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Optimization of the drying of *Moringa oleifera* leaves by determination of thermophysical parameters

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ABSTRACT

Moringa oleifera leaves are increasingly used as a dietary supplement. The present study deals with the estimation of its thermophysical properties. It is based on the Clausius-Clayperon and Gibbs-Helmholtz equations. This study required knowledge of the sorption isotherms obtained by the static gravimetric method in the relative humidity range of 5.4 to 97% and the temperatures of 30, 35, 45 and 55 °C. The BET models (1938), Smith (1947), Henderson (1952), Iglesias (1981) and GAB (1985) are used for the smoothing of the experimental points. The isotherms obtained are of type II and characterized by a sigmoid shape. The theoretical curves of GAB and Smith show a better similarity with the experimental curves. The monolayer moisture content (Xm) is 8.54/7.62% at 30 °C; 7.0/5.52% at 35 °C; 6.74/ 5.41% at 45 °C and 5.45/4.65% at 55 °C respectively for the GAB and BET models. The net isosteric heat *(qst)* and desorption differential entropy *(ΔS)* tend towards zero for very high moisture contents. The activation energy of desorption of the *Moringa oleifera* leaves in the temperature range tested is -13.1010 kJ/mol. Isokinetic temperature *(Tβ)* and the average harmonic temperature *(Thm)* are respectively 314.172 K and 314.459 K while the free energy *(ΔGβ)* is 308.18 J/mole.

Keywords: Desorption isotherm, Modelization, Isosteric heat, Differential Entropy, Activation energy.

INTRODUCTION

The *Moringa oleifera* leaves, a plant with the multiple uses, are used as a food supplement for the fight against protein related energy malnutrition and micronutrient deficiencies (Houndji et al., 2012) because of their nutritional (Songre-Ouattara et al., 2016), therapeutic (Okorondu et al., 2013; Ndiayesy et al., 2016), agribusiness (Mawouma and Mbofung, 2014) properties. The mastery of drying operations is essential to guarantee over long periods, a better conservation of these leaves. The knowledge of water activity in the matter has considerable interest in food technology. Indeed, the thermodynamic activity of water conditions the speed and intensity of the chemical reactions (oxidation, Maillard

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reaction), enzymatic reactions, the development and the physiology of the microorganisms and modifies most of the rheological, mechanical and organoleptic properties of foods (Kakou et al., 2015; Simo-Tagne et al., 2016). The sorption isotherms, are curves which present for a given temperature T, the equilibrium moisture content (*Xeq*) of a product according to the value of water activity (a_w) or relative humidity (HRE) of air in equilibrium with the product (Ahouannou et al., 2010). In accordance with the fixed relative humidity, the product can adsorb or lose moisture with the surroundings, thus the phenomena of adsorption or desorption, respectively, can be present (Coronel et al., 2016). During a drying process, the desorption isotherms inform about the limit values of moisture content of the product during the process and consequently promote the optimization of the operation (Benhamou et al., 2010). In the case of storage operations, the isotherm has as role to indicate the hygroscopic nature of a product (Ahouannou et al., 2010; Aguirre-Ldredd et al., 2017), which allows predicting the influence of the variation of the relative humidity of the atmosphere of storage on the hygroscopic product stability, and to make an estimate of the water quantity which would be adsorbed depending on the storage time. The knowledge and understanding of moisture sorption isotherms for food products is of great importance to the optimisation of the process of drying, for assessing packaging problems, for modelling moisture changes which occur during drying, for predicting shelf-life stability, for ingredient mixing predictions, etc. (Aguirre-Ldredd et al., 2017). Thus, we can predict the product storage life in a certain atmosphere (Ahouannou et al., 2010). Various mathematical models were proposed to describe the isothermal curves of water vapor sorption of the foodstuffs. These models, and in particular the simplest expressions (linear) of the water content according to the water activity are particularly useful in agribusiness (Coronel et al., 2016). All these models, which are the theoretical base or empirical, can help to understand the capacity of water adsorption by the product in the monolayer or multilayer and sometimes to determine the adsorbent surface of the product.

This research aims at determining the isotherm desorption of *Moringa oleifera* leaves and then to evaluate the thermodynamic properties to optimise the hygroscopic equilibrium conditions in order to improve the quality of the product and a better conservation during its drying and stocking process.

MATERIALS AND METHODS

Modelization isotherms

The theoretical reproducibility of the desorption curves obtained experimentally was made following five (5) models described in the literature and commonly used for an optimal adjustment. It is:

- ***BET Model (1938)***

The BET model is most often applied for fruits and foods. This equation provides the value of the monolayer moisture content, which is an important parameter in the study of food deterioration. This model is valid until aw = 0.5 only (Akoy et al., 2013). The BET model is represented by the following equation:

$$X_{eq} = \frac{X_m\, C\, a_w}{(1-a_w)(1+(C-1)a_w)} \quad (1)$$

Where: Xeq = equilibrium moisture content (gH_2O/gms); Xm= BET monolayer moisture content (gH_2O/gms); C= BET constant related to the net heat of sorption; a_w = water activity.

To obtain the two *Xm* and *C* parameters, equation {(Eq.1)} was linearized (Timmermann, 2003) as follows:

$$\frac{a_w}{(1-a_w)X_{eq}} = \frac{1}{CX_m} + \frac{C-1}{CX_m}a_w \qquad (2)$$

Equation {(Eq.2)} can easily be transformed into a linear equation having the following form:

$$\frac{a_w}{(1-a_w)X_{eq}} = Aa_w + B \quad (3)$$

where: $A = \frac{C-1}{CX_m}$; $B = \frac{1}{CX_m}$

A linearization of the curve $\frac{a_w}{(1-a_w)}X_{eq} = f(a_w)$ by the least squares method, allows determining the slope (A) and the ordinate at the origin (B). The Xm and C parameters are then determined by the following relationships:

We know that

$$f(a_w) = \frac{a_w}{(1-a_w)}X_{eq}$$

$$so\ X_m = \frac{1}{(A+B)} \quad (4) \quad \text{and}$$

$$C = \frac{A+B}{B} \quad (5)$$

- ***Smith (1947)***

It's an equation with two parameters frequently used to simulate the isotherms of the biological products. It is form:

$$X_{eq} = K_1 - K_2 ln(1-a_w) \qquad (6)$$

A linearization of the curve $X_{eq} = f\big(ln(1-a_w)\big)$ allows determining the constants K_1 and K_2 of the equation.

- ***Henderson equation (1952)***

It is an empirical equation developed by Henderson and which is written as follows:

$$ln(1-a_w) = -K_1 T\left(X_{eq}\right)^{K_2} \quad \text{or}$$

$$X_{eq} = \left[\frac{-1}{TK_1}ln(1-a_w)\right]^{\frac{1}{K_2}} \qquad (7)$$

A linearization of the curve $\ln[-ln(1-a_w)] = f(X_{eq})$ by least squares allows to determine the constants K_1 and K_2 of the model.

- ***Iglesias and Chirife (1982)***

In the study of the behaviour in moisture sorption of rich foods in carbohydrates where there is dissolution of sugars, these authors propose the following empirical equation:

$$X_{eq} = K_1\left(\frac{a_w}{1-a_w}\right) + K_2 \qquad (8)$$

A linearization of the curve $X_{eq} = f\left(\frac{a_w}{1-a_w}\right)$ by least squares allows determining the constants K_1 and K_2 of the model.

- ***GAB Model (1985)***

This model not only allows calculating monolayer moisture content but also the heat sorption of monolayer and multilayer. It is applicable for the water activities ranging between 0.05 and 0.95 (Ferradji et al., 2008). The GAB equation is given by the following equation (Kakou et al., 2015):

$$X_{eq} = \frac{X_m\,C\,Ka_w}{(1-Ka_w)(1-Ka_w+CKa_w)} \qquad (9)$$

Where: Xeq = equilibrium moisture content (gH_2O/gms); *Xm* = GAB monolayer moisture content (gH_2O/gms); C=constant related to the monolayer heat of sorption; K = factor related to the heat of sorption of the multilayer. This equation has a similar form to BET, but has an extra constant K. BET is actually a special case of GAB, where K=1. The GAB parameters were determined following the method of the transformed form of the GAB isotherm (Timmermann, 2003). The GAB model can be rearranged to a polynomial equation as follows:

$$\frac{a_w}{X_{eq}} = \frac{K}{X_m(\frac{1-C}{C})}a_w{}^2 + \frac{C-2}{X_mC}a_w + \frac{1}{X_mKC} \quad (10)$$

The equation {(Eq.10)} can be represented by the form:

$$\frac{a_w}{X_{eq}} = \alpha a_w{}^2 + \beta a_w + \varepsilon \qquad (11)$$

Where:

$$\alpha = \frac{K}{X_m}\frac{C}{1-C}\ ; \qquad \beta = \frac{C-2}{X_mC}\ ;$$

$$\varepsilon = \frac{1}{X_mKC}$$

A polynomial direct nonlinear regression method of a_w/Xeq versus a_w was carried out using Microsoft Excel (2010) software in order to determine the values of the quadratic coefficient term α, the linear term coefficient β and the constant ε. Then the GAB parameters were calculated as follows:

$$K = \frac{\sqrt{f} - \beta}{2\varepsilon} \qquad (12)$$

$$X_m = \frac{1}{(\beta + 2K\varepsilon)} \qquad (13)$$

$$C = 2 + \frac{\beta}{K\varepsilon} \qquad (14)$$

Where: $f \equiv \beta^2 - 4\alpha\,\varepsilon$

The temperature dependency of the GAB parameters was given by the following Arrhenius-type equations:

$$K = K_o\, exp\frac{\Delta H_k}{RT} \quad et \quad C = C_o\, exp\frac{\Delta H_C}{RT}$$

with

$$\Delta H_C = H_m - H_n \quad et \quad \Delta H_k = L_v - H_n$$

Where:

C_o and K_o, are adjustable constants for the temperature effect; R= universal gas constant, (8.314 J/mol/K); T= absolute temperature (K); $H_{m=}$ total heat of sorption of the monolayer; H_n= total heat of sorption of the multilayer; L_v: latent heat of condensation of water liquid, whether 43.98 kJ/mol on the field (20 -80 °C) (Ferradji et al., 2008).

Thermodynamic properties

Determination of Isosteric Heat of Sorption

Clausius-Clapeyron equation, because of its theoretical basis, is often used in determining the total heat of sorption (Qst) of agricultural products (Kakou et al., 2015; Shittu et al., 2015). At a constant amount of sorbed water, the equation is expressed as follows:

$$\left.\frac{dlnP}{dT}\right|_X = \frac{Qst}{R_O T^2} \qquad (15)$$

Where P is the water vapour pressure of the product at the specified temperature, T, and Ro is the universal gas constant. For pure water, equation {(Eq.15)} becomes

$$\frac{dln\, P_O}{dT} = \frac{Lv}{R_O T^2} \qquad (16)$$

Where Po is the saturation water vapour pressure at the temperature, T and Lv is the heat of vaporization of pure water. Subtracting equation {(Eq.16)} from equation {(Eq.15)} yields

$$\left.\frac{dln\frac{P}{P_O}}{dT}\right|_X = \left.\frac{dln\, a_w}{dT}\right|_X = \frac{q_{st}}{R_O T^2} \qquad (17)$$

Where $q_{st} = Q_{st} - L_{v,}$ is the net isosteric heat of sorption (kJ/mol) with equilibrium moisture content (gH_2O/ms). Integrating equation {(Eq.17)} yields

$$\ln a_w = \left(\frac{-q_{st}}{R_O}\right)\frac{1}{T} + C_{st} \qquad (18)$$

Where: $C_{st,}$ is the constant of integration.

The chart representation of the curve - *ln (aw) = f(1/T)* with one moisture content constant with the value of R near, enables us to determine the slope $-q_{st}/R_o$ and the constant of C_{st} integration. Slope of isosteric and for each moisture content Xeq, we can deduce the corresponding net isosteric heat and plot the curve q_{st} = f (Xeq). A mathematical model which expresses the total heat of sorption as function of moisture is commonly cited in the literature. The equation is given as follows:

$$\text{Qst} = Lv\,[aexp(bXeq)] \qquad (19)$$

One exponential empirical correlation {(Eq.20)} can be established to describe a relation between the isosteric heat of desorption and the equilibrium moisture content (Edoun and Kuitche, 2014).

$$q_{st} = q_o\, exp\left(-\frac{X_{eq}}{X_o}\right) \qquad (20)$$

Where: q_o is the isosteric heat of sorption of the first molecule of water in the food (kJ/mol);

X_o is a characteristic moisture content (gH_2O/gms) of the food material; it is the moisture content at which the net isosteric heat of desorption has been reduced by 63%

(Edoun and Kuitche, 2014; Benseddik et al., 2014).

Enthalpy-Entropy compensation theory

The change in molar differential entropy was calculated from Gibbs-Helmholtz equation.

$$\Delta s = -\frac{q_{st} - \Delta G}{T} \qquad (21)$$

$$\Delta G = RT_O ln(\frac{P}{P_0}) = RT_O ln(a_w) \qquad (22)$$

ΔG is the free energy (kJ mol^{-1}) and Δs is the differential entropy (kJ $mol^{-1}K^{-1}$). Combining {(Eq.21)} and {(Eq.22)} gives a final relationship:

$$ln(a_w) = -\frac{q_{st}}{RT_O} + \frac{\Delta s}{R} \qquad (23)$$

The values of q_{st} and Δs were calculated from the slope of the line when ln (a_w) was plotted against 1/T at different constant moisture contents, (q_{st}/R) and the intercept (Δs/R) respectively. The enthalpy-entropy compensation theory assumes that a linear relationship exists between enthalpy and entropy as follows:

$$q_{st} = T_\beta(\Delta S) + \Delta G_\beta \qquad (24)$$

The value of T_β, which is the isokinetic temperature (K) and ΔG_β, which is the free energy at the isokinetic temperature were calculated from linear regression of q_{st} against ΔG_β values. The isokinetic temperature T_β represents the temperature at which all reactions in the series proceed at the same rate, and ΔG_β is a criterion to determine whether water vapor sorption process for material is a spontaneous (-ΔG) is or non-spontaneous process (+ΔG).T_β and ΔG_β are obtained by plotting the curve qst= f (ΔS).

The validity of the compensation theory was tested by comparing the isokinetic temperature (T_β) with the harmonic mean temperature Th_m, which is defined as (Giraldo et al., 2011; Shittu et al., 2015):

$$Th_m = \frac{n}{\sum_{i=1}^{n}\left(1/T_n\right)} \qquad (25)$$

Where: n is the total number of isotherm. The isokinetic temperature ($T\beta$) is calculated by linear regression for all the sets of data with a confidence interval of 95%:

$$T_\beta = T_\beta \pm t_{m-2^\alpha}/2\sqrt{Var(T_\beta)} \qquad (26)$$

Where:

$$T_\beta = \frac{\sum(q_{st} - \overline{q_{st}})(\Delta S - \overline{\Delta S})}{(\Delta S - \overline{\Delta S})^2} \qquad (27)$$

$$Var(T_\beta) \quad (28)$$

m is the number of (qst, ΔS) even of data, ($\overline{q_{st}}$) is the mean enthalpy, and is $\overline{\Delta S}$ the mean entropy.

Activation Energy

The activation energy is the free enthalpy which separate from the state energy transition and that of the initial state. The energy activation is roughly constant in a given interval of temperature. While inspiring to us by the equation Arrhenius, a correlation between the monolayer moisture content, X_m (GAB or B.E.T) and the temperature is established (29):

$$X_m = X^O exp\left(\frac{-E_a}{RT}\right) \qquad (30)$$

Where: E_a, activation energy **(**J/mol), X^o, the frequency collision (%MS). The graphic representation ln (X_m) = f ($1/T$), allows to determine the slope -Ea/R and the ordinate in the beginning *(ln* X^o*).*

Determination of desorption isotherms

The gravimetric static method was used for the determination of desorption isotherms of *Moringa oleifera* leaves. The experiment consists in putting the samples to be desorbed in isothermal bottles hermetic containing solutions salts saturated and maintained at temperature and relative humidity constants in a controlled drying oven (Ahouannou et al., 2010). The desorption experiments are carried out with 30 °C (ambient temperature), 35 °C, 45 °C and 55 °C and at nine values of relative humidity (Table 1).When the various equilibrium masses are obtained for the various desired climatic conditions, the samples tested are taken again then immediately placed in the drying oven of desiccation regulated with 103 °C±2. This operation allow to obtain the dry extracts of the studied samples, which undergo in this condition, the total loss free waters and bound that they contain (Ahouannou et al., 2010). The samples are regularly weighed and if at the end of 24 hours their masses do not vary any more, then the dry extract is obtained. Thus, the mass measured for each sample is regarded as the mass anhydrous (Ms). From this parameter obtained, we defined the various equilibrium moisture contents of the samples. The equilibrium moisture content of the product on dry basis is calculated by the following expression:

$$X_{eq}(\%) = 100\,\mathrm{X}\,\frac{(\mathrm{M_{eq}} - \mathrm{M_s})}{\mathrm{M_s}} \qquad (31)$$

Xeq = equilibrium moisture content of the sample (%bs); Me = equilibrium mass of the sample tested (g); Ms = mass anhydrous of the sample tested (g). For a given temperature, the various couples values obtained (H_{ri}, X_{eqi}) for i=1,.., n∈N, has allowed to plot experiments isotherms of desorption of the *Moringa oleifera* leaves. Consequently, the equilibrium moisture content of the product can be expressed by the following relation:

$$X_{eq} = f(a_w)_{T_s} \qquad (32$$

Where: Xeq = equilibrium moisture content of the sample (%bs); Ts= equilibrium temperature of the system in Kelvin, a_w = Water activity of the product, in decimal fraction, given by the relation:

$$a_w = \frac{P_V}{P_{vsat}} = \frac{H_r(\%)}{100} \qquad (33)$$

Where: P_v = Vapor pressure at the surface of the product; Pvsat = Vapor pressure saturation at the temperature of the system. The relation between water activity, the temperature and the solutions saturated salt works prepared in distilled water (Table 1) are determined by equation (Labuza et al., 1985):

$$ln(aw) = \frac{K_1}{T} - K_2 \qquad (34)$$

Statistical analyses

The modelization of desorption isotherms requires the statistical analysis methods of regression and correlation to assert the best results obtained, without a great margin of error. The regression analysis is carried out, under the software Excel 2010, by using the method of least squares. The coefficient correlation (r) was the first criterion of selection of the best equation to describe the curves of desorption. In addition to the calculation of r, calculations of the values of EMR (Relative Average Error), EST (Standard Error of the Moisture Content) and ei (Residual Error) have allowed to justify the choice of the model. The residual error allows knowing if the residues between the values predicted and experimental are tiny. The best model is that which presents the greatest value close to r and the smallest values of errors EMR, EST and ei (Benhamou et al., 2010).

$$r = \sqrt{\frac{\sum_{i=1}^{n}(X_{eqi'}pre - \overline{X_{eqi'}}exp)^2}{\sum_{i=1}^{n}(X_{eqi'}exp - \overline{X_{eqi'}}exp)^2}} \qquad (35)$$

$$EST = \sqrt{\frac{\sum_{i=1}^{n}(X_{eqi'}exp - X_{eq_{i,}}pre)^2}{df}} \qquad (36)$$

$$EMR = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{X_{eq_{eqi'}}exp - X_{eq_{i,}'}pre}{X_{eq_{i'}}exp}\right| \qquad (37)$$

$$Ei = X_{eqi'}exp - X_{eq_{i}'}pre \qquad (38)$$

Where: *Xeqi' exp:* i^{em} equilibrium moisture content experimental; *Xeqi'pre*: i^{em} equilibrium moisture content predicted % (MS); $\overline{X_{eqi'}}exp = \frac{1}{N}\cdot\sum_{i=1}^{N}X_{eq_{i,}}exp$: moisture mean content experimental; N:number experimental points, {in our case, N=9} and df are degree of freedom of the regression model {df = N - n} where n indicates the number of constants of each model.

Table 1: Standards values of water activity according to salts and the temperature.

Salts	Equations	a_w			
		30 °C	**35 °C**	**45 °C**	**55 °C**
LiBr	Ln a_w = (620.6358 x 1/T) - 4.8327	6.20	6.00	5.70	5.40
KOH	Ln a_w = (2094.4890 x 1/T) - 9.4977	7.20	6.70	5.90	5.60
LiCl	Ln a_w = (10.8233 x 1/T) - 2.2193	11.30	11.3	11.20	11.00
MgCl2	Ln a_w = (151.0652 x 1/T) - 1.6271	32.40	32.10	31.10	29.9
CoCl2	Ln a_w = (982.7329 x 1/T) - 5.0477	61.8	58.60	52.60	48.00
KI	Ln a_w = (258.1545 x 1/T) - 1.2388	67.89	66.96	65.26	63.78
NaCl	Ln a_w = (23.1092 x 1/T) - 0.3607	75.1	74.90	74.50	74.40
KCl	Ln a_w = (157.0587 x 1/T) - 0.6967	83.6	83.00	81.70	80.7
K_2SO_4	Ln a_w = (52.7544 x 1/T) - 0.2046	97.00	96.70	96.10	96.00

Source **:** (Labuza et al., 1985)

RESULTS

Obtaining the points of desorption isotherms

The hygroscopic equilibrium desorption of the *Moringa oleifera* leaves is reached at the end of 38 days for the last points of the curve. The values of equilibrium moisture content experimental *(Xeq)* are presented in the Table 2 which follows**.** On this Table 2, on observes with the increase of the temperature, it occurs, a reduction of the moisture content, which wants to say that the product becomes less hygroscopic.

Modelization of the desorption isotherms

The Table 3 presents the parameters models used and the statistical criteria of the choices realised. The high values of r^2 and the low values of EST and EMR indicate a good adjustment of all these models to the experimental results. Among these models, GAB and Smith give a highest values coefficient of correlation respectively (R=1) and (R = 0.999 to 1) and weakest values of EST and EMR in the range of temperature tested. Thus, GAB and Smith seem to be adapted to describe the desorption isotherms in the very high field of the water activities. These results are in agreement with the work realised on desorption isotherms where the GAB model simulated better, on a broad range of water activity, experimental data of the authors hereafter: Ferradji et al. (2008); Ahouannou et al. (2010); Kakou et al. (2015).The monolayer moisture contents of BET and GAB models are dependent on the temperature with values relatively very close, respectively 7.62 and 8.53 with 30 °C; 5.52 and 7% with 35°C; 5.4 and 6.74 with 45°C and 4.65 and 5.45 with 55°C.

The curves of desorption isotherms which result from three theoretic models are confronted with the experimental points and are illustrated on the Figure 1.

On this Figure1, we observe that the theoretical curves obtained coincide well with the experimental results. The theoretical models GAB and Smith are quite satisfactory to reproduce theoretically the isotherms desorption of the *Moringa oleifera* leaves in the field drive of the water activities from 5.4 to 97%. The BET model presents a perfect simulation with the experimental curve but in the beach of water activities lower than 0.35.

It is possible to observe on the isotherms reproduced by the models GAB and Smith, that three zones are identifiable (Figure 2):

- Monolayer Zone (zone 1): Constitution of one monolayer molecular on the surface of the product. It is characteristic of the action of the forces of Van Der Waals between the absorbent groupings and the water molecules. The adsorption of the water molecules is done gradually until constituting one monolayer covering all external surface and one part of the pores of the product. Water is in a rigid state because of the importance of the bonding strengths between the water molecules and surface. The passage to the following zone is carried out when all surfaces is saturated;
- Multilayer Zone (zone 2): Adsorption of the molecules on the monolayer initial. The isotherm is linear in this zone and water is in an intermediate state between solid and liquid.
- Zone of free water and of the solvation (Zone3): Water is present in the liquid state in the pores of material. The thickness of the film is sufficient so that water is present at the liquid state in the pores of material. Water microcapillary constitutes a continuous phase.

The curves of residues resulting from the confrontation of the experimental points and the theoretical curves of GAB and Smith (Figure 3) are almost confused with x-axis in the beach of water activities ranging between 5.4 to 97% and at the temperature of 55 °C, meaning that these residues are almost, null.

We also note that it is with 55 °C that the curves of residues between the isotherms experimental and predicted by BET (Figure 4) are confused perfectly with the x-axisin the beach of the activities of water ranging between 5.4 to 35%.

Thermodynamic properties

Net isosteric heat and differential entropy

The thermodynamic functions such as net isosteric heat (q_{st}) and the differential entropy (ΔS) calculated from desorption isostere (figure 5) allows to evaluate the heat quantity necessary to dry the product.

It is noted that the variation logarithmic curve of the water activity (a_w) according to the temperature reverse gives affine lines (isostere), which results in the existence of a proportionality between water activity and the temperature. The moisture content of the product is related to these two parameters. The net isosteric heat (q_{st}) and the differential entropy (ΔS) of desorption for the temperatures of 30 at 55 °C, according to moisture content are presented on the Figure 6. These curves show that for higher moisture contents, the net isosteric heat (qst) and the differential entropy (ΔS) desorption tends towards zero. The experimental data of the net isosteric heat and the differential entropy were correlated with satisfaction (R = 0.999) by the GAB model in its transformed form, represented by the equation {(Eq. (39)}:

$$a_w = \left[2 + z * C - \{(2 + z * C)^2 - 4(1 - C)\}^{\frac{1}{2}}\right] / \left[2K * (1 - C)\right] \quad (39)$$

Where $z = \left(\frac{X_m}{X_{eq}} - 1\right)$

The values of *Xo* and *q*

reaction and that the relationship between the enthalpy and the entropy is linear (Arsalan and Torgrul, 2006; Benhamou et al., 2010).

Activation Energy

The activation energy is the energy quantity necessary to initiate a reaction. The variation logarithmic curve of the GAB and BET monolayer *(Xm)* moisture contents according to the temperature reverse is presented on the Figure 8. A linearization of the curve ln (*Xm*) = f (1/T) {(Eq.19)}, by least squares made allow to determine the slope -Ea/R and the ordinate in the beginning lnX^{O}. Thus, the values of the activation energy (Ea) given from the GAB and BET monolayer are respectively of -13.1009539 K/mol and -13.674442 K/mol with a frequency collision respective (X^{O}) of 0.45646 and 0.30546 (%MS).

Table 2: Equilibrium moisture content, *Xeq* (gH_2O/ g ms) of desorption isotherms.

T= 30 °C		**T= 35 °C**		**T= 45 °C**		**T= 55 °C**	
a_w	**Xeq**	**a_w**	**Xeq**	**a_w**	**Xeq**	**a_w**	**Xeq**
6.20	4.45	6.00	3.35	5.7	3.11	5.40	3.01
7.20	5.11	6.70	4.46	5.9	3.98	5,60	3.41
11.30	6.37	11.30	5.85	11.2	5.02	11.00	4.25
32.40	10.20	32.10	7.59	31.1	7.23	29.90	6.19
61.80	16.20	58.60	13.01	52.6	11.03	51.00	9.01
67.89	17.88	66.96	16.03	65.6	14.29	63.78	11.39
75.10	21.94	74.90	20.99	74.5	17.60	74.40	14.49
83.60	27.53	83.00	25.42	81.7	21.03	80.70	16.82
97.00	39.25	96.70	35.87	96.1	29.86	95.40	25.87

Table 3: Values of the estimated parameters and statistical criteria of choice

T (°C)		**GAB (n=5)**	**BET (n=2)**	**Smith (n=2)**	**Henderson (n =2)**	**Iglesias (n=2)**
30	**Xm**	0.08539977	0.07620234	-	-	-
	C	19.6628262	20.3676674	-	-	-
	K	0.81684454	-	-	-	-
	Co	23.04354687	-	-	-	-
	Ko	4.8874E-19	-	-	-	-
	K1	-	-	0.05708544	0.86108253	0.00929291
	K2	-	-	0.10319489	1.92329812	0.11908612
	R	1	0.9992354	1	0.98428792	0.989
	EST	0.110185	0.9406	0	0.01470782	7.49549E-06
	EMR	0.054165305	0.01.2727708	0	0.23111111	0.054041124
	Xm	0.07005121	0.05522413	-	-	-

35	**C**	18.8319155	35.3178036	-	-	-
	K	0.85778751	-	-	-	-
	Co	22.01300452	-	-	-	-
	Ko	4.96669E-19	-	-	-	-
	K1	-	-	0.04553394	0.77455377	0.00967159
	K2	-	-	0.09962828	1.82895141	0.1028673
	R	1	0.9924578	0.999999966	0.97375255	0.951
	EST	0. 6185	11.86	5.71429E-17	0.02187081	0.00012117
	EMR	0.0349304632	0.197408235	1.67626E-05	0.34366667	0.24409369
45	**Xm**	0.06742878	0.05409165	-	-	-
	C	18.4569659	27.6989425	-	-	-
	K	0.824693	-	-	-	-
	Co	8.630004053	-	-	-	-
	Ko	3.8565E-19	-	-	-	-
	K1	-	-	0.04271906	0.88159482	0.0095338
	K2	-	-	0.08552536	1.91181752	0.08785777
	R	1	0.995678	0.999801159	0.97996575	0.9987
	EST	0.2509	6.773	1.42857E-09	0.0142482	5.71828E-08
	EMR	0.014007752	0.12383273	0.0981981	0.22388889	0.006212759
55	**Xm**	0.05450447	0.04657808	-	-	-
	C	24.4546232	32.6023403	-	-	-
	K	0.83794319	-	-	-	-
	Co	11.7024607	-	-	-	-
	Ko	3.71298E-19	-	-	-	-
	K1	-	-	0.02634887	1.21721762	0.0100649
	K2	-	-	0.07717861	2.00976287	0.06971325
	R	1	0.99989	1	0.71731644	0.636
	EST	0.001497	0.929	7.0434E-33	0.16719257	0.00922926
	EMR	0.0006609308	0.019485469	2,61241E-13	2.62717778	4.11865821

n = Parameters number of model

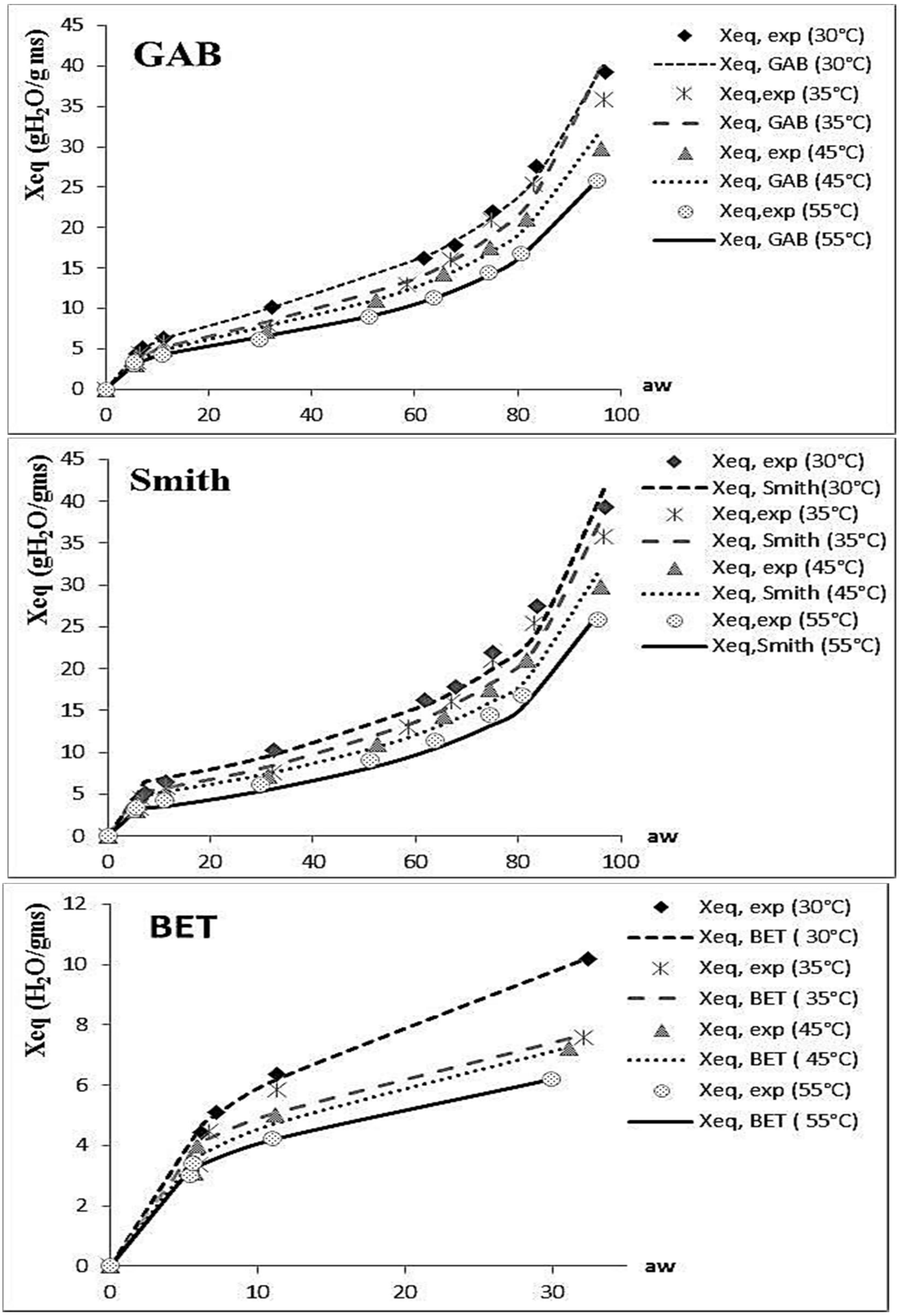


Figure 1: Experimental and modelled desorption curves of *Moringa oleifera* leaves.

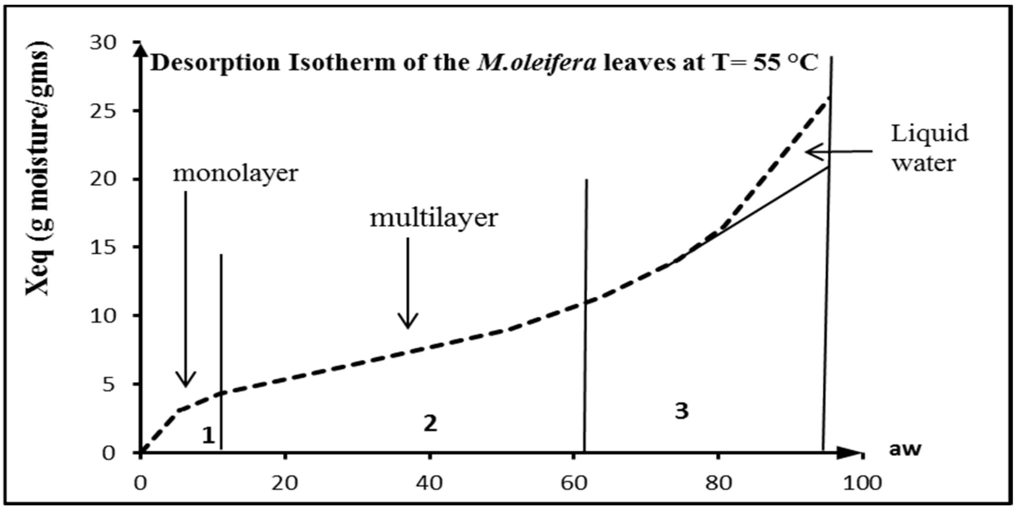
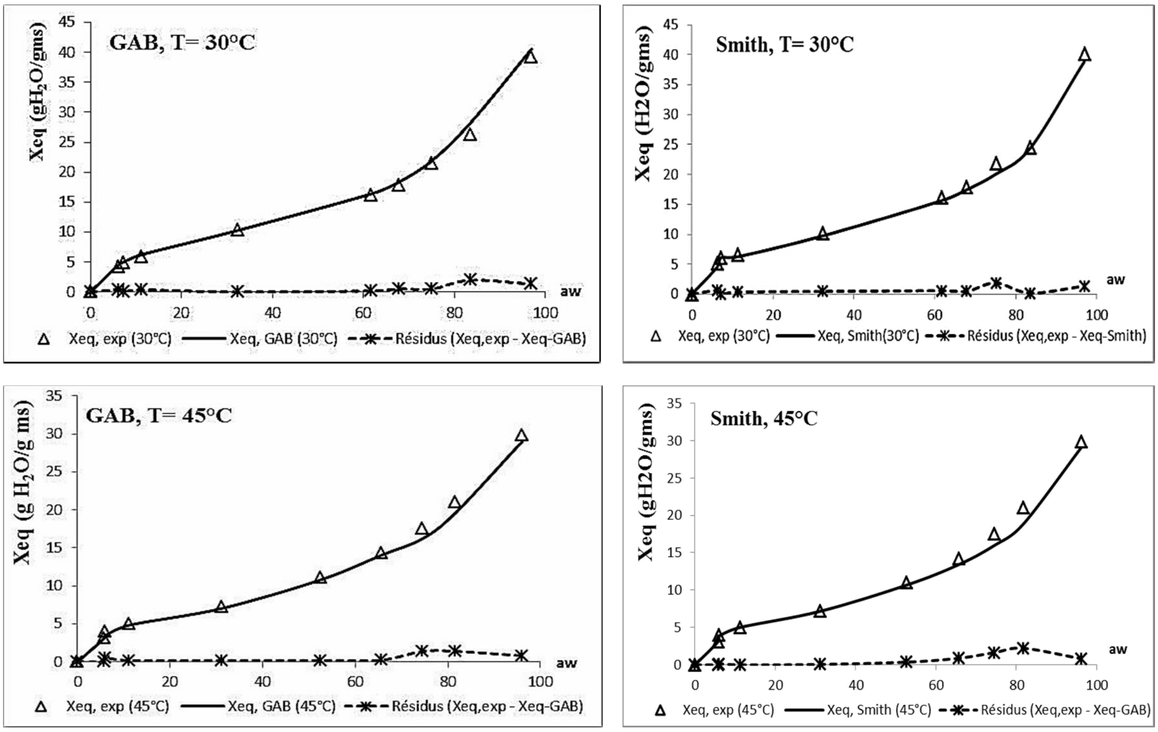


Figure 2: Experimental curve of desorption of the *Moringa oleifera* leaves showing the three zones isotherms.



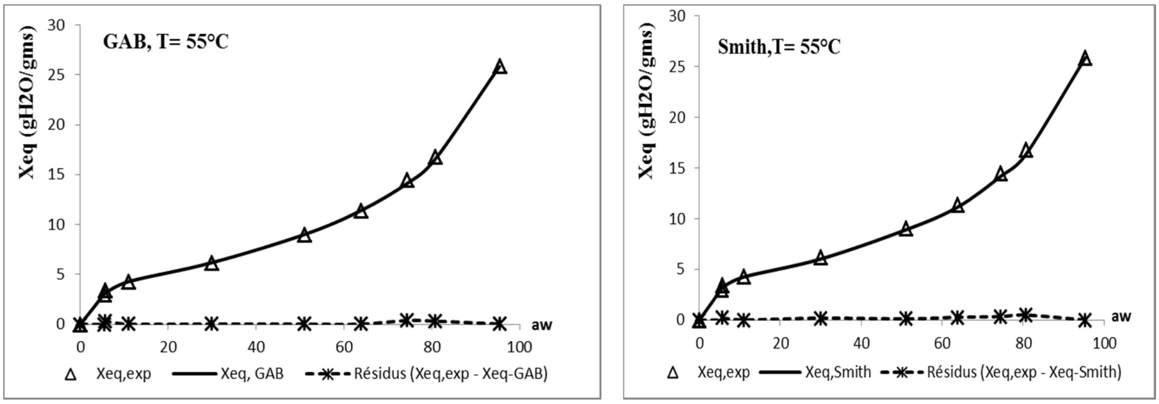


Figure 3: Curves of residues between the isotherms experimental and predicted by GAB and Smith at 30, 45 and 55 °C.

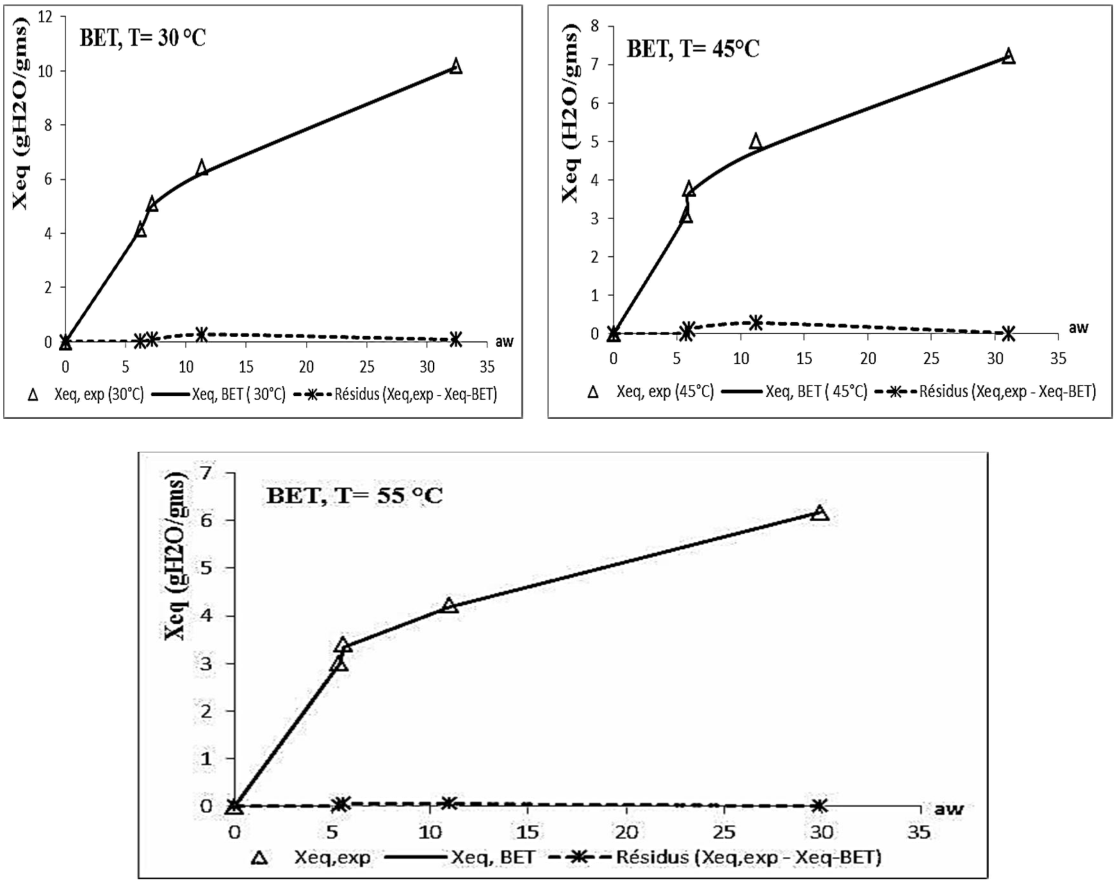


Figure 4: Residues curves between the isotherms experimental and predicted by BET 30 °C, 45 °C and 55 °C.

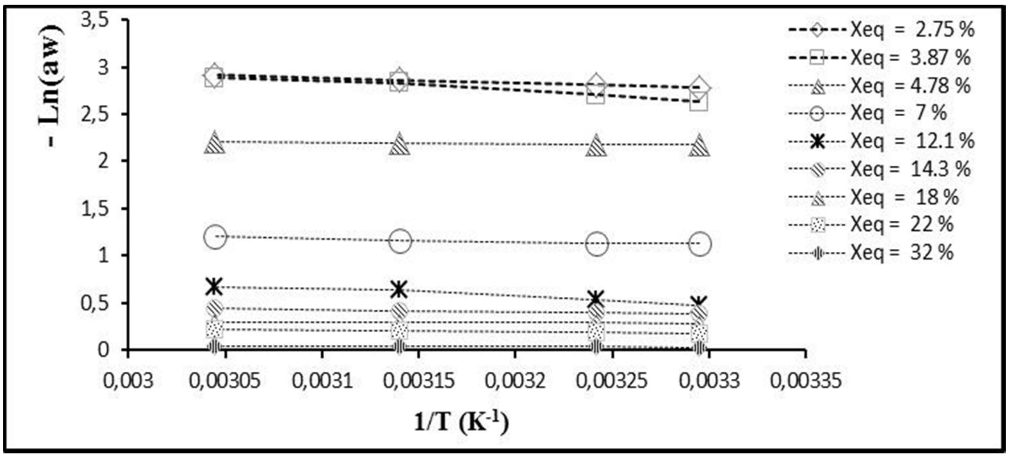


Figure 5: Variation logarithmic curve of a_w according to the temperature reverse.

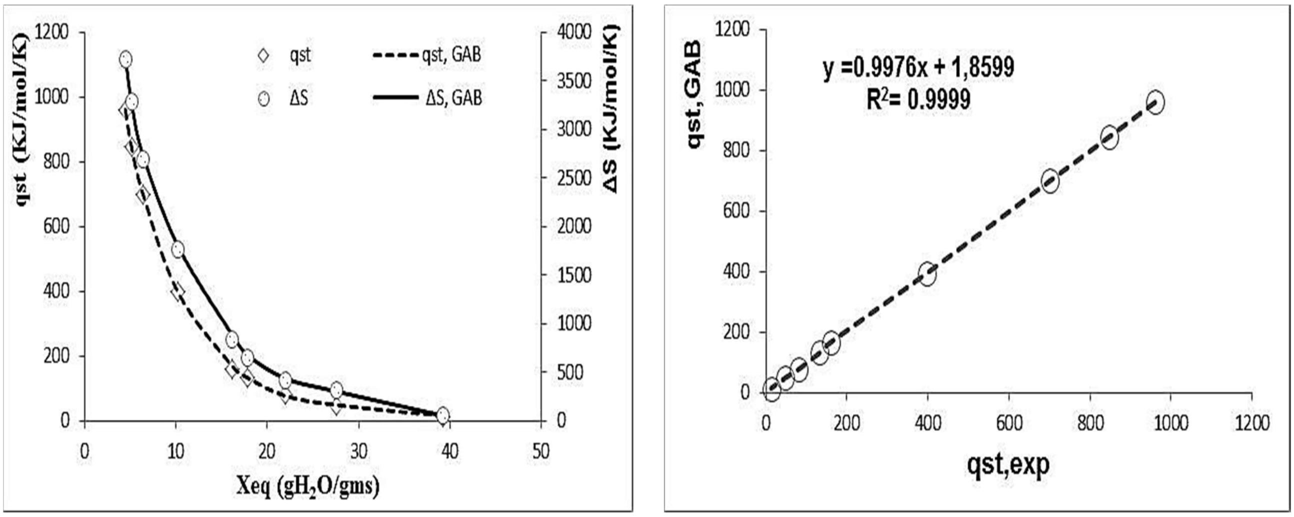


Figure 6: Isosteric heat and differential entropy experimental and predicted by GAB.

Table 4: values of X_o and q_o for the *Moringa oleifera* leaves.

Parameters	**T= 30 °C**	**T= 35 °C**	**T= 45 °C**	**T= 55 °C**
X_o(gH$_2$O/gms)	0.08075639	0.07649098	0.06249227	0.05261513
q_o(KJ/mol)	16.4329266	16.3095454	16.3956327	16.378185
r^2	0.965724	0.934134	0.98546	0.99999

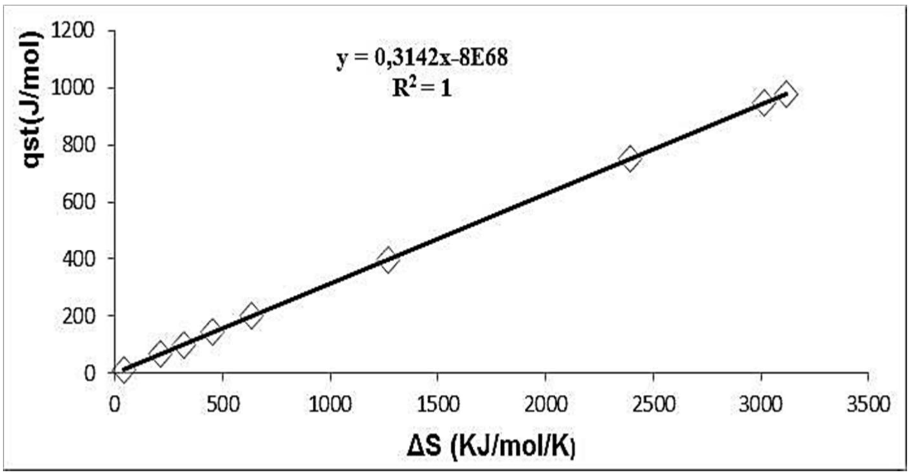


Figure 7: Enthalpy-entropy compensation theory of the *Moringa oleifera* leaves.

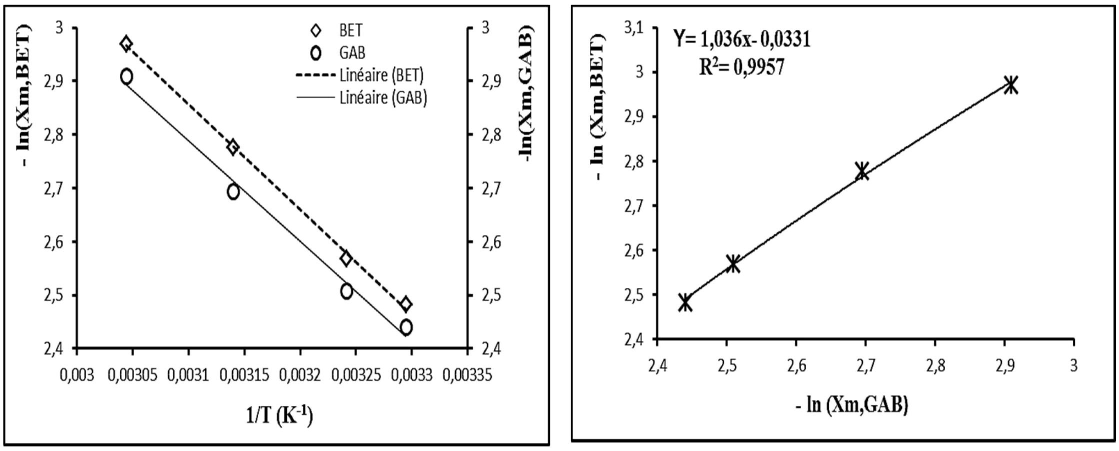


Figure 8: Variation logarithmic curve of the GAB and BET monolayer (Xm) moisture.

DISCUSSION

Experimental points of desorption isotherms

The Table 2 shows that with the increase of the temperature, it occurs, a reduction of the moisture content. That can be explained by the increase of thermic agitation (binding energy of high moisture); indeed, for high temperatures, the state of excitation of the water molecules is more significant, involving a reduction of the attraction forces of the water molecules between them (Benhamou et al., 2010; Shittu et al., 2015).

Modelization of the desorption isotherms

The values of the parameter C of GAB equation in the Table 3 allows to characterize the isotherms of sorption. According to Medeiros et al. (2006), when C≤10, the isotherm is type III whereas for C≥10, the isotherm is type II. In this study, the values of the parameter C are higher than 10 whatever the temperature. Thus, the isotherms of desorption obtained are type II (Figure 1). They are thus of form sigmoidal. That implies a formation of monolayer then polylayer. This type of isotherm is characteristic of the hygroscopic behaviour of the majority of the foodstuffs (Kakou et al., 2015). These results are in agreement with the behaviour of the biological products (Benhamou et al., 2010; Ahouannou et al., 2010). The positive value of the parameter K of GAB, whatever the temperature, indicates that, the heat of sorption of multilayer is lower than the latent heat of condensation of pure water. The three zones of isotherms observed (figure 2) prove easily that the middle is nonporous or macroporous and that the isotherm of desorption of *Moringa oleifera* leaves is characteristic of absorption multimolecular: progressive thickening of the absorptive layer. The curves of residues (figure 3) confirm well weakest of Standard Error of the moisture content (EST), of Average Error Relating (EMR) and of the Residual Error (ei) obtained to this temperature.

Net isosteric heat and differential entropy

The Figure 6 show that for higher moisture contents, the net isosteric heat (qst) and the differential entropy (ΔS) desorption tends towards zero. That illustrates the strong contact of water with the substrate, the isosteric heat of desorption (q_{st}) becomes negligible in front of the latent heat. The existence of polar sites of great activity in the *Moringa oleifera* leaves which are covered with water molecules forming the monolayer (Benseddik et al., 2014) could explain this fact. According to other authors (Boki et al., 1990; Salgado et al., 1994), this phenomenon is due to the fact that in a very restricted field of moisture, when the moisture content increases, certain products inflate and favours the opening of new sites of adsorption of strong joining, which increases isosteric heat. In the Table 4, one observes with the increase in the temperature, it occurs a reduction in the moisture content characteristic (X_o). The net heat of isosteric desorption of the first water molecules in the product (q_o) is almost constant with 16.3 kJ/mol in the beach of temperatures tested. These results are comparable with those obtained by Benseddik et al. (2014) for other foodstuffs. Indeed, the parameter q_o provides significant information on the physicochemical interactions of water with the major components of product and the state of water in the product. It is about an essential parameter, for the estimate of the requirements in energy during drying (Benseddik, 2014).

Enthalpy-Entropy compensation theory

The curves (Figure 3) show a perfect linearity (R=1) between the enthalpy and the differential entropy of desorption of the *Moringa oleifera* leaves. Values of the isokinetic temperature (T_β) and the harmonic mean (*Thm*) temperature are respectively of 314.17159 K and 314.45944 K. The free energy ($\Delta G\beta$) is 308.18 J/mol. The value of $T\beta$ obtained for the *Moringa oleifera* leaves is lower than those reported for oatmeal biscuit and oat flakes (430.9 and 443.4 K, respectively) (Kaymak-Ertekin and Gedik, 2014) but within the range reported for garlic (348 K) (Madamba et al., 1996), sucuk (323.4 K) (Polatoglu et al., 2011); marjoram leaves (357.84 K) (Benhamou et al., 2010), the mangos (463 ± 4K) (Gabas et al., 2007), albumin powder and spaste (330.7K) (Shittu et al., 2015). Kakou et al. (2015) on the other hand obtained very low value (0.0034 K) for cocoa broad beans. The harmonic mean *Thm* *(*314, 45944 K) confirms well the relevance of the isokinetic theory for the water desorption of *M. oleifera* leaves. Values of (T_β) and *(Thm)* obtained show that the process enthalpy is involved. Indeed, according to Leffler (1995), if $T_\beta < Thm$, the process enthalpic is involved, on the other hand if $Thm < T\beta$, the process is regarded as controlled entropy. The free energy of *Moringa oleifera* leaves is 308.18 J/mol, which firstly indicates the water vapor sorption process by is a non-spontaneous process. In fact, the process enthalpy-entropy compensation expresses the structuring-destructuring of water thermodynamically. The variation of the enthalpy corresponds to the variations of energy which occur between the water molecules and that of the matrix during the operations of sorption. Whereas the entropy defines the degree of order of the water adsorbed in the matter and allows the interpretation of some process, such as dissolution, crystallization and the expansion (Koumoutsakos and Avramidis, 1999). The knowledge of the change of isosteric heat, and thus also of the change of differential entropy, calculated starting from the Gibbs-Helmholtz equation, is interesting, because it offers an additional level of information to characterize the association of two molecules.

Activation energy

Indeed, the (Ea) negative values (-13.1009539 K/mol and -13.674442 K/mol) obtained explain why the process of desorption of *Moringa oleifera leaves* is exothermic. The bringing together of the variation logarithmic curve of GAB and BET monolayer (*Xm*) gives a line closely connected translating by the existence of a proportionality between the monolayer (*Xm*) of GAB and BET with a proportionality factor is equal to 1.036 and one coefficient of correlation R = 0.9957.

Conclusion

The desorption curves of the *Moringa oleifera* leaves obtained are type II proving a strong hygroscopicity. The theoretical curves of the models tested coincide well with the experimental points. This study reveals that the GAB and Smith theoretical curves present the best agreement with the experimental curve in the very high domain of water activities and for the temperature of 55 °C. A variation in the temperature in range 30 and 55 °C entrained a strong influence on the equilibrium curves but in proportions largely acceptable for better preserving the *M. oleifera* leaves. An exponential empirical correlation is established to describe the dependence of the heat sorption with the equilibrium moisture content. The enthalpy-entropy compensation and of the isokinetic theory are applied successfully for desorption of the *Moringa oleifera* leaves, which shows that the process of leaves desorption is exothermic, non-spontaneous and is done by controlled enthalpic mechanisms. Lastly, knowing the equilibrium moisture contents of the *M. oleifera leaves*, we can now plan to determine their kinetics of drying in a solar drier functioning in forced convection.

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