) and (d)) should be described via the multilayer model. In this case, many adsorbed layers are formed based on charge neutralization between cations (\(\text{Al}^{3+}\)) and anions (\(\text{SO}_4^{2-}\)).

3.2. Analysis of physicochemical parameters

The monolayer model equation was governed by three parameters (number of aluminum ions per receptor site \(n\), density of porphyrin sites \(P_M\) and \(c_{1/2}\) (Eq.9)). The multi-layer adsorption can be interpreted via five physicochemical variables (\(n\) and \(P_M\) (steric variables), \(L\) (number of adsorbed layers), and \(c_1\) and \(c_2\) (Eqs. 11 and 12)).

All fitting parameters values are given in Table 2. The study of the adsorption models parameters attributes interesting microscopic interpretations of the porphyrins complexation.

3.2.1. Steric interpretation
Basically, the parameters \( n \) and \( P_M \) are typified by a steric aspect. The product of these parameters is the result of the maximum adsorption capacity [47].

The evolution of the two steric parameters versus temperature is reported in Fig. 5.

From Fig. 5a, the \( n \) values are found inferior to 1 for the four adsorption systems. For example, regarding the values of this parameter that are inferior to 0.5, it is clear that the adsorption process is a multi-interaction process (the ions can be interacted with at least two adsorption sites) [43]. In this situation, we define the coefficient \( n' = 1/n \) representing the number of receptor sites interacting with one adsorbed particle [25, 42]. In fact, the equilibrium equation of the adsorption reaction (Eq. 1) can be written as [24, 25]:

\[
A + n'S \rightleftharpoons A-S_{n'}
\]

where, \( A \) is the adsorbate (aluminum particles), \( S \) is the receptor site of porphyrin \( H_2TPP \) or \( H_2TTPP \), \( A-S_{n'} \) is the formed complex (aluminum-porphyrins).

The \( n' \) values of the two tested adsorbents are indicated in Table 3.

Generally, an increase in the value of \( n' \) reflects that an aluminium particle is associated with many porphyrin sites which suggest that it can easily escape from a receptor site to a neighbor one. Comparing the \( n' \) values of the four adsorption systems we find that \( n'(H_2TPP) > n'(H_2TTPP) \) for the two adsorbates. We find also that till four receptor sites of tetraphenylporphyrin (\( H_2TPP \)) can be bonded with one aluminum ion. This leads to conclude that the interaction between the aluminum ions and the tetraphenylporphyrin cavities is weak so the adsorbed aluminum can move from the adsorbent site at any time. On contrary, all \( n' \) values of \( H_2TTPP \) are near the unit which reflects a strong interaction \( Al^{3+}-H_2TTPP \). Therefore, it can be concluded that the use of \( H_2TTPP \) favors the stability of aluminum-porphyrin complex.
Furthermore, it is noted from Fig. 3 that the temperature exerts exactly the same influence on the four complexation systems: once the temperature increases, the adsorption capacities increase. This is often explained from Fig. 5 which shows that the values of the coefficients n (Fig. 5a) and PM (Fig. 5b) rise with the temperature. It can be concluded that the thermal agitation effect favors the adsorption dynamics: the rise of temperature active other receptor site to contribute in the complexation process.

For aluminium sulfate adsorptions, the number L is also a steric parameter which characterizes the number of layers that are adsorbed with the second energy level (-E2). According to Fig. 5c, the increase of the temperature disfavors the formation of layers in the multi-layer region indicating a strong interaction between the adsorbates far from the surface [47].

3.2.2. Energetic calculation

According to Eqs. 9, 11 and 12, the molar adsorption energies of the four complexation systems can be calculated by means of the energetic coefficients c1/2, c1 and c2 of the two physical models [38, 47]:

For aluminum chloride adsorption:

$$-\Delta E_{1/2} = RT \ln \left( \frac{c_{1/2}}{S(AlCl_3)} \right)$$

(14)

For aluminum sulfate adsorption:

$$-\Delta E_1 = RT \ln \left( \frac{c_1}{S(Al_2(SO_4)_3)} \right)$$

(15)

$$-\Delta E_2 = RT \ln \left( \frac{c_2}{S(Al_2(SO_4)_3)} \right)$$

(16)
According to Table 4, for aluminum sulfate adsorption, it is obviously remarked that the calculated values of $|(-\Delta E_1)|$ which characterizes the aluminum-porphyrin interaction are greater than those of $|(-\Delta E_2)|$ (interaction between the adsorbed layers [38]). Therefore, we can conclude that the interaction $|(-\Delta E_1)|$ should be compared to the others adsorption systems energies ($|(-\Delta E_{1/2})|$) to evaluate the stability of the formed metalloporphyrin complexes.

Comparing the $|(-\Delta E_{1/2})|$ and the $|(-\Delta E_1)|$ values of the four complexation systems (Table 4 and Fig. 6), we observe that: $|(-\Delta E_{1/2})|$ (AlCl$_3$-H$_2$TTPP) > $|(-\Delta E_1)|$ (Al$_2$(SO$_4$)$_3$- H$_2$TTPP) > $|(-\Delta E_{1/2})|$ (AlCl$_3$- H$_2$TPP) > $|(-\Delta E_1)|$ (Al$_2$(SO$_4$)$_3$- H$_2$TPP). This result indicates that the affinity of the porphyrins H$_2$TTPP cavities to the aluminum ions is more important compared to the tetraphenylporphyrin sites and confirms that aluminum chloride- porphyrin (H$_2$TTPP) is the best adsorption system suited for metalloporphyrin complex application.

Moreover, the adsorption energies $|(-\Delta E_{1/2})|$ of AlCl$_3$-H$_2$TTPP are superior to 40 kJ/mol for all the temperatures. For this system, the adsorption is carried out via a chemical process involving covalent bonds [43, 48 and 49]. Whereas, all the others adsorption mechanisms take place via a physical process since they present adsorption energies values lower than 40 kJ/mol [46, 48 and 50].

Finally, it can be seen that all the adsorption energies rise with the expansion of the temperature (Fig. 6). This can be interpreted by the endothermic behavior of the four adsorption mechanisms.

4. Results and discussion

The development of the two advanced adsorption models (mono-layer and multi-layer) allows to the determination of the physicochemical parameters which govern the complexation dynamic. The variations of these physicochemical parameters against the temperature are interpreted in order to compare the performance of the adsorption materials.
It is noticed that the thermal agitation causes an increase of n and P_M. these two parameters shows the same behavior via the temperature because firstly, they are both steric coefficients and secondly, they are related to the monolayer adsorbed quantity Q_{a,mono} with the following expression Q_{a,mono} = n \times P_M. It is the same remark for the adsorption energies. We discovered that the value of |(-\Delta E_{1/2})|, |(-\Delta E_1)| and |(-\Delta E_2)| increase by increasing the temperature. The behavior of these parameters is in agreement with the expansion of the adsorbed amounts via the temperature shown in Fig. 3 for the four complexation systems. On the other hand, the parameter L decreases with the rise of temperature for the multi-layer adsorption of aluminum sulfate. This parameter showed a behavior opposite to the adsorbed quantity behavior so it is not dominant in the adsorption mechanism.

Overall, the four adsorption systems can be evaluated based on their energetic aspects. In this work, we concluded that the adsorption energies |(-\Delta E_{1/2})| and |(-\Delta E_1)| are the dominant elements in the adsorption processes because |(-\Delta E_2)| is not considered since it characterizes the adsorption process in the multi-layer region (adsorbate-adsorbate interaction). Thus, the selection of the best adsorption materials that can be used for metallo-porphyrin application depends on the interpretations given by |(-\Delta E_{1/2})| and |(-\Delta E_1)|.

The analysis of the performance of the four adsorption systems, by the intermediate of the adsorption energies, showed that aluminum chloride-tetrakis(4-tolylphenyl)porphyrin(H_2TTPP) is the best adsorbate-adsorbent system in terms of stability and can be used in a genuine industrial application.

5. Conclusion

It was ensured in this work that the experimental QCM tool is useful to control the adsorption of aluminum chloride and aluminum sulfate on porphyrins H_2TTPP and H_2TPP. By analyzing the experimental isotherms, the AlCl_3- H_2TTPP complex was found the best
adsorption system in terms of reproducibility since it showed the highest adsorbed quantities. Theoretically, physical models were suggested for the microscopic analysis of experimental results. The aluminum chloride adsorption was described by a mono-layer model whereas the adsorption isotherms of aluminum sulfate were modeled by the LBL multilayer model. The physicochemical parameters of these models gave interesting microscopic insights about the two porphyrins complexation. Indeed, it was found that the aluminum adsorption was governed by a multi-interaction process for the four adsorption systems. The thermal agitation caused an increase of the density of occupied sites $P_M$ which indicated that some porphyrin sites contribute to the adsorption only at high temperature. The energetic study, through adsorption energies calculation, demonstrated that the adsorption of AlCl$_3$ on H$_2$TTPP is a chemisorption process involving covalent bonds.

**Author contribution statement**

The contribution of each author is detailed as follows:

1- Dr. Mohamed Ben Yahia, Dr. Zaineb Elqahtani are responsible for the achievement of the experimental part and the materials used (Quartz Crystal Microbalance apparatus) for the measurement of experimental adsorption isotherms of aluminum ions onto porphyrins molecules.

2- Pr. Nada Alfryyan, Dr. Shatha Aldaghfaq and Pr. Fatma Aouaini are responsible for the theoretical characterization of the experimental isotherms. They developed the advanced statistical physics models in order to interpret the complexation phenomenon at the microscopic scale.

All authors reviewed the manuscript.
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6. References

[1] J. Fuchs, S. Weber, R. Kaufmann, Genotoxic potential of porphyrin type photosensitizers with particular emphasis on 5-aminolevulinic acid: implications for clinical photodynamic therapy, Free Radical Biology & Medicine. 28 (2000) 537-548.

[2] G. Simonneaux, H. Srour, P. Le Maux, S. Chevance, D. Carrie, Metalloporphyrin Symmetry in Chiral Recognition and Enantioselective Catalysis, Symmetry. 6 (2014) 210-221.

[3] B. Saha, A. G. Petrovic, A. Dhamija, N. Berova, S. P. Rath, Complexation of Chiral Zinc(II) Porphyrin Tweezer with Achiral Aliphatic Diamines Revisited: Molecular Dynamics, Electronic CD, and $^1$H NMR Analysis, Inorg. Chem. 58 (2019) 11420-11438.

[4] J. Du, C. Miao, C. Xia, Y. M. Lee, W. Nam, W. San, Mechanistic Insights into the Enantioselective Epoxidation of Olefins by Bioinspired Manganese Complexes: Role of Carboxylic Acid and Nature of Active Oxidant, ACS Catal. 8 (2018) 4528-4538.

[5] E. Stulz, S. M. Scott, N. F. Ng, A. D. Bond, S. J. Teat, S. L. Darling, N. Feeder, J. K. M. Sanders, Construction of Multiporphyrin Arrays Using Ruthenium and Rhodium Coordination to Phosphines, Inorg. Chem. 42 (2003) 6564- 6574.

[6] M. M. Pereira, L. D. Dias, M. J. F. Calvete, Metalloporphyrins: Bioinspired Oxidation Catalysts, ACS Catal. 8 (2018) 10784-10808.
[7] M. Costas, Selective C–H oxidation catalyzed by metalloporphyrins, Coord. Chem. Rev. 255 (2011) 2912-2932.

[8] M. Guo, T. Corona, K. Ray, W. Nam, Heme and Nonheme High-Valent Iron and Manganese Oxo Cores in Biological and Abiological Oxidation Reactions, ACS Cent. Sci. 5 (2019) 13-28.

[9] M.K. Peters, S. Hamer, T. Jäkel, F.Röhricht, F. D. Sönntichsen, C. von Essen, M. Lahtinen, C. Naether, K. Rissanen, R. Herges, Spin Switching with Triazolate-Strapped Ferrous Porphyrins, Inorg. Chem. 58 (2019) 5265-5272.

[10] Q. Liu, C. Guo, Theoretical studies and industrial applications of oxidative activation of inert C-H bond by metalloporphyrin-based biomimetic catalysis, Sci. China. Chem. 55 (2012) 2036-2053.

[11] N. Chaudhri, L. Cong, A. S. Bulbul, N. Grover, W. R. Osterloh, Y. Fang, M. Sankar, K. M. Kadish, Structural, Photophysical, and Electrochemical Properties of Doubly Fused Porphyrins and Related Fused Chlorins. Inorg.Chem. 59 (2020) 1481-1495

[12] D. K. Stevenson, R. Ji. Wong, Metalloporphyrins in the management of neonatal hyperbilirubinemia, Semin. in Fetal. Neonat. M. 15 (2010) 164-168.

[13] M. S. Liao, S. Scheiner, Electronic structure and bonding in metal porphyrins, metal=Fe, co, Ni, cu, Zn, J. Chem. Phys. 117 (2002) 205-219.

[14] I. H. A. Badr, M. E. Meyerhoff, Highly Selective Optical Fluoride Ion Sensor with Submicromolar Detection Limit Based on Aluminum(III) Octaethylporphyrin in Thin Polymeric Film, J. Am. Chem. Soc. 127 (2005) 5318-5319.
[15] L. Li, Y. Zhang, Y. Li, Y. Duan, Y. Qian, P. Zhang, Q. Guo, J. Ding, Polymeric Membrane Fluoride-Selective Electrodes Using Lewis Acidic Organo-Antimony(V) Compounds as Ionophores, ACS Sens. 5 (2020) 3465-3473.

[16] N. K. Joon, N. He, T. Ruzgas, J. Bobacka, G. Lisak, PVC-Based Ion-Selective Electrodes with a Silicone Rubber Outer Coating with Improved Analytical Performance, Anal. Chem. 91 (2019) 10524-10531.

[17] X. Xie, E. Bakker, Ion selective optodes: from the bulk to the nanoscale, Anal. Bioanal. Chem. 407 (2015) 3899-3910.

[18] Y. Qin, H. Guo, X. Sheng, X. Wang, F. Wang, Aluminum Porphyrin Complex with High Activity and Selectivity for Cyclic Carbonate Synthesis, Green Chem. 17 (2015) 2853-2858.

[19] P. P. Kumar, B. G. Maiya, Aluminium(III) porphyrin based dimers and trimers: synthesis, spectroscopy and photochemistry, New J. Chem. 27 (2003) 619-625.

[20] S. Richeter, J. Thion, A. v. d. Lee, D. Leclercq, Synthesis, structural characterization and properties of aluminum (III) meso-tetraphenylporphyrin complexes axially bonded to phosphinate anions, Inorg. Chem. 45 (2006) 10049-10051.

[21] D. Wang, P. Mousavi, P. J. Hauser, W. Oxenham, C. S. Grant, Quartz crystal microbalance in elevated temperature viscous liquids: Temperature effect compensation and lubricant degradation monitoring, Colloids and Surfaces A: Physicochem. Eng. Aspects. 268 (2005) 30-39.

[22] G. de Ruiter, M. Lahav, M. E. van der Boom, Pyridine Coordination Chemistry for Molecular Assemblies on Surfaces, Acc. Chem.Res.47 (2014) 3407-3416.
[23] S. H. Cho, S. T. Nguyen, T. Hupp, Manganese porphyrin multilayer films assembled on ITO electrodes via zirconium phosphonate chemistry: chemical and electrochemical catalytic oxidation activity, Topics in Catalysis. 34 (2005) 101-107.

[24] M. Ben Yahia, M. B. Yahia, F. Aouaini, S. Knani, H. Al-Ghamdi, E. S. Almogait, A. B. Lamine, Adsorption of sodium and lithium ions onto helicenes molecules: Experiments and phenomenological modeling, J. Mol. Liq. 288 (2019) 110988.

[25] S. Knani, N. Khalifa, M. Ben Yahia, F. Aouaini, M. Tounsi, Statistical physics study of the interaction of the 5, 10, 15, 20-tetrakis (4-tolylphenyl) porphyrin (H₂TTPP) with magnesium ion: New microscopic interpretations, Arab. J. Chem. 13 (2020) 4374-4385.

[26] A. Nakbi, M. Bouzid, F. Ayachi, F. Aouaini, A. B. Lamine, Investigation of caffeine taste mechanism through a statistical physics modeling of caffeine dose-taste response curve by a biological putative caffeine adsorption process in electrophysiological response. Prog. in Biophys. Mol. Bio. 147 (2019) 70-85.

[27] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Korakoff, A simplified synthesis for meso-tetraphenylporphine, J. Org. Chem. 32 (1967) 476-476.

[28] K. Kurzątkowska, D. Shpakovsky, J. Radecki, H. Radecka, Z. Jingwei, E. Milaeva, Iron (III) porphyrin bearing 2,6-di-tert-butylphenol pendants deposited onto gold electrodes for amperometric determination of L-histidine, Talanta. 78 (2009) 126-131.

[29] X. Huang, Q. Bai, J. Hu, D. Hu, A Practical Model of Quartz Crystal Microbalance in Actual Applications, Sensors. 17 (2017) 1781-1785.

[30] B. Ballarin, S. Masiero, R. Seeber, D. Tonelli, Modification of electrodes with porphyrin-functionalised conductive polymers, J. Electroanal. Chem. 449 (1998) 173-180.
[31] C. K. O’Sullivan, G.G. Guilbault, Commercial quartz crystal microbalances theory and applications, Biosens. Bioelectr. 14 (1999) 663-670.

[32] X. Huang, K. Nakanishi, N. Berova, Porphyrins and Metalloporphyrins: Versatile Circular Dichroic Reporter Groups for Structural Studies, Chirality. 12 (2000) 237-255.

[33] M. P. Soriaga, Ultra-high vacuum techniques in the study of single-crystal electrode surfaces, Progress in Surface Science. 39 (1992) 325-443.

[34] G. Sauerbrey, Use of quartz vibration for weighing thin films of a microbalance, Z. Phys. 155 (1959) 206-212.

[35] V. Tsionsky, E. Gileadi, Use of the quartz crystal microbalance for the study of adsorption from the gas phase, Langmuir. 10 (1994) 2830-2835.

[36] K. K. Kanazawa, J. G. Gordon, Frequency of a quartz microbalance in contact with liquid, Anal. Chem. 57 (1985) 1770-1771.

[37] M. Urbakh, L. Daikhin, Influence of the Surface Morphology on the Quartz Crystal Microbalance Response in a Fluid, Langmuir. 10 (1994) 2836-2841.

[38] M. Ben Yahia, S. Knani, H. B. L. Hsan, M. B. Yahia, H. Nasri, A. B. Lamine, Statistical studies of adsorption isotherms of iron nitrate and iron chloride on a thin layer of porphyrin, J. Mol. Liq. 248 (2017) 235-245.

[39] I. Langmuir, The adsorption of gases on plane surfaces of Glass, Mica and Platinium, Am.Chem.Soc. 40 (1918) 1361-1403.

[40] F. M. H. Freundlich, Over the adsorption in solution, J. phys. chem. 57 (1906) 385-471.

[41] A. Ben Lamine, Y. Bouazra, Application of statistical thermodynamics to the olfaction mechanism, Chem. Senses. 22 (1997) 67-75.
[42] S. Knani, M. Mathlouthi, A. Ben Lamine, Modeling of the psychophysical response-curves using the grand canonical ensemble in statistical physics, Food Biophys. 2 (2007) 183-192.

[43] L. Sellaoui, E. F. Soetaredjo, S. Ismadji, B. A. Petriciolet, C. Belver J. Beda, B. A. Lamine, A. Erto, Insights on the statistical physics modeling of the adsorption of Cd$^{2+}$ and Pb$^{2+}$ ions on bentonite-chitosan composite in single and binary systems, Chem. Eng. J. 354 (2018) 569-576.

[44] H. Alyousef, F. Aouaini, M. Ben Yahia, New insights on physico-chemical investigation of water adsorption isotherm into seed of dates using statistical physics treatment: Pore size and energy distributions, J. Mol. Liq. 298 (2020) 112041.

[45] B. Diu, C. Guthmann, D. Lederer, B. Roulet, Physique Statistique, Hermann, Paris, 1989.

[46] M. Bouzid, Q. Zhu, D. M. Geoff, A. Ben Lamine, New insight in adsorption of pyridine on the two modified adsorbents types MN200 and MN500 by means of grand canonical ensemble, J. Mol.Liq. 263 (2018) 413-421.

[47] F. Aouaini, S. Knani, M. Ben Yahia, N. Bahloul, N. Kechaou, A. Ben Lamine, Application of Statistical Physics on the Modeling of Water Vapor Desorption Isotherms, Dry. Tech. 32 (2014) 1905-1922.

[48] C.L. Sun, C.S. Wang, Estimation on the intramolecular hydrogen-bonding energies in proteins and peptides by the analytic potential energy function, J. Mol. Struct. 956 (2010) 38-43.

[49] B. yon Oepen, W. Kördel, W. Klein, Sorption of nonpolar and polar compounds to soils: Processes, measurements and experience with the applicability of the modified OECD-guideline 106, Chemosphere. 22 (1991) 285-304.
[50] B. Yavorski, A. Detlaf, Aide mémoire de Physique. Edition Mir-Mouscou, Le-Livre (SABLONS, France), France, 1975.