Water adsorption/desorption isotherms and thermodynamic properties of African mussels

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Abstract— This study is focused in adsorption isotherms for African mussels determined in the range of 303.15 to 323.15 K through the static gravimetric method. The balance was obtained after 15 days for desorption and 12 days for adsorption. The thermal hysteresis effect is negligible in the range of temperatures tested. For the modeling of sorption isotherms, and for predicting the hygroscopic behavior during storage or drying of African mussels, four mathematical models were used; the models of GAB, LESPAM, Peleg and Enderby, and best adjustments were found for GAB and Peleg models with $r > 0.99$ and no pattern distribution of residual plots. Compensation theory was confirmed, with linear relationship between enthalpy and entropy show that water adsorption was considered driven by enthalpy, clarifying the mechanisms of water vapor sorption in African mussels .

Index Terms— Sorption, entropy, enthalpy, isokinetic temperature, compensation theory

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1 INTRODUCTION

ODAY, aquaculture industry is experiencing significant development in Morocco. Much research is conducted in the biological field, in particular the reproductive cycle. But few studies have focused on issues related to the conservation of these products. However, a food product if it is not dried in good conditions may degrade and therefore lose all of its nutrients and its organoleptic quality.

This work is a participatory approach with the local association of women gatherers of mussels in the province of Chtouka Aït Baha, in southern Morocco and aims to:

- Modernize the sector to improve the traceability of products, their taste and health quality,
- Improve valuation on the national and international market: further processing ...
- Reduce energy costs, the impact on the environment by using clean and abundant solar energy,
- Preserve the socio-economic fabric.

The knowledge of the hygroscopic nature of a material is a key to the proper appreciation of the drying process. In fact, a material to be dried is then used for a particular application generally requiring precise water content related to the stability of the product.

In the hygroscopic area, where the water that moves is either bound water or water vapor, there is a macroscopic relation between the equilibrium moisture content of the product and the surrounding environment. This relationship, the sorption isotherm, binds the water content at the temperature and the relative humidity of the environment. It is characteristic of the many interactions between the solid skeleton and the water molecules that take place on a microscopic scale [1]. This curve expresses:

Ordinate: the equilibrium moisture content of the product, expressed in kg water per 100 kg of dry matter (% DM).

X-axis: either the water vapor concentration of the atmosphere in equilibrium with the product, expressed as equilibrium relative humidity (ERH) or the water activity in the product $\left(a_w \right)$.

Given the complexity of the phenomena occurring during the sorption of water, four mathematical models based on more or less physical considerations were tested. two models with three parameters (LESPAM and GAB) and two models with four parameters (Peleg and Enderby). The determination and modeling of sorption isotherms in different temperatures gives information about the product conditions during storage, since the material stability can be predicted by the availability of water molecules in front of variations in temperature and relative humidity.

Thermodynamic parameters are variables responsible by providing insights about the material microstructure, as well as theoretical interpretations for matrix–water interactions. Among them, it could be found the differential enthalpy, differential entropy and free Gibbs energy. Differential enthalpy is valuable for designing equipment involved in water removal processes, once it represents the binding strength of water to the food compounds. On the other hand, differential entropy represents the amount of available sorption sites in a specific energy level. Free Gibbs energy intend to correlate these two functions, corresponding qualitatively to the difference between the total energy available (enthalpy) and the unavailable energy (entropy) [2-4]. The presence of a linear correlation states that the isokinetic, or enthalpy–entropy, compensation theory exists due to changes in the sorbent-sorbate interaction [5]. The corresponding slope is the isokinetic temperature, representing the temperature at which all reactions in series proceed at the same rate.

Our work aims to:

Determine the sorption isotherms of the African mussels, to optimize the balance hygroscopic conditions for a recovery and better preservation during the storage operation,

Provide an adequate water transfer model based on a comparison of water content profiles calculated and measured [6, 7].

Study and calculate the thermodynamic properties of the African mussels.

2 EXPERIMENTAL PROTOCOL

2.1 Materials and procedure

The procedures for obtaining the sorption isotherms of water

from food products are described by several authors [8, 9]. Among these procedures, are used dynamic methods where the sample is placed in a temperature of gas stream and humidity kept constant, without air agitation, or static procedures where the sample to adsorb or desorbs is placed in chambers containing saturated salt solutions and kept at constant temperature and relative humidity until it reaches thermodynamic equilibrium.

Static gravimetric method was used to determine the isotherms of water sorption along the temperature range [10]. Different equilibrium relative humidity's $(ERH = a_w \times 100)$ were reached by using glass desiccators with saturated salt solutions of KOH, (MgCl2, 6H2O), K2CO3, NaNO3, KCl et (BaCl2, 2H2O) dissolved into de-ionized water. Saturated salt solutions were prepared to obtain an a_w range from 0.0572 to 0.8980. Table 1 contains the specifications for each salt. These solutions are prepared in sealed jars and held isothermal in a regulated oven temperature [8-11]. The sample is suspended in the jar, above salts, (Figure 1) and thus remains in a stabilized atmosphere in temperature and humidity.

Table 1: Salt specifications and their standard values of the equilibrium relative humidity.

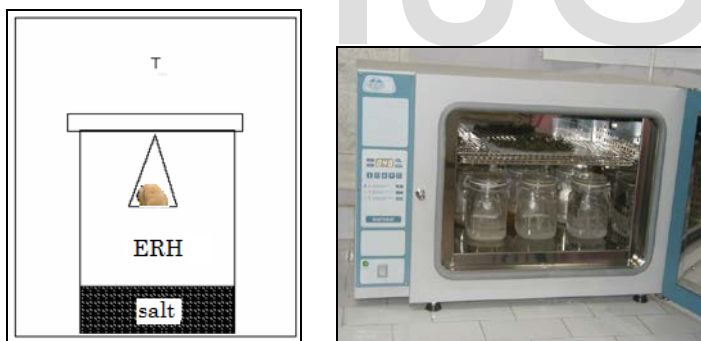|	KOH	(MgCl₂, 6H₂O)	K₂CO₃	NaNO₃	KCl	(BaCl₂, 2H₂O)
303.15 K	7.38	32.38	43.17	72.75	83.62	89.80
313.15 K	6.26	31.59	42.30	71.00	82.32	89.10
323.15 K	5.72	30.54	40.91	69.04	81.20	88.23

Fig.1: Experimental device for measuring the sorption isotherms

The weighing of the samples is regularly performed until the measured weight no longer changes: then we reached mois-

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ture equilibrium.

The solids content determined from the sample is then known, for a given humidity, the sample moisture content. If the sample placed in the chamber is wet, there

is obtained the desorption curve, i.e. that the sample loses water to reach equilibrium. By cons, if the sample is initially dry, adsorption curve was obtained.

Figures 2 and 3 illustrate these results. Table 2 contains all values of a_w obtained from the study reported by Labuza [12] for each salt solution versus experimental data of X_{eq} at each specific temperature.

Table 2: Experimental data of equilibrium moisture content versus specific equilibrium relative humidity (ERH) in the studied temperatures

303,15 K			313,15 K		
ERH	des	ads	ERH	des	ads
7.38	4.5151	4.2211	6.26	2.8507	2.9114
32.38	8.3408	7.2116	31.59	7.4834	6.4301
43.17	9.2004	8.5412	42.30	8.2754	7.5610
72.75	23.7217	19.2200	71.00	17.9892	15.2112
83.62	44.4850	39.1532	82.32	33.6238	31.2816
89.80	64.1522	58.2231	89.10	59.3031	55.2113

323,15 K		
ERH	des	ads
5.72	2.5675	2.6312
30.54	5.7608	5.6115
40.91	7.8129	7.2111
69.04	14.2246	13.1212
81.20	33.2511	31.2212
88.23	42.4348	41.1763

2.2 Isotherms modeling

The mean equilibrium moisture content was plotted against water activities to represent the water adsorption by the six isotherms obtained. Although isotherms provide information about equilibrium moisture, their modeling also gives water activity values for specific equilibrium moisture content. The resolution method used in this work is the Levenberg-Marquardt algorithm with CurveExpert 3.1 software and the software OriginPro 8.0 (OriginLab Corporation, Northampton,

MA, USA), non-linear regressions were performed to adjust the mathematical models commonly found in literature (table 3).

$X_{eq_{i,pre}}$: The predicted equilibrium moisture content (% DM)

N : number of data points; in our case (N = 6)

d_f : Degree of freedom from the regression model;

d_f = N - n

n : number of variables of each model

2.3 Optimal storage conditions

How to handle the product during handling, storage and conservation requires to experimentally determining the optimal equilibrium relative humidity for the conservation of African mussels. Indeed the sorption isotherm may especially be modeled as a function of third degree; the central portion (conservation line) corresponds to the area of better stability of the food products.

2.4 Thermodynamic approach

The temperature dependence of the isotherm can be represented by the net isosteric heat of sorption, which assumes to be invariant with temperature. Plotting $\ln(a_w)$ as a function of $\left(\dfrac{1}{T}\right)$ in a fixed equilibrium moisture, the net isosteric heat of sorption or enthalpy of sorption (q_{st}) can be determined by the slope from Clausius-Clapeyron equation (Equation 4). The application of this method requires the measurement of adsorption and desorption isotherms at least three temperatures [14]. In addition, the q_{st} is also defined as the difference between integral heat of sorption (Q_{st}) and the heat of vaporization of water (L_v) [11]:

Table 3 : Proposed models

Model name	Mathematical expression	reference
LESPAM	$X_{eq}=A.exp\left(\dfrac{B.(HRE)}{\theta}\right)+C$	[28]
Enderby	$X_{eq}=\left[\dfrac{A}{1-B(HRE)}+\dfrac{C}{1-D(HRE)}\right](HRE)$	[32]
GAB	$X_{eq}=\dfrac{ABC(HRE)}{\left[1-B(HRE)\right]\left[1-B(HRE)+BC(HRE)\right]}$	[33]
Peleg	$X_{eq}=A(HRE)^C+B(HRE)^D$	[34]

The fit accuracy for each model was evaluated based on the adjusted coefficient of determination (r), the root mean square error (RMSE) and residual distribution. Adjustments with low r and high RMSE and/or clear pattern in residual plots should be discarded [13]. These statistical parameters are defined as follows:

$$r=\sqrt{\dfrac{\sum_{i=1}^{N}\left(Xeq_{i,pre}-\overline{Xeq_{i,exp}}\right)^2}{\sum_{i=1}^{N}\left(Xeq_{i,exp}-\overline{Xeq_{i,exp}}\right)^2}}$$

(1)

$$RMSE=\dfrac{100}{N}\sum_{i=1}^{N}\left|\dfrac{X_{eq_{i,exp}}-X_{eq_{i,pre}}}{X_{eq_{i,exp}}}\right|$$

(2)

$$\overline{Xeq_{i,exp}}=\dfrac{1}{N}\sum_{i=1}^{N}Xeq_{i,exp}$$

(3)

With :

$X_{eq_{i,exp}}$: The experimental equilibrium moisture content (% DM)

$$\dfrac{\partial \ln(a_w)}{\partial\left(\dfrac{1}{T}\right)}=-\dfrac{Q_{st}-L_v}{R}=\dfrac{-q_{st}}{R}$$

(4)

Q_{st} : Isosteric heat of sorption (kJ.mol⁻¹)

q_{st} : Net isosteric heat of sorption (kJ.mol⁻¹)

T : Absolute temperature (K)

R : Gas constant (8.3145 J.mol⁻¹.K⁻¹)

Lv : Latent heat of vaporization of pure water (43.53 kJ.mol⁻¹) at 35°C

Since thermodynamic properties can express the behavior of water sorption, Equation (5) represents the variation in molar differential entropy of adsorption (ΔS) by Gibbs-Helmholtz equation :

$$\Delta S=\dfrac{q_{st}\Delta G}{T}$$

(5)

Considering that Gibbs free energy is calculated as:

$$\Delta G = RT\ln(a_w)$$

(6)

Combining Equation (5) and Equation (6), the change in Gibbs free energy is expressed by variations on both enthalpy and entropy, resulting in Equation (7):

$$\ln(a_w) = \frac{-q_{st}}{RT} + \frac{\Delta S}{R}$$

(7)

In this way, enthalpy of sorption and entropy can be calculated from Equation (7) by same procedure as described for net isosteric heat of sorption, extracting values of slope $\left(\dfrac{q_{st}}{R}\right)$ and the linear coefficient $\left(\dfrac{\Delta S}{R}\right)$.

Correlating the obtained values of q_{st} versus ΔS for adsorption and desorption data, a linear tendency is expected to confirm the compensation theory for sorption [15]:

$$q_{st\beta} = T_\beta \Delta S + \Delta G_\beta$$

(8)

In this relation, T_β is the isokinetic temperature and represents the temperature at which all reactions in the series proceed at the same rate.

Another test for validating the compensation theory is comparing the isokinetic temperature with the harmonic mean temperature T_{hm} [16, 17], that is defined as:

$$T_{hm} = \frac{n}{\sum\limits_{i=1}^{n}\left(\dfrac{1}{T}\right)}$$

(9)

3 RESULTS AND DISCUSSION

3.3 Sorption isotherms

The equilibrium data of African mussels kind Perna Perna is obtained in 6 days for desorption and 11 days for adsorption. The moisture contents $\left(X_{eq}\right)$ are summarized in table 2 for three temperatures 303.15, 313.15 and 323.15 K.

By the graph in figure 2, curves shape seemed to follow a sigmoid behavior, typical of type II isotherms [18]. This kind of isotherm can be classified into three regions: the first one correspond to the monolayer moisture strongly bounded into the product matrix; the second is almost linear corresponding to the multilayered water; and the third region is related to the free water available for chemical reactions [19].
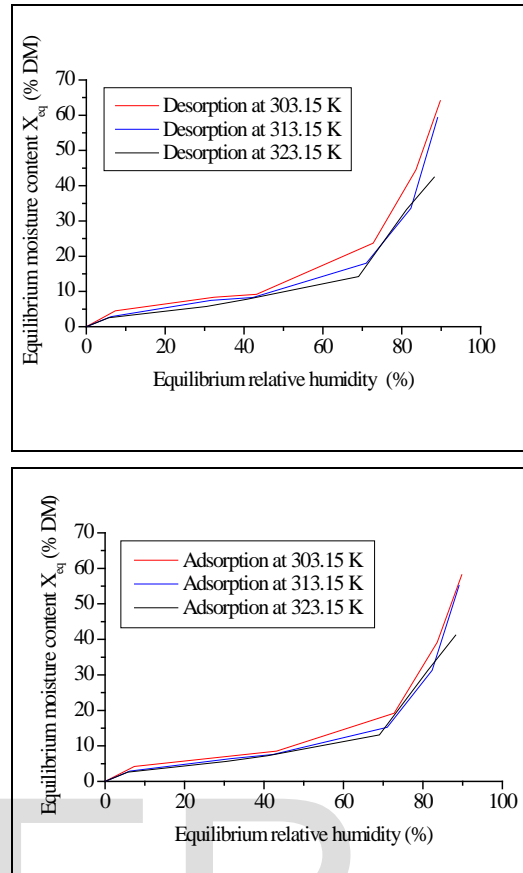

Fig. 2: Desorption and adsorption isotherms in the mussel/water system

The experimental curves obtained show that for a given water activity, the equilibrium moisture content increases with decreasing temperature. Similar results have been reported in the literature [20- 23].

The adsorption and desorption isotherms at 303.15 K, of African mussels, are accompanied by a less pronounced hysteresis phenomenon (Figure 3). This phenomenon is explained by considering that the rigid structures of pores are related with the environment by capillarity. During adsorption, the fine capillaries desorb water since the environment has a higher relative humidity than that of the pores. When the partial pressure of the steam air becomes greater than that of the liquid in the capillaries, moisture changes within the pores. [24].
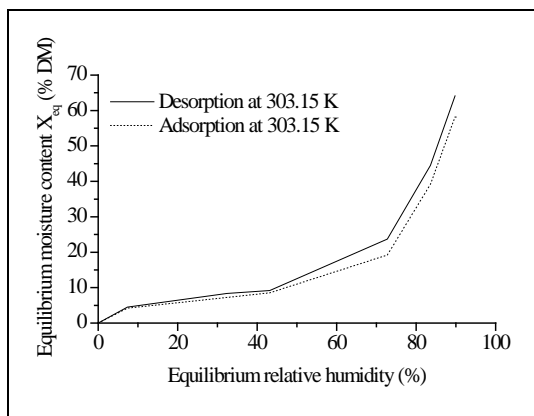
Fig. 3: Memory effect of the African mussels on their hygroscopic properties

	GAB	LESPAM	Enderby	Peleg
A	4.6180	0.1067	3.4414	11.9349
B	0.9912	208.074	0.9972	132.1656
C	19.3721	3.8888	3.4414	0.5232
D			0.9946	9.5432
r	0.9990	0.9947	0.9946	0.9999
RMSE %	13.2376	16.7865	17.6543	4.1234

3.2 Modeling of sorption isotherms of the African mussels

The experimental adsorption and desorption residues and modeled by the equations used in Table 2 are illustrated in Figures 4 and 5. After evaluation of fitting parameters to the experimental data disposed in Table 4 and 5 shows that the model of Peleg indicated good accuracy of experimental data. According to Al-Muhtaseb et al. [25] and Telis et al. [26], GAB model is considered the most versatile model available in literature for sorption isotherms. The same authors concluded that GAB model represents adequately the sorption isotherms of starchy products, such as potato and wheat starch, and lignocellulosic materials such as persimmon skin.

Table 4: Parameters of the proposed models fitted to desorption data

	GAB	LESPAM	Enderby	Peleg
A	7.7332	0.2498	5.4559	12.1861
B	0.9838	183.07	1.0226	106.8504
C	5.7267	3.7644	89.4284	0.3727
D			-17.8584	6.5962
r	0.9977	0.9957	0.9997	0.9999
RMSE %	18.4562	23.1456	7.2231	5.3245

Table 5: Parameters of the proposed models fitted to adsorption data
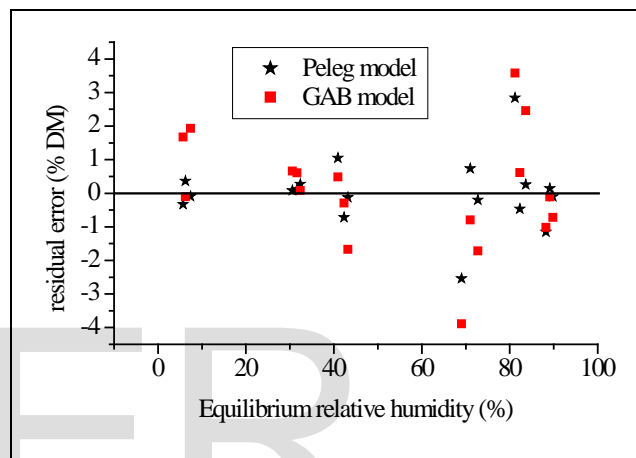

Fig. 4: Residual plot distributions on desorption isotherms of the African mussels
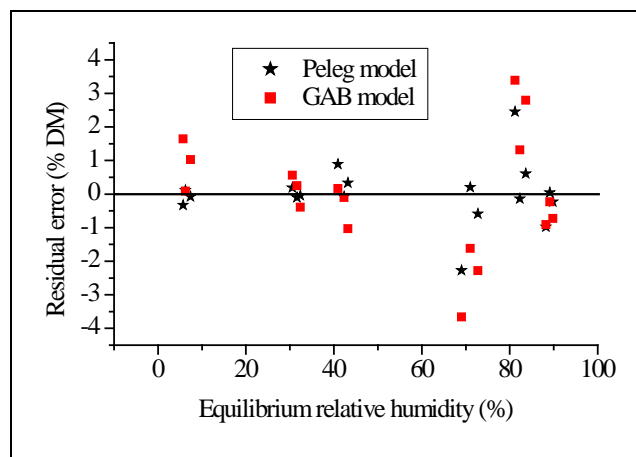

Fig. 5: Residual plot distributions on adsorption isotherms of the African mussels

3.3 Optimal storage conditions

Figure 6 illustrates the technique for balancing optimal relative humidity to maintain African mussels kind Perna Perna.

The calculation method comprises a polynomial decomposition of the equilibrium moisture content of all experimental results as a function of the equilibrium relative humidity. This allows calculating the value for which the second derivative of X_{eq} vanishes (inflection point) and therefore the optimum retention of the relative humidity. The experimentally value found corresponds to 35.63 % compatible with water contents references.
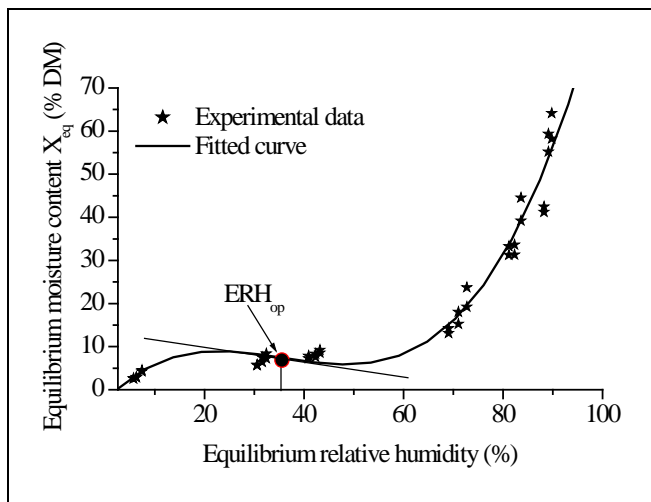

Fig. 6: Optimum equilibrium relative humidity ERH_{op} for the conservation of African mussels

3.4 Thermodynamic properties

The isosteric heat of sorption can be calculated from the sorption isosteres, given by equation 4, for constant equilibrium moisture content. Figure 7 shows the isosteric heats of adsorption and desorption of the African mussels at temperatures ranging between 303.15 to 323.15 K.
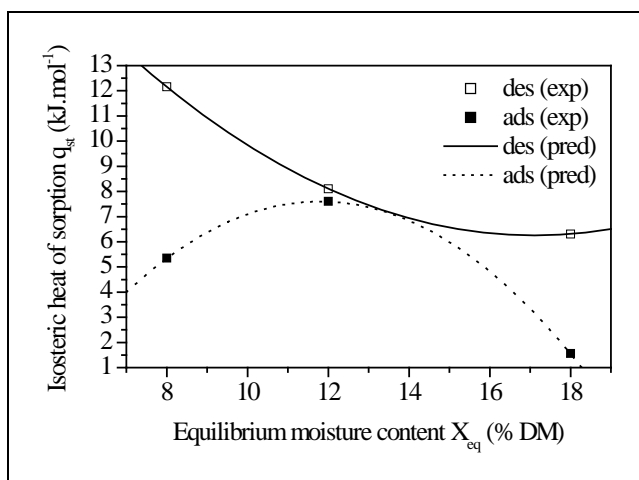

Fig. 7: Isosteric heat of sorption for African mussels as a function of equilibrium moisture content.

This curve shows that the isosteric heat is larger for small values of the water content, illustrating the strong bonding of water with the substrate, and it becomes negligible compared

with the latent heat of vaporization of water for high water levels [27]. The energy needed for desorption process is greater than the energy necessary to the phenomenon of adsorption. Similar results are cited by other authors [28- 30].

The experimentally values obtained were correlated with satisfaction by the following polynomial equations (r=1):

$$q_{st}(des) = 27.1029 - 2.4388 \times X_{eq} + 0.0713 \times X_{eq}^2$$

$$(10)$$

$$q_{st}(ads) = -14.2717 + 3.7101 \times X_{eq} - 0.1573 \times X_{eq}^2$$

$$(11)$$

Focusing on the thermodynamic approach, the behavior of water adsorption can be evaluated according to the differential enthalpy and entropy by Equation (4) in a range of X_{eq} from 0.08 to 0.18. As expected, the change in enthalpy was represented by values ranging from 1 to 12 kJ.mol^{-1} while entropy presented positive values ranging from 2 to 30 J.mol^{-1}.K^{-1}. Both, in modulus, tend to lower values as the moisture content increases (Figures 7 and 8). The enthalpy, similarly as isosteric heat of sorption, illustrates the required energy to do a useful work. At higher moisture contents, less energy is needed to remove a same amount of water in more dried sample due to the fewer available binding sites to promote sorption [31]. On the other hand, entropy represents lost work or energy not available to perform a determined process. Samples with low moisture content present higher values of entropy, indicating that more energy (or enthalpy values) are necessary to remove the water molecules in that conditions [32-34].
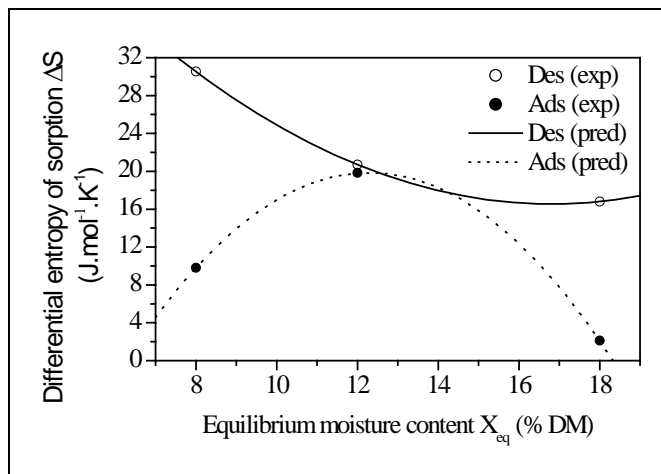

Fig. 8: Differential entropy of sorption for African mussels as a function of equilibrium moisture content.

The experimental values obtained are correlated with a coefficient of determination equal to 1, by the following polynomials:

$$\Delta S(des) = 67.4773 - 6.0618 \times X_{eq} + 0.1804 \times X_{eq}^2$$

$$(12)$$

$$\Delta S(ads) = -62.5781 + 13.4128 \times X_{eq} - 0.5455 \times X_{eq}^2$$

$$(13)$$

One first important requirement to confirm the enthalpy-entropy compensation theory, is the presence of a linear relationship between enthalpy and entropy. The linear tendency observed in Figure 9, with $r > 0,9990$, means that the change in enthalpy is accompanied by simultaneous changes in both entropy and Gibbs free energy. In turn, Gibbs free energy tends towards to assume values around zero as the moisture content increases, indicating that dehydration process is more spontaneous ($-\Delta G_\beta$) or not (ΔG_β).
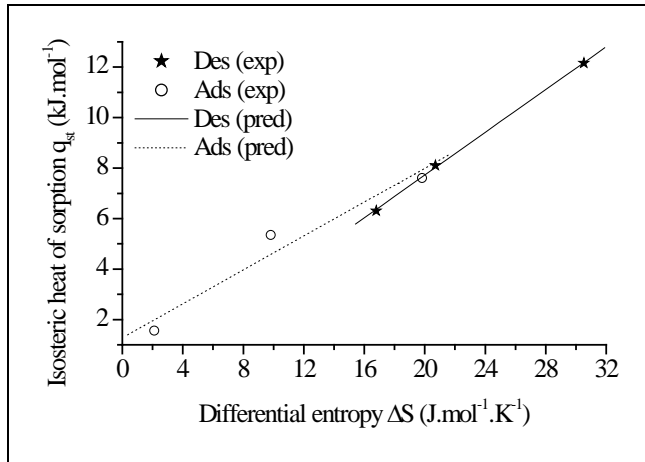

Fig. 9: Linear regression of isosteric heat of sorption versus differential entropy values

The experimentally values obtained for the African ussels are:

T_β (K)	T_β (K)	ΔG_β (J.mol^{-1})	ΔG_β (J.mol^{-1})
(desorption)	(adsorption)	(desorption)	(adsorption)
423.40	335.76	-744.65	1280.31

4 CONCLUSIONS

The water sorption behavior of Africain mussels was evaluated in order to optimize drying Kinetics and minimize the energy expenses involved in dehydration processes. Thus, adsorption and desorption isotherms of Perna Perna mussels were studied in temperatures from 303.15 to 323.15 K, presenting increasing values of equilibrium moisture content when relative humidity increased and temperature decreased. These data could be well-fitted to the GAB and Peleg models with great accuracy (r> 0.9990 and RMSE<0.0130).

The optimal equilibrium relative humidity for the conservation of the African mussels is 35.63% consistent with optimum storage range between 20% and 40%.

Thermodynamic properties were determined as a function of equilibrium moisture content. In an interval of X_{eq} of 0.05–0.18, enthalpy and entropy values ranged from 1 to 12

kJ.mol^{-1} and from 2 to 30 J.mol^{-1}.K^{-1}, respectively. The linear relationship between them showed that lower energy is necessary to remove a certain amount of water at higher moisture contents, which is associated to the decrease in the number of available sites to sorption followed by a reduction of interactions between African mussels matrix and water molecules in the multilayer. This phenomenon makes the water removal process "more spontaneous" when African mussels presents higher moisture contents. It was found a higher value of 423.40 ± 6.64 K for desorption isokinetic temperature and 335.76 ± 4.27 K for adsorption isokinetic temperature than for harmonic temperature (312.94 K), confirming the consideration of enthalpy driven process to water adsorption of African mussels.

Nomenclature

A, B, C, D	model coefficients	X_{eq}	Equilibrium moisture content (% DM)
ads	adsorption	RMSE	Root mean square error (%)
a_w	water activity (-)	r	Cœfficient of determination
B_0, C_0, h_1, h_2	coefficients GAB model	T	Absolute temperature (K)
DM	dry matter	ΔS	entropy (J.mol^{-1}.K^{-1})
exp	experimental	ΔG	free energy (J.mol^{-1})
pred	predicted by model	θ	temperature (°C)
des	desorption		

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