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Experimental determination and modeling of desorption isotherms and isosteric heat of onion

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ABSTRACT: It is essential to know the desorption isotherms to control the drying processes of agricultural products, food. The objective of this work is to determine the sorption isotherms of the local onion: the Violet de Galmi cultivated in the Niayes area. Desorption isotherms were studied for water activities ranging from 0.05 to 0.9 and for temperatures of 40 °C, 50 °C and 60 °C using the static gravimetric method. Six saturated salt solutions were used (KOH, K2CO3, NaBr, CuCl2, KCl and NaCl). The results show that the desorption isotherms of onion are type II and the equilibrium water content is temperature dependent. The experimental results are then smoothed by five models: Guggenheim - Anderson - De Boer (GAB), Brunauer - Emmett and Teller (BET), Henderson, Oswin and Peleg for the description of the equilibrium state of this product. From the modeling, it was concluded that both the Peleg model and the GAB model describe the desorption isotherms of onion well, but the Peleg model has the smallest relative errors, thus defining the Peleg model as the best model. From the results obtained, the isosteric heat of desorption is determined using the Clausius-Clapeyron equation.

KEYWORDS: Onion, Galmi violet, desorption isotherm, isosteric heat, modeling.

1 INTRODUCTION

The onion is a universal herb, consumed in all regions of the world, particularly in Senegal. There are several varieties, some of which are particularly rich in antioxidants. The onion is part of the large family of alliaceous plants and, like garlic, it is attributed certain beneficial properties for health. In the kitchen, it is an essential ingredient and is found in many culinary specialties. Several varieties are grown in Senegal, but those recommended for bulb production are: Violet de Galmi, Noflay, Yaakar, Red Creole, Early Yellow of Valencia, Early texas Grano, Late Spanish Yellow, Valencia, Red of Amposta, Spanish Red. The consumption of onions in Senegal is estimated by ARM to be between 15,000 and 18,000 tons/month, i.e approximately 200,000 to 250,000 tons per year, which places Senegal among the main onion consuming countries with an average per capita consumption of 13 kg per year [1]. However, due to the serious conservation and storage problems faced by farmers, huge post-harvest losses are recorded, about 30% of the production [2], [3]. This is why solar drying has become the preferred means of preserving and enhancing the value of onions. The knowledge of the sorption isotherm is particularly important for the drying of a product. It allows to calculate the equilibrium water content (Xeq) of the product with the drying air which is the limit towards which the water content of the product will tend at the end of drying. The value of the equilibrium water content is also an important parameter appearing in the models which allow to predict the evolution of the water content of the product during its drying, then during its storage [4].

In the present work, it is proposed to determine experimentally by the static gravimetric method and at different temperatures, the desorption isotherms of onion: Galmi's Violet. The desorption isotherms are also used to calculate the amount of heat required to evaporate the water molecules to the equilibrium water content. The knowledge of this total heat quantity is important for the sizing of drying and storage equipment to a lesser extent [5].

2 MATERIALS AND METHODS

2.1 RAW MATERIAL

The type of onion used in this study is Violet de Galmi, grown in the Niayes area (Dakar). The products are sent directly to the laboratory after collection.

Fig. 1. Onion: the violet of Galmi

2.2 EXPERIMENTAL METHOD

The static gravimetric method has been used for the determination of desorption curves of onion. In particular, this is the saturated salt method [6], [7]. This method ensures moisture regulation by contact with aqueous salt solutions above which the water vapor pressure, at a given temperature, is perfectly known. Five solutions of saturated salts are used: KOH, K2CO3, NaBr, CuCl2, NaCl, KCl. These solutions allow to obtain relative humidities varying from 0.05 to 0.9. They are prepared in hermetically sealed jars and are maintained in a temperature-controlled oven. The sample is suspended in the jar, above the salts, and thus remains in a temperature and hygrometry stabilized environment. The experiment is performed at three temperatures 40°C, 50°C and 60 °C.

Table 1 gives the water activity values of the different solutions used at different temperatures [8].

Table 1. Water activity values of the different solutions used

Saline solutions used	Water activities		
	40°C	**50°C**	**60°C**
KOH	0,063	0,057	0,056
K_2CO_3	0,422	0,456	0,45
NaBr	0,532	0,509	0,497
$CuCl_2$	0,68	0,655	0,633
NaCl	0,747	0,744	0,745
KCl	0,823	0,812	0,803

The mass of the product used for desorption is 8.0000 ± 0.0001 g. The monitoring of mass losses is ensured by a precision balance ± 0.0001 g. The hygroscopic equilibrium is obtained when the exchange between the product and the ambient air is completed. As soon as the wet masses are determined, the samples are introduced into an oven at 105 °C for 24 h in order to determine their dry masses.

2.3 Modeling Of Desorption Isotherms For Onion

Several mathematical models, describe the relationship between equilibrium water content, equilibrium relative humidity and temperature. In this study, five models are used to smooth out the desorption isotherms of the product: BET, GAB, Henderson, Oswin and Peleg. The goal is to determine the most appropriate model (s) for describing the desorption isotherms of onion. Table 2 lists the five models studied [9].

Table 2. Mathematical models of sorption isotherms

Authors	Models	Parameters	Domain
BET	$X_{eq} = \frac{ACa_w}{(1-a_w)(1-a_w+Ca_w)}$	*A, C*	monolayer
GAB	$X_{eq} = \frac{ABCa_w}{(1-Ka_w)(1-Kaw+CKa_w)}$	*A, B, C*	complete curve
Oswin	$X_{eq} = A\left[\frac{a_w}{1-a_w}\right]^B$	*A, B*	complete curve
Henderson	$X_{eq} = \left[\frac{\ln(1-a_w)}{-A}\right]^{1/B}$	*A, B*	complete curve
Peleg	$X_{eq} = Aa_w^{K_1} + Ba_w^{K_2}$	*K_1, K_2*	complete curve

Where A, B, C, K1, K2 are constants relative to the models and T the temperature in degree Kelvin. The parameters of these models vary with temperature.

The models are compared based on the correlation coefficient (R2), relative error (P), root mean square error (RMSE), and the average of the sum of the squared errors the reduced chi-2 (χ^2) obtained from the full Origin Pro version 8.5 software where RMSE and χ^2 give the difference between the experimental and modeled values. The best model will be the one with the largest correlation coefficient (almost equal to 1) and the smallest values of P, RMSE and χ^2. These parameters can be calculated by the following equations 1, 2, 3 and 4:

$$R^2 = [\frac{\sum_{i=1}^{N}(X_{exp,i}-\overline{X_{exp,\iota}})\times(X_{mod,i}-\overline{X_{mod,\iota}})}{\sqrt{\sum_{i=1}^{N}(X_{exp,i}-\overline{X_{exp,\iota}})^2\times\sum_{i=1}^{n}(X_{mod,i}-\overline{X_{mod,\iota}})^2}}]^2 \quad (1)$$

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}\left(X_{exp,i} - X_{mod,i}\right)^2\right]^{\frac{1}{2}} \quad (2)$$

$$\chi^2 = \frac{\sum_{i=1}^{N}\ (X_{exp,i}-X_{mod,i})^2}{N-n} \quad (3)$$

$$P(\%) = \frac{100}{n}\sum_{i=1}^{N}\frac{X_{exp}-X_{mod}}{X_{exp}} \quad (4)$$

Where;

Xexp, i: the ith reduced water content obtained experimentally
Xmod,i: the ith reduced water content obtained with the studied model
N: the number of measurement points
n: the number of parameters

3 Results And Discussion

3.1 Desorption Isotherms Of Onion At Different Temperatures

The experimental results of desorption of onion at different temperatures (40, 50, and 60°C) are presented in Figure 2. These represent the evolution of the equilibrium water content Xeq as a function of the water activity of the medium for the temperatures studied. This is observed for activities that range from 0.05< Aw < 0.9.

The curves show a sigmoidal shape similar to those presented by several products [10], [11]. It can be seen that the water content increases with increasing water activity. It is also noted that an increase in temperature is accompanied by an increase in water activity for a constant water content.

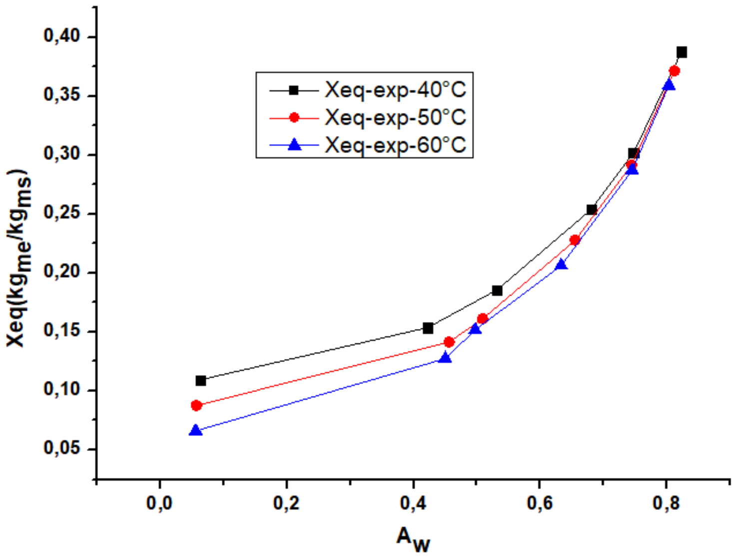

Fig. 2. Desorption isotherms of onion at 40°C, 50°C and 60°C

For a given water activity, it is also observed that the equilibrium water content of the onion decreases with increasing temperature, which corroborates the results obtained by many authors for high protein products [10], [12], [13], [14]. For high temperatures the excitation state of the molecules is higher, leading to a decrease in the attractive forces of the water molecules between them. At constant temperatures, the water activity (Aw) increases with the equilibrium water content (Xeq).

To ensure the microbiological quality of the product and its preservation, the water activity (Aw) should be between 0.2 and 0.3 [15]. This activity value corresponds to equilibrium water contents between 0.08 < Xeq < 0.12 in desorption for air temperatures between 40°C,50°C and 60° C.

3.2 Modeling Of Desorption Isotherms

Table 3 gives the fitting parameters on the experimental results.

Table 3. Values of the fitting parameters of the desorption isotherms

	Models	RMSE	χ^2	R^2	P (%)
40°C	BET	0,04518	0,00204	0,80706	39,09057
	GAB	0,00464	$2,15566.10^{-5}$	0,99796	1,149158
	Oswin	0,02881	$8,3002.10^{-4}$	0,92154	12,01775
	Henderson	0,0406	0,00165	0,84423	19,16239
	Peleg	0,00402	$1,61857.10^{-5}$	0,99847	0,01478
50°C	**Models**	**RMSE**	χ^2	R^2	**P (%)**
	BET	0,03601	0,0013	0,88209	38,52918
	GAB	0,00489	$2,38712.10^{-5}$	0,99783	0,67009
	Oswin	0,02637	$6,95295.10^{-4}$	0,93678	18,08784
	Henderson	0,03606	0,0013	0,88177	30,29559
	Peleg	0,00434	$1,87989.10^{-5}$	0,99829	0,02427
60°C	**Models**	**RMSE**	χ^2	R^2	**P (%)**
	BET	0,0262	$6,86594.10^{-4}$	0,94122	37,23584
	GAB	0,00606	$3,6681.10^{-5}$	0,99686	0,69661
	Oswin	0,01956	$3,82539.10^{-4}$	0,96725	20,81058
	Henderson	0,02771	$7,67602.10^{-4}$	0,93429	34,28331
	Peleg	0,007	$4,90636.10^{-5}$	0,9958	0,08126

The measured and calculated onion desorption isotherms for the Peleg model and the ABM model for the different temperatures studied are presented by Figure 3. These isotherms are in agreement with the analysis of the calculated R^2, P, RMSE and χ^2 values.

Contrary to some authors who claim that the BET model performs better for water activities between 0.05 and 0.45, and the ABM model is better for products with high water content [16], [17], regardless of the range of activity considered and temperature, the Peleg model has the lowest relative errors. Among the models tested, the Peleg model provides the best fit to the experimental desorption isotherms of onion followed by the ABM model.

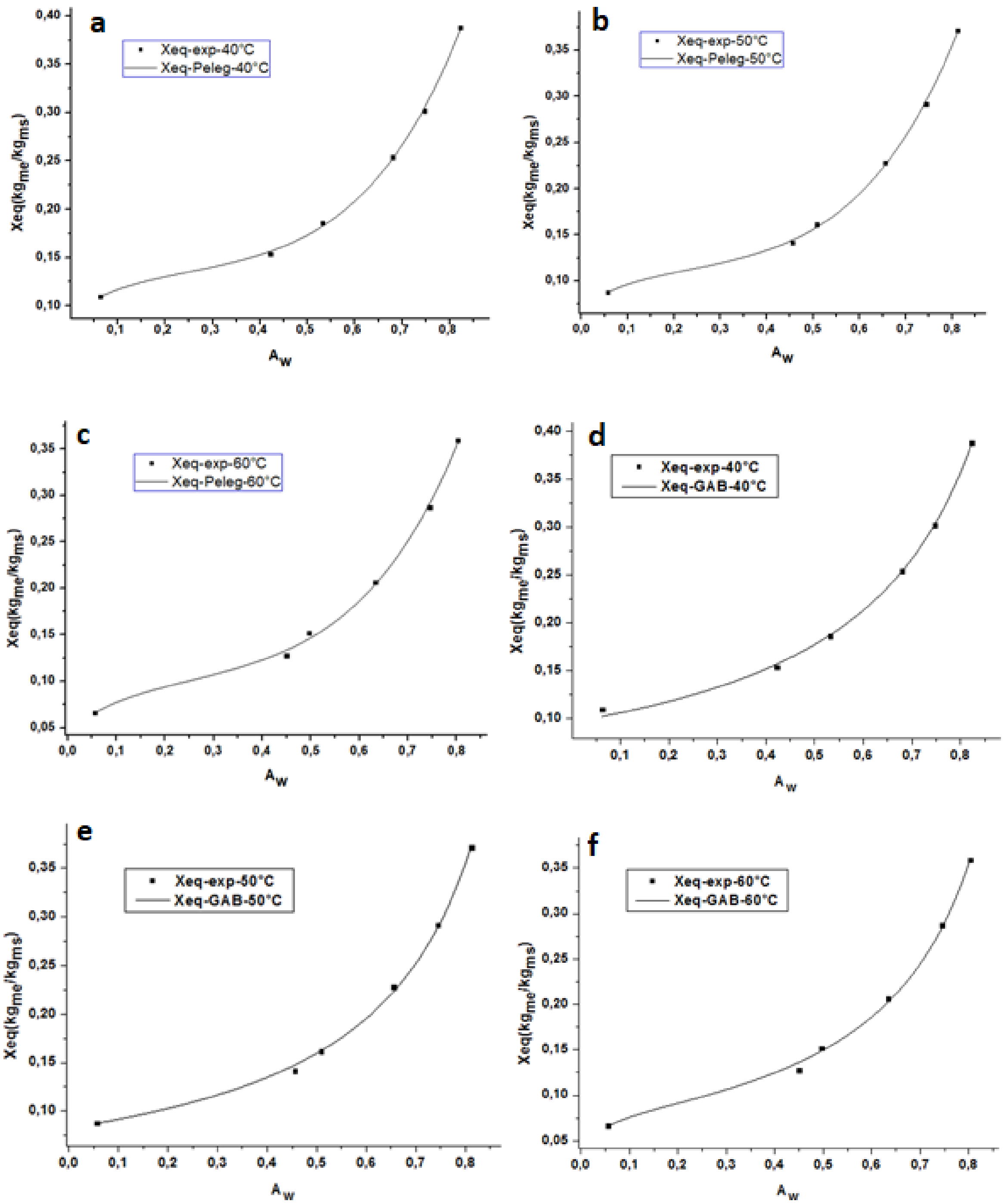

***Fig. 3.** Desorption isotherms of onions obtained by the: a Peleg Model at 40°C; b Peleg Model at 50°C; c Peleg Model at 60°C; d GAB Model at 40°C; e GAB Model at 50°C; f GAB Model at 60°C*

The values of the coefficients A, B, C, K1 and K2 of the Peleg model are obtained from the software by setting initial values at the beginning of the program. These values are given in Table 4 below.

Table 4. Parameter values of the Peleg and ABM models

40°C	**Models**	**A**	**B**	**C**	**K_1**	**K_2**
	GAB	0,0778	0,97786	67,38192		
	Peleg	0,16426	0,532792		0,14754	4,43138
50°C	**Models**	**A**	**B**	**C**	**K_1**	**K_2**
	GAB	0,08319	0,95731	2151,3819		
	Peleg	0,56536	0,14221		4,26535	0,16926
60°C	**Models**	**A**	**B**	**C**	**K_1**	**K_2**
	GAB	0,09648	0,91195	$5,129.10^{43}$		
	Peleg	0,14537	0,58484		0,27462	4,45875

3.3 Determination Of The Isosteric Heat Of Desorption Of The Onion

The isosteric heat is equal to the sum of the latent heat of vaporization of water (Lvap) and the net isosteric heat of desorption (Qst). It is given by the equation of Clausis Clapeyron (4). The isosteric heats are calculated from the isosteres of desorption, i.e the curve giving ln (Aw) as a function of 1/T at a constant water content (Figure 4) according to equation (5) [11].

$$Q_s = Q_{st} + L_{vap} \ (5)$$

$$ln(Aw) = -\left(\frac{Q_{st}}{R}\right)\frac{1}{T} + K \ (6)$$

This isosteric heat is calculated from the desorption isosteres plotted in Figure 4.

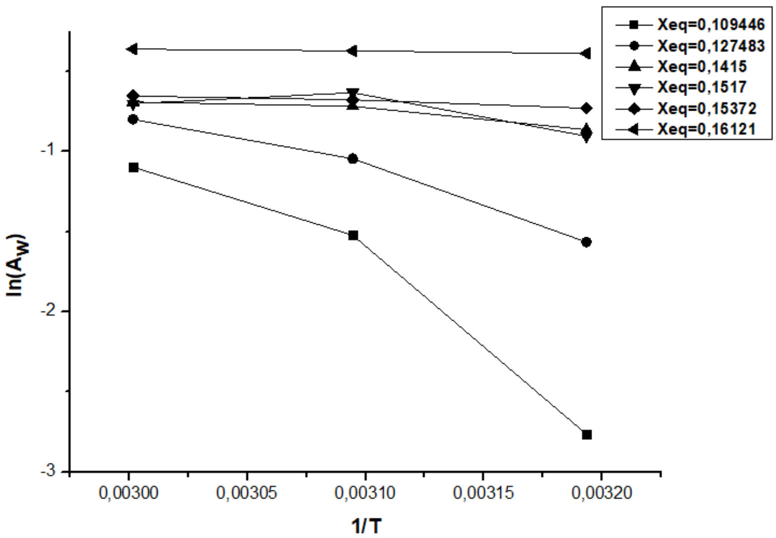

Fig. 4. Desorption isosters of onion as a function of inverse temperature for different water contents

Figure 5 shows that the isosteric heat of desorption decreases with increasing equilibrium water content. The high values of isosteric heat, at low water contents, indicate strong water binding in the product to be dried. The isosteric heat of desorption decreases continuously with increasing water content, going towards the latent heat of vaporization of pure water (0.13338 kJ/mol). This indicates that the adsorbed water vapor can behave like pure water when the water content is high. The rapid decrease in isosteric heat for low water content of the product is due to theexistence of the polar sites of high activity in the product which are covered with water molecules forming the molecular monolayer [18]. Other authors [19], [20] have explained this phenomenon by the fact that in a very restricted range of humidity, when the water content increases, some products swell and promote the opening of new adsorption sites of strong bonds, which increases the isosteric heat.

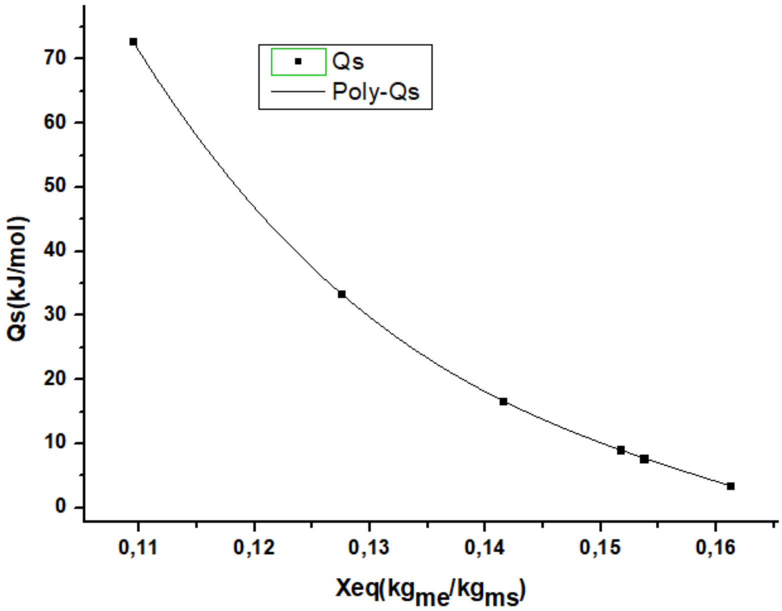

Fig. 5. Isosteric heat of desorption as a function of water content

The correlation of Qs is given by equation 7:

$$Qs = 19031Xeq^4 - 308370Xeq^3 + 143733Xeq^2 - 23831Xeq + 1337 \quad (7)$$

$$R^2 = 0{,}99999$$

These results are in agreement with those generally observed for most food products (such as the case of spearmint leaves) [21]. The knowledge of the isosteric heat of desorption is therefore very important for a good design of drying equipment. Indeed, for example, it turns out that to reach the water activity values allowing to ensure the stability of onion (0.2 < Aw < 0.3), i.e. equilibrium water content values between 0.08 (dry basis) and 0.12 (dry basis) depending on the drying air temperature, an energy of at least 40 kJ/mol is required.

4 Conclusion

The knowledge of sorption isotherms is an essential step to better understand and comprehend the problems related to the conservation, experimentation and modeling of drying processes. The results obtained show that the sorption isotherms of onion follow well the general shape of the sorption curve and that the Peleg and GAB models describe these sorption isotherms well. However, the Peleg model provides the lowest average relative errors regardless of the temperature considered. Thus, the Peleg model is the most adequate model for the onion sorption isotherms. We also note that the net isosteric heat of onion decreases with increasing water content. Finally, knowing the equilibrium water content of the onion, it is possible to determine its behavior in a solar dryer operating in forced convection.

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