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Bioactive composition, sorption isotherms and isosteric heats of Lazoul (*Allium roseum* L.) leaves.

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Abstract - *Allium roseum* leaves were found to be rich in polyphenols and flavonoids and had high antioxidant activity. *Allium roseum* leaves thermo-physical characterization shows that the increase in water activity and the decrease in temperature significantly augment the equilibrium water content of *Allium roseum* leaves. A significant difference between desorption and adsorption (hysteresis effect) was found at lower temperature (20°C) and it disappeared at higher temperatures. GAB and Peleg models were found to better describe the relationship between equilibrium moisture content, water activity and temperature. The isosteric heats of desorption and adsorption were determined from experimental sorption isotherms and then correlated with corresponding equilibrium moisture contents. Desorption isosteric heat decreased continuously with the increase of the equilibrium moisture content, and was always higher than adsorption heat. In this case and from a moisture content of 0.15 kg water/kg db, adsorption isosteric heat was constant and about 40.68 kJ/mol.

Keywords: Rosy garlic leaves / bioactive composition / sorption isotherms / modeling / isosteric heat of sorption.

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1. Introduction

Rosy garlic *(Allium roseum)*, a spontaneous edible plant, is specific of the south-east of Tunisia. *Allium roseum* leaves are traditionally consumed by local population as a condiment in food, often substituting onion. It has also been empirically used as an herbal remedy for its numerous therapeutic properties. Currently, pharmaceutical interest for traditional therapeutic resources focuses on plant derived natural product. Rosy garlic in the south east of Tunisia (Medenine region) is well known for its expectorant properties and anti rheumatism virtues among others. It may hence arouse great interest as a potential bioactive molecules source.

Allium genus includes approximately 700 species, the most widely used of which are onions (*Allium cepa*), garlic (*Allium sativum*), leeks (*Allium porrum*), chives (*Allium schoenoprasum*), and shallots (*Allium ascalonicum*). *Allium* species are extensively employed as food flavoring because of their characteristic taste. They are also considered as significant sources of bioactive and beneficial molecules such as sulphurous (Calvey et al. 1998; Jones et al. 2004; Li et al. 2007; Mondy et al. 2002) and phenolic compounds (Bonaccorsi et al. 2008; Bozin et al. 2008; Lanzotti 2006).

Allium roseum is a seasonal plant, currently available only during the wet season. It is a plant with high water content during its vegetative phase (Ben Haj Said et al. 2014; Ben Haj Said et al. 2013) which causes physical, chemical, enzymatic and microbiological changes during the storage and the processing. These changes are particularly influenced by the moisture content, the water activity and the storage temperature. Moisture sorption by the product from the atmosphere (adsorption) or by the atmosphere from the product (desorption) occurs during drying, storage and packaging until reaching equilibrium. Hence, a comprehensive knowledge of *Allium roseum* sorption behavior is indispensable and would allow a better understanding, between equilibrium moisture content, water activity and temperature relationships, which are expressed as sorption isotherms.

Moisture sorption isotherm data are used to evaluate the product residual moisture content and to predict the maximum moisture amount gained or loosed by the product material during storage or drying. The adsorption isotherms data are used for choosing and deciding of storage conditions, while desorption isotherms allow to establish drying processes. Thus, moisture sorption isotherm, are especially indispensable to find optimal processing and storage conditions that allow product stability (Cordeiro et al. 2006). Experimental sorption isotherms data are also used to calculate the net isosteric heat of sorption, which is essential to estimate energy requirements of dehydration processes. Comparison between the product net isosteric heat and the latent heat of vaporization of pure water may thus be done. Such moisture content level corresponds to the bound water amount contained in the food material. Several empirical and semi-empirical models have been proposed to describe the relationship between the equilibrium moisture content, the temperature and the water activity of food products (Brunauer et al. 1938; Caurie 1970; Halsey 1948; Henderson 1952; Oswin 1946; Peleg 1993; Smith 1947). Nevertheless, no one model is found universal enough to predict the material equilibrium moisture content throughout the whole range of water activities, and for all types of foods. Hence, experimental and modeling investigations are essential to thermo-physical characterization and sorption isotherms determination of agricultural products.

Little information is available about *Allium roseum* leaves characterization and no available results in the literature were found about the study of sorption behavior of *Allium roseum*. Therefore, the main objectives of this study were (i) to determine the bioactive composition of rosy garlic leaves, (ii) to obtain experimental desorption and adsorption isotherms at different temperatures, (iii) to check several moisture sorption equation for their ability to predict rosy garlic sorption behavior and (iv) to estimate desorption and adsorption isosteric heats of *Allium roseum* leaves.

2. Material and methods

2.1. Plant material

Allium roseum, locally called Lazoul, used in this investigation, was collected at its vegetative stage from Medenine which is an arid region with a mean annual fall ranging from 150 to 200 mm, in the south-east of Tunisia. Botanical identification was carried out in the Range Ecology Laboratory of the Institute of Arid Areas (Medenine, Tunisia).

2.2. Bioactive composition

2.2.1. Separation and characterization of volatile sulfur compounds

Allium roseum leaves were crushed. Compounds emitted in a closed 4-ml vial at room temperature were trapped at 60°C for 30 min and transferred to the GC–MS injector by headspace SPME (Teyssier et al. 2001).

2.2.2. Sample extract preparation

Leaves extract was obtained by magnetic stirring for 30 min of 2.5 g of fresh or dried powdered leaves with 25 ml of absolute methanol. The mixture was kept in dark at 4°C for 24 hours and then filtered. The methanolic extract was stored at 4°C until analysis (Ben Haj Said et al. 2013).

2.2.3. Total polyphenols content (TPC)

Total polyphenols content was assayed using the Folin–Ciocalteu reagent following the method based on the reduction of a phosphowolframate–phosphomolybdate complex by phenolic compounds to blue reaction products (Dewanto et al. 2002).

2.2.4. Total flavonoïds content (TFC)

Total flavonoïds content was measured using a colorimetric method based on the formation of the complex aluminum-flavonoïd (Dewanto et al. 2002).

2.2.5. Antioxidant activity

The antioxidant activity was estimated by the method used by Miliauskas et al. (2004) and Chan et al. (2009) with some modifications. This method is based on the determination of the diphenylpicrylhydrazyl radical (DPPH·) scavenging activity. All samples were analyzed in three replications for each extract concentration. Radical-scavenging ability was calculated as IC_{50} ($\mu g\ ml^{-1}$), the extract concentration required to cause a 50% inhibition, and expressed as TEAC in kg trolox equilvalents (TE) /100 kg as follows:

$$\mathrm{TEAC\,(mg\,trolox/100g)} = \frac{IC_{50(trolox)}}{IC_{50(sample)}} \times 10^5 \qquad (1)$$

The IC_{50} of trolox used for calculation of TEAC was determined with the same way as the samples.

2.3. Color measurement

Surface color of *Allium roseum* leaves were evaluated using a handheld tristimuli colorimeter (Konica Minolta CR-410, Japan). L*, a* and b* CIE color space coordinates show the degree of brightness, the degree of redness (a) or greenness (-a), and the degree of yellowness (b) or blueness (-b), respectively. For each sample, L*, a* and b* parameters were measured three times directly on the product. Color intensity or chromacity (C) and hue value (α) were calculated using the following relations:

$$C = \sqrt{(a^{*2} + b^{*2})} \qquad (2)$$

$$\alpha = \tan^{-1}\left(\frac{b^*}{a^*}\right) \qquad (3)$$

2.4. Experimental sorption isotherms determination

Allium roseum leaves equilibrium moisture contents data for water adsorption and desorption were determined at 20, 30, 40, 50 and 60°C. The static gravimetric method was applied using saturated salt solutions to maintain a fixed relative humidity. The salts used are NaOH, $MgCl_2$, K_2CO_3, $SrCl_2$, NaCl, KCl and $BaCl_2$. These salts have a range of relative humidity of 4.56–90.69%.

Equilibrium moisture content was reached when three consecutive weight measurements (analytical balance: AXIS AGN220C, Germany), separated by 24 hours showed a difference less than 0.001g. Both adsorption and desorption isotherms experiments were duplicated.

Once equilibrium reached, equilibrium moisture content (Xeq) was calculated as follows:

$$X_{eq} = \frac{(MH_{eq} - MS)}{MS} \qquad (4)$$

Where MHeq and MS are the masses before and after drying, respectively.

2.5. Statistical analysis

Equilibrium moisture content (X_{eq}) data were reported as mean values ± standard deviation (SD) and expressed as kg water/kg d.b. One-way variance analysis (ANOVA) was carried in order to evaluate the influence of water activity and temperature on equilibrium moisture content by using Statistical Analysis System (SAS) version 9. For all statistical analyses, the level of significance is fixed at 5%.

2.6. Sorption isotherms modeling

Experimental evolutions of equilibrium moisture content for different water activities and temperatures were described by using different models (Table 1) chosen from the most used equations in literature to describe desorption and adsorption processes of agricultural products.

Table 1. Mathematical models for sorption isotherms modeling.

Model name	Model expression
BET (Brunauer et al. 1938)	$X_{eq} = \left(\frac{ACa_w}{(1-a_w)(1+(A-1)a_w)}\right)$
GAB (Van den Berg et al. 1981)	$X_{eq} = \left(\frac{CABa_w}{(1-Ba_w)(1-Ba_w+ABa_w)}\right)$
Henderson-Thompson (Henderson 1952)	$X_{eq} = \left(\frac{\mathrm{Ln}(1-a_w)}{-A(T+B)}\right)^{\frac{1}{C}}$
Halsey (Halsey 1948)	$X_{eq} = A\left(-\frac{B}{\mathrm{Ln}\,(a_w)}\right)^{\frac{1}{C}}$
Oswin (Oswin 1946)	$X_{eq} = A\left(\frac{a_w}{(1-a_w)}\right)^{B}$
Peleg (Peleg 1993)	$X_{eq} = A\,a_w^B + C\,a_w^D$
Caurie (Caurie 1970)	$X_{eq} = \exp\,(A + B\,a_w)$
Smith (Smith 1947)	$X_{eq} = A - (B(\mathrm{Ln}\,(1-a_w)))$

Non-linear optimization method was used to determine the parameters of the equations cited in table 1. The parameters of each model were determined by minimizing the difference between calculated and experimental data. The adequacies of the models were evaluated by using three statistical parameters: the standard error (S), the correlation coefficient (r) and the percent average relative deviation (P). These parameters are defined as following:

$$S = \sqrt{\frac{\sum_{i=1}^{n_{exp}}(Xeq_{expi} - Xeq_{cal_i})^2}{n_{exp} - n_{param}}} \tag{5}$$

$$r = \sqrt{1 - \frac{\sum_{i=1}^{n_{exp}}(Xeq_{expi} - Xeq_{cal_i})^2}{\sum_{i=1}^{n_{exp}}(\overline{X}_{eq} - X_{eq})^2}} \tag{6}$$

$$P = \frac{100}{n_{exp}}\sum_{i=1}^{n_{exp}}\left|\frac{Xeq_{cali} - Xeq_{expi}}{Xeq_{expi}}\right| \tag{7}$$

Where Xeq_{cal} is the value of the equilibrium moisture content calculated by using the tested model, Xeq_{exp} is the experimental value of the equilibrium moisture content, n_{param} is the number of the model parameters and n_{exp} is the number of experimental points.

2.7. Sorption isosteric heats determination

The net isosteric heats of sorption (q_{nst}) can be calculated by using the following correlation which is derived from the Clausius–Clapeyron equation.

$$\mathrm{Ln}\,(a_w) = -\left(\frac{q_{nst}}{R}\right)\left(\frac{1}{T}\right) + K \tag{8}$$

In Eq. (8) a_w, R, T and K are, respectively, the water activity, the universal gas constant, the absolute temperature and a constant.

Experimental sorption isotherms are plotted as $\mathrm{Ln}(a_w)$ versus 1/T for fixed values of equilibrium moisture contents (the isosteres curves). The net isosteric heats of sorption could be calculated for each value of equilibrium moisture content from the slope of the isosteres curves which is equal to $-q_{nst}/R$.
Values of the isosteric heat of sorption (Qst) are obtained by adding pure water latent heat of vaporization (L) to the net isosteric heat of sorption:

$$Q_{st} = q_{n\,st} + L \tag{9}$$

3. Results and discussion

3.1. Bioactive composition

3.1.1. Volatile sulfur compounds

Five volatile sulfur compounds have been detected, by SPME analysis, in fresh *Allium roseum* leaves, four disulfides (dimethyl-disulfide, methyl-2-propenyl-disulfide, cis-propenyl-methyl-disulfide, trans-propenyl-methyl-disulfide) and a trisulfide (dimethyl-trisulfide) (Figure 1).

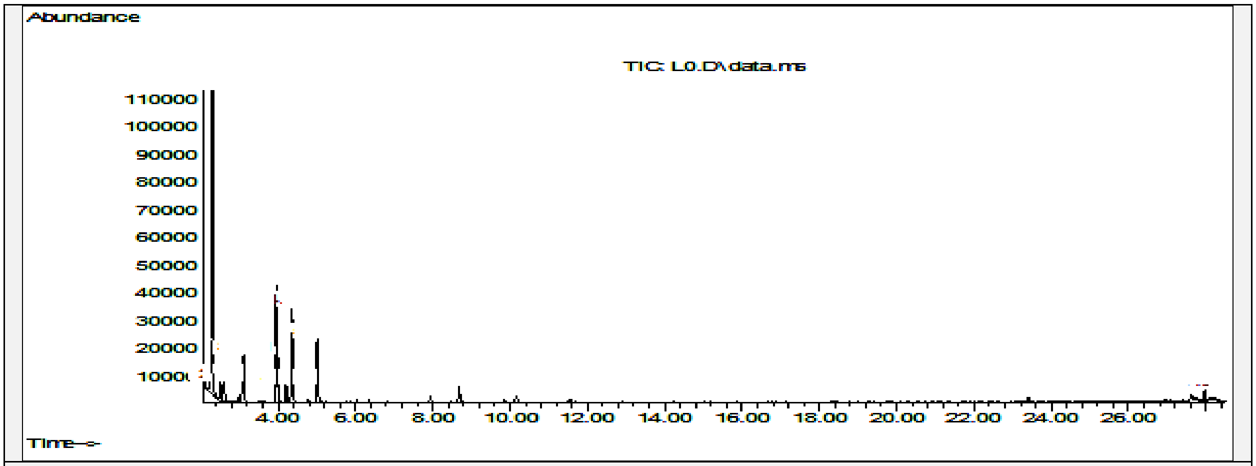

Figure 1. Chromatogram of *Allium roseum* leaves volatile sulfur compounds.
1. Dimethyl-disulfide; 2. methyl-2-propenyl-disulfide; 3. Cis-propenyl-methyl-disulfide;
4. Trans-propenyl-methyl-disulfide; 5. Dimethyl-trisulfide

Dimethyl-trisulfide and methyl-2-propenyl-disulfide are also found abundant in the *Allium roseum* flowers essential oil collected from Bengardane (South-East of Tunisia) (Zouari et al. 2011) and Sfax areas (Central Tunisia) (Zouari et al. 2013). For chive leaves (*Allium schoenoprasum*), only disulfides were detected. It is about dimethyl-disulfide, dipropyl-disulfide, methyl-propyl-disulfide, methyl-l-propenyl-disulfide and propyl-1-propenyl-disulfide (Mellouki et al. 1994). Dimethyl-disulfide (47.57%) is the major volatile sulfur compound found in *Allium roseum* leaves. According to Mellouki et al. (Mellouki et al. 1994), chive leaves are also very rich in dimethyl-disulfide. For chives leaves, it is the dipropyl-disulfide which occupies first place. This compound has been not detected in *Allium roseum* leaves. For garlic (*Allium sativum*), three major volatile sulfur compounds have been detected and are, by order of abundance, the di-2-propenyl-trisulfide, the methyl-2-propenyl-trisulfide and the di-2-propenyl-disulfide. The methyl-2-propenyl-disulfide and the dimethyl-trisulfide, abundant compounds in *Allium roseum* leaves, have been also detected in garlic

3.1.2. Phenolic compounds and antioxidant activity

Fresh *Allium roseum* leaves contain 1.645±0.343 kg GAE/100 kg d.b. of total polyphenols. Najjaa et al. (2011) found 0.74 ±0.089 and 0.75 ± 0.13 kg catechol equivalent/100 kg d.b. of total phenolic compounds in flower and leaf, respectively. Differences in total phenolic contents found could be attributed to extraction and dosage adopted methods. Flavonoïds are the major subclass of polyphenols found in *Allium* species (Pérez-Gregorio et al. 2011). The total flavonoïds content determined in fresh *Allium roseum* leaves was 3.344±0.185 kg QE/100 kg d.b (Ben Haj Said et al. 2013). These compounds could exhibit antioxidant properties approximately comparable to commercial synthetic antioxidants. The antioxidant capacity of fresh *Allium roseum* leaves was 5.375±0.064 kg TE/100 kg d.b. This suggests the potential use of this category of plants as conservator and antioxidant additives in foods in order to preserve their organoleptic quality and to prevent lipid oxidation (Yang et al. 2011).

3.2. Color

The values for the CILAB L*, a* and b* color coordinates of the fresh *Allium roseum* leaves were 28.89±1.6, −5.28±0.49 and 7.78±0.73, respectively. For the all examined leaves, the parameter a* is negative indicating the green color of the leaves. The values of chromacity (C) and hue value (α) were 9.41±0.87 and -0.10±0.02, respectively. The hue angle (H°=180°+ α) of fresh *Allium roseum* leaves was about 180°, which represents a color in the yellow/green region (hue angle between 90° and 180°).

3.3. Experimental sorption isotherms

The hygroscopic equilibrium of *Allium roseum* leaves was reached in 10 days for desorption and adsorption. Experimental desorption isotherms of *Allium roseum* leaves obtained at 20, 30, 40, 50, 60°C are shown in Figure 2.

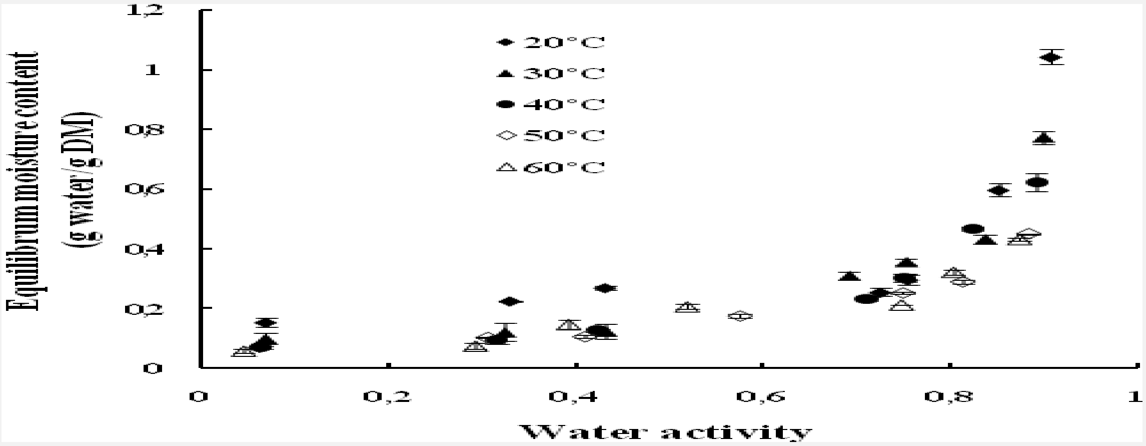

Figure 2. Desorption isotherms of *Allium roseum* leaves at different temperatures.

Allium roseum leaves desorption isotherms have a sigmoid form (typical S-shape curves) and are of type II on BET classification. Equilibrium moisture content increased very slowly at low water activity and showed a steep increase at high relative humidity (from a water activity of 0.8). According to Pezzuti and Crapiste (1997) and Moriera et al. (2009), at low and intermediate values of water activity, water is mainly retained by physical adsorption on the polymeric compounds. Sugar dissolution increases and becomes important causing a steep increase in moisture content at higher water activities. Statistical analysis of sorption data indicated that water activity affect significantly (P<0.05) equilibrium moisture content.

The temperature effect on desorption isotherm is principally observed for higher water activity values. The ANOVA analysis shows a significant effect of temperature on equilibrium moisture content of *Allium roseum* leaves (P<0.05). For a given water activity, higher temperatures give lower equilibrium moisture content. For example, at a water activity value of 0.75, the equilibrium water contents were 0.21 kg water/kg d.b. at 60°C, 0.25 kg water/kg d.b. at 50°C, 0.30 kg water/kg d.b. at 40°C and 0.36 kg water/kg d.b. at 30°C. These results indicate that an increase in temperature will not favor water sorption. This can be explained, according to Moreira et al. (2005), by less hygroscopic capacity of the material due to a reduction in the total number of active sites for water binding at higher temperatures (Toğrul and Arslan 2007). This behavior could be also ascribed to water molecules excitation state. For high temperatures, the state of molecules excitation is elevated and caused a reduction in the attraction forces between water molecules and in turn an increase in the degree of water desorption.

Adsorption isotherms (Figure 3) show practically the same tendencies as those of desorption. Same interpretations that for desorption isotherms can be made for adsorption isotherms. In fact, the water activity and the temperature present a statistically significant effect (P<0.05) on equilibrium moisture content of *Allium roseum* leaves.

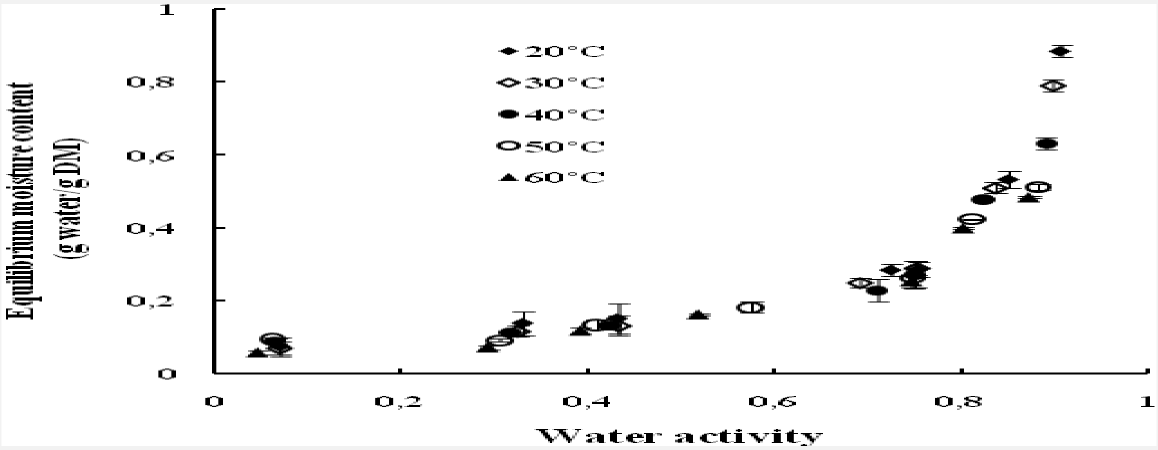

Figure 3. Adsorption isotherms of *Allium roseum* leaves at different temperatures.

As shown in Figure. 3, certain differences are observed. Indeed, temperature effect appears only with values of water activity higher than 0.9. Moreover, temperature effect is less important in the case of adsorption. This may be ascribed to the pre-drying to which the samples, in the case of adsorption, were subjected. These differences in the temperature effect on equilibrium moisture content between desorption and adsorption isotherms are also reported for turnip top leaves (Moreira et al. 2005), *Maytenus ilicifolia* leaves (Cordeiro et al. 2006).

Difference in equilibrium moisture content, for the same water activity, between adsorption and desorption processes is observed. This phenomenon, which is the hysteresis effect, may be attributed to reaction irreversibility and to structural and physicochemical changes occurred during the pre-drying to which the samples, in the case of adsorption, were submitted. Similar results were reported for garlic (Pezzutti and Crapiste 1997). The hysteresis effect is statistically significant (P<0.05) at 20°C (Figure 4) and disappears with increasing temperature (Figure 5).

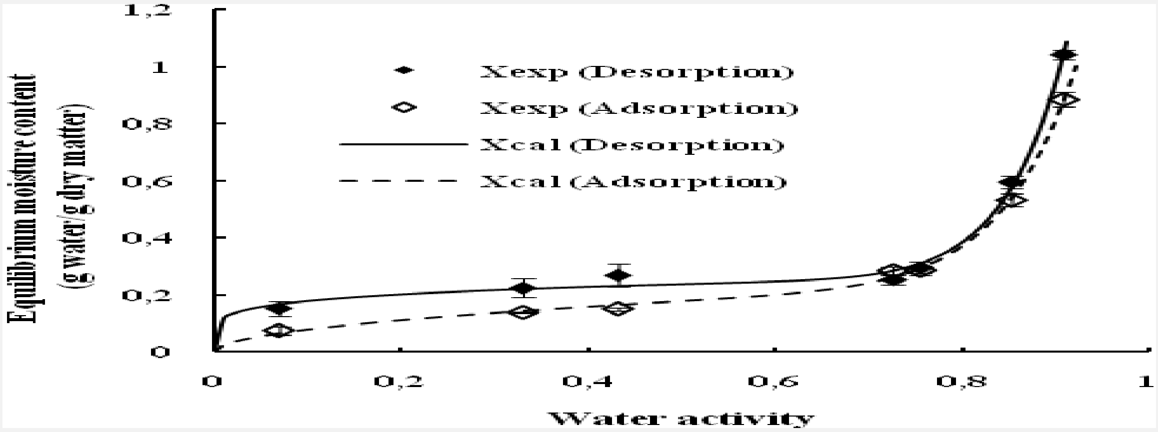

Figure 4. Experimental and calculated data (Peleg model) of sorption isotherms of *Allium roseum* leaves at a temperature of 20°C.

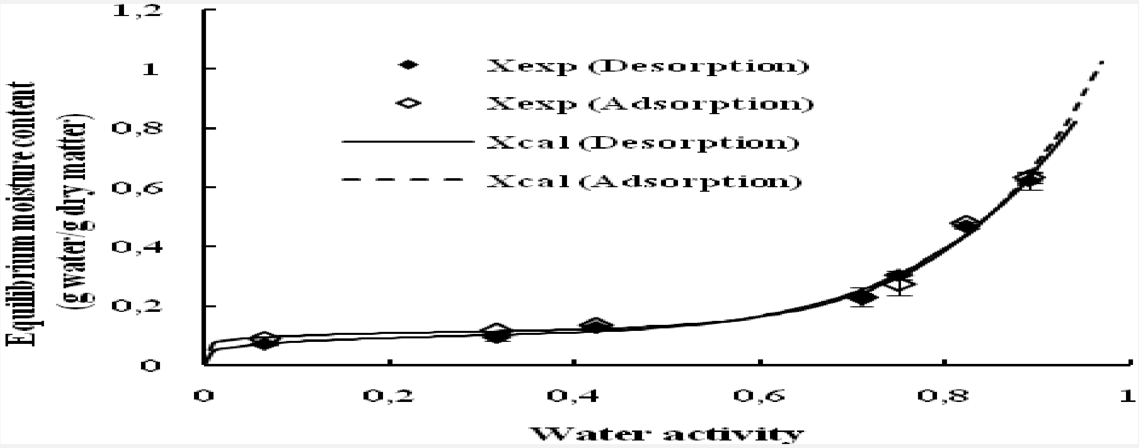

Figure 5. Experimental and calculated data (Peleg model) of sorption isotherms of *Allium roseum* leaves at a temperature of 40°C.

For example, at a water activity value of 0.43, *Allium roseum* leaves equilibrium moisture contents were 0.269 kg water/kg d.b. in desorption and 0.151 kg water/kg d.b. in adsorption at 20°C and 0.127 kg water/kg d.b. in desorption and 0.133 kg water/kg d.b. in adsorption at 40°C. These results can be explained, according to Moreira et al. (2009), by changes of the sorption properties, having for result the elimination of hysteresis, which include the elastic properties of the product, the structural changes of the pores and the modifications of the surface characteristics occurred at high temperatures. These structure modifications of the products cause, under certain experimental conditions, the hysteresis elimination because of the capillary condensation absence.

3.4. Sorption isotherms modeling

The model coefficients for all the eight models were estimated by non-linear regression analysis. The goodness of fit of the models is characterized by the highest value of correlation coefficient (r) and lowest values of standard error (S) and percent average relative deviation (P). The estimated values of models coefficients and the respective values of the correlation coefficients (r), the standard errors (S) and the percent average relative deviation (P) are shown in Tables 2-3.

Table 2. Parameter values for models used to describe desorption isotherms of *Allium roseum* leaves.

Model name	T (°C)	Model parameters				Statistical parameters		
		A	B	C	D	r	S	P
BET	20	7.484×10^{9}	-	0.093	-	0.967	0.087	26.052
	30	2.958×10^{9}	-	0.079	-	0.989	0.039	10.158
	40	3.295×10^{11}	-	0.072	-	0.989	0.034	07.901
	50	1.523×10^{11}	-	0.056	-	0.980	0.029	13.337
	60	1.184×10^{9}	-	0.059	-	0.944	0.048	16.825
GAB	20	16.124×10^{10}	1.013	0.084	-	0.969	0.095	25.366
	30	53.482×10^{8}	0.989	0.085	-	0.990	0.041	09.667
	40	34.803	0.979	0.082	-	0.992	0.032	09.484

	50	321.079	0.952	0.071	-	0.995	0.016	05.256
	60	47.970	0.924	0.082	-	0.967	0.042	15.955
Henderson-Thompson	20	0.338	-12.907	0.529	-	0.897	0.170	45.603
	30	-0.309	-39.566	0.755	-	0.965	0.077	26.060
	40	0.280	-28.559	0.747	-	0.980	0.051	27.494
	50	-0.247	-72.518	1.075	-	0.967	0.042	19.478
	60	-0.332	-80.245	1.264	-	0.951	0.050	23.982
Caurie	20	-6.193	6.805	-	-	0.882	0.162	46.027
	30	-3.960	3.993	-	-	0.960	0.074	25.165
	40	-4.224	4.170	-	-	0.980	0.045	26.547
	50	-3.571	3.036	-	-	0.971	0.035	18.703
	60	-3.052	2.417	-	-	0.951	0.045	17.327
Halsey	20	0.336	0.332	1.134	-	0.950	0.120	33.915
	30	0.321	0.312	1.266	-	0.988	0.046	13.602
	40	0.302	0.293	1.251	-	0.992	0.033	09.379
	50	0.275	0.253	1.508	-	0.994	0.018	07.844
	60	0.281	0.262	1.606	-	0.969	0.040	16.184
Oswin	20	0.157	0.805	-	-	0.931	0.126	39.973
	30	0.166	0.681	-	-	0.981	0.051	18.624
	40	0.149	0.686	-	-	0.988	0.035	15.784
	50	0.135	0.579	-	-	0.983	0.027	14.787
	60	0.160	0.489	-	-	0.965	0.038	20.315
Peleg	20	3.176	14.308	0.267	0.177	0.997	0.033	06.517
	30	8.407	29.859	0.497	1.310	0.987	0.055	18.652
	40	0.999	5.851	0.127	0.213	0.997	0.022	05.338
	50	0.150	0.295	0.671	6.531	0.989	0.028	07.475
	60	0.262	0.655	1.028	12.207	0.975	0.042	20.252
Smith	20	0.036	0.322	-	-	0.862	0.175	40.251
	30	0.003	0.285	-	-	0.953	0.079	24.513
	40	-0.005	0.257	-	-	0.967	0.171	22.460
	50	0.022	0.178	-	-	0.972	0.035	15.053
	60	0.042	0.173	-	-	0.961	0.041	17.243

Table 3. Parameter values for models used to describe adsorption isotherms of *Allium roseum* leaves.

Model name	T (°C)	Model parameters				Statistical parameters		
		A	B	C	D	r	S	P
BET	20	105.152	-	0.081	-	0.997	0.024	06.654
	30	1.948×10^{10}	-	0.080	-	0.998	0.019	07.020
	40	1.861×10^{10}	-	0.074	-	0.984	0.039	08.637
	50	-1.829×10^{10}	-	0.067	-	0.970	0.044	12.560
	60	-2.27×10^{10}	-	0.074	-	0.945	0.055	18.095
GAB	20	12.157×10^{3}	1.009	0.075	-	0.998	0.021	07.245
	30	77.881	1.006	0.077	-	0.998	0.018	03.054
	40	80.356×10^{5}	0.987	0.078	-	0.988	0.039	06.895
	50	14.297×10^{5}	0.956	0.083	-	0.986	0.034	09.183
	60	27.677	0.961	0.081	-	0.986	0.034	19.820
Henderson-Thompson	20	0.313	-11.657	0.569	-	0.971	0.084	36.776
	30	-0.300	-38.990	0.615	-	0.979	0.064	32.431
	40	-0.315	-50.509	0.816	-	0.962	0.068	30.095
	50	-0.288	-64.704	0.989	-	0.963	0.054	20.746
	60	-0.302	-78.402	1.340	-	0.912	0.077	34.382
Caurie	20	-5.594	5.965	-	-	0.961	0.086	39.568
	30	-4.990	5.235	-	-	0.974	0.064	34.061
	40	-3.845	3.735	-	-	0.962	0.060	28.657
	50	-3.350	2.991	-	-	0.973	0.042	16.499
	60	-2.693	2.227	-	-	0.933	0.061	31.470
Halsey	20	0.308	0.304	1.095	-	0.993	0.040	16.773
	30	0.305	0.307	1.109	-	0.996	0.027	11.965
	40	0.307	0.307	1.336	-	0.986	0.041	13.380
	50	0.300	0.285	1.464	-	0.983	0.038	13.007
	60	0.322	0.302	1.705	-	0.966	0.049	34.255
Oswin	20	0.134	0.815	-	-	0.987	0.051	25.850
	30	0.139	0.793	-	-	0.991	0.038	20.971
	40	0.164	0.637	-	-	0.978	0.046	19.607

	50	0.165	0.566	-	-	0.975	0.040	15.860
	60	0.206	0.461	-	-	0.944	0.055	30.601
Peleg	20	0.253	0.512	2.010	11.66	0.999	0.018	05.476
	30	0.189	0.389	1.509	8.444	0.999	0.015	03.912
	40	0.130	0.122	1.091	6.457	0.994	0.030	05.368
	50	0.152	0.199	0.642	6.588	0.976	0.039	15.987
	60	0.206	0.184	1.063	8.306	0.980	0.043	45.992
Smith	20	-0.027	0.318	-	-	0.934	0.112	34.522
	30	-0.028	0.307	-	-	0.949	0.089	32.785
	40	0.018	0.248	-	-	0.957	0.064	24.317
	50	0.031	0.213	-	-	0.970	0.044	18.704
	60	0.076	0.196	-	-	0.948	0.053	37.639

The correlation coefficient (r) values varied from 0.862 to 0.997 for desorption and from 0.912 to 0.999 for adsorption whereas the standard error (S) values ranged from 0.022 to 0.175 for desorption and from 0.015 to 0.112 for adsorption and the percent average relative deviation (P) varied from 5.256 to 46.027% for desorption and from 3.054 to 45.992% for adsorption. Among eight models used to fit sorption isotherms of *Allium roseum* leaves, GAB and Peleg models were found to better describe equilibrium moisture content, water activity and temperature relationship for both desorption and adsorption processes. Hence, these models may be used to predict *Allium roseum* leaves equilibrium moisture content at a temperatures range of 20-60°C within a range of 4.5–90% relative humidity with a high accuracy.

Figure 6 and Figure 7 show the adequacy between experimental and calculated (GAB model) data of desorption and adsorption isotherms of *Allium roseum* leaves.

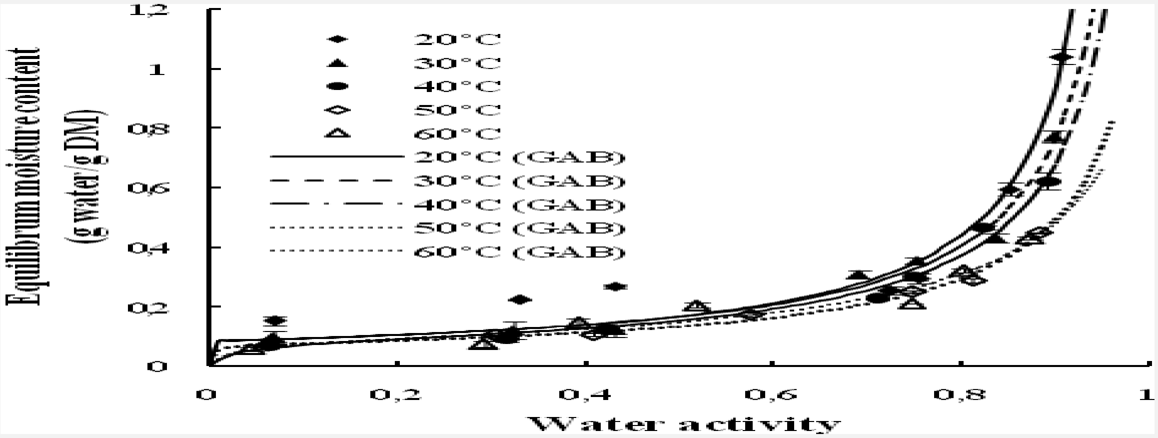

Figure 6. Experimental and calculated data (GAB model) of *Allium roseum* leaves desorption isotherms at different temperatures.

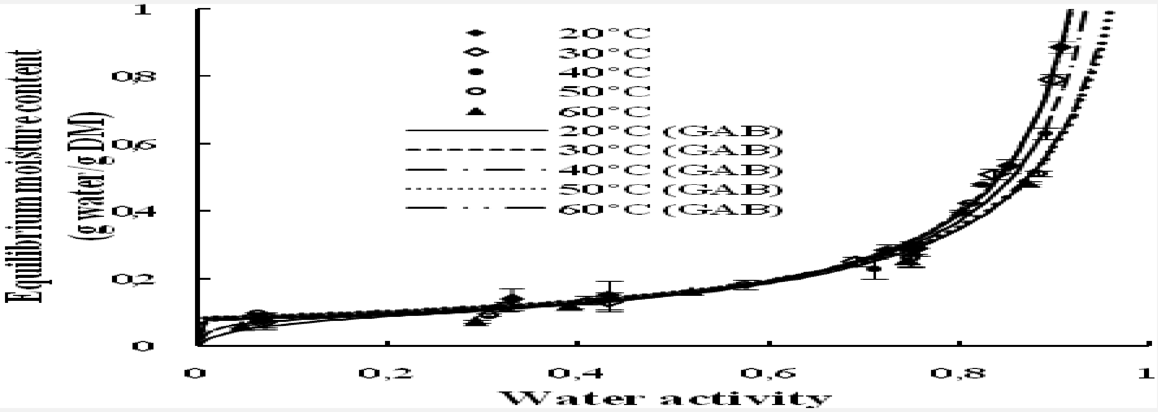

Figure 7. Experimental and calculated data (GAB model) of *Allium roseum* leaves adsorption isotherms at different temperatures.

3.5. Net isosteric heats of sorption

The isosteric heats of sorption at various water contents were calculated from the plot of Eq. (5) using the slopes of the isosteres curves at the five temperatures (Figure 8 and Figure 9).

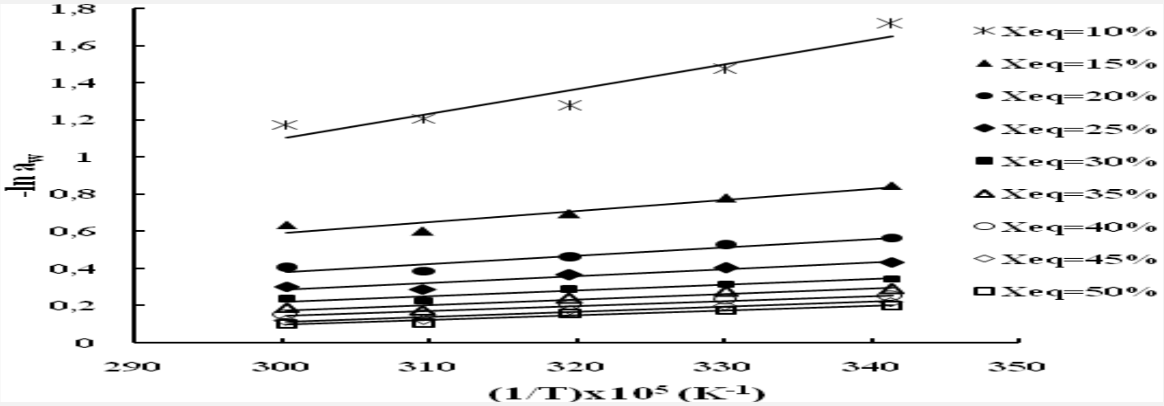

Figure 8. Isosteres plots of *Allium roseum* leaves desorption at different equilibrium moisture content levels.

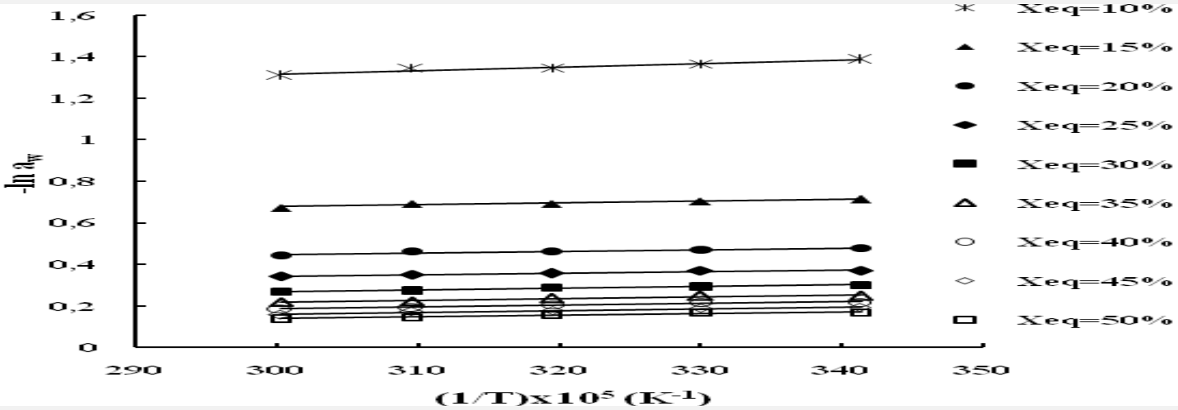

Figure 9. Isosteres plots of *Allium roseum* leaves adsorption at different equilibrium moisture content levels.

Evolutions of isosteric heats of sorption obtained at different equilibrium moisture content of *Allium roseum* leaves for desorption and adsorption are presented in Figure 10.

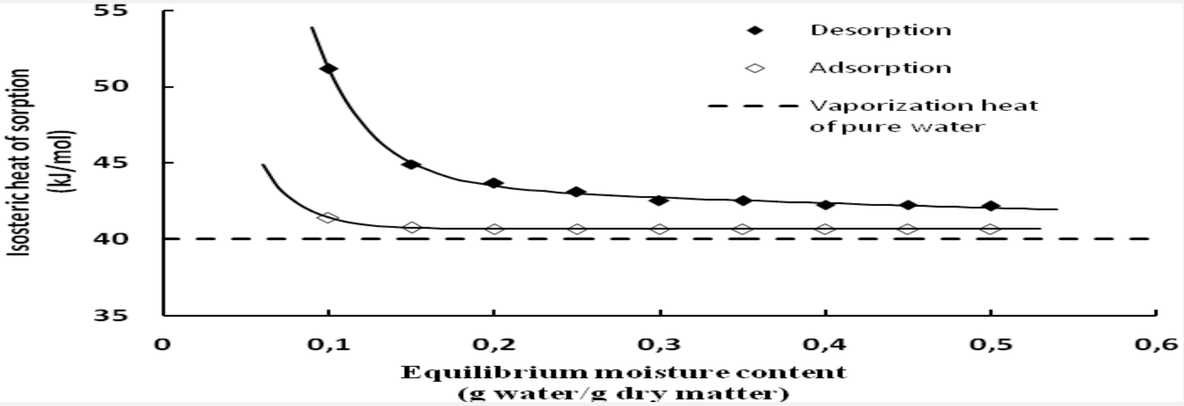

Figure 10. Experimental and calculated values of *Allium roseum* leaves isosteric heats of sorption.

Figure 10 shows that sorption heats decrease with increasing *Allium roseum* leaves equilibrium moisture content. Two zones can be distinguished in Figure 10. For low moisture contents (lesser than 0.15 kg/kg d.b.), the isosteric heat greatly decreases when the moisture content increases. For moisture content higher than 0.15 kg/kg d.b., desorption isosteric heat decreases slowly with moisture content increase and adsorption isosteric heat remains almost constant and equal to the latent heat of vaporization of pure water (L=40.014 kJ/mol). This behavior is due to higher binding energy at lower moisture levels (Madamba et al., 1996). Similar effects of moisture content on the sorption energy were also reported for garlic (Madamba et al. 1996; Pezzutti and Crapiste 1997). At the same equilibrium moisture content, desorption isosteric heat was higher than the isosteric heat of adsorption. This may be attributed to reaction irreversibility resulting from the leaves pre-drying (Moreira et al. 2010).

The adjustment of the isosteric heats (Q_{st}) values of sorption versus corresponding equilibrium moisture contents was done by an exponential equation (Eq. (10)).

$$Q_{st} = a \exp\left(b X_{eq}\right) + c \exp\left(d X_{eq}\right) \qquad (10)$$

Estimated parameters values of the equation used for fitting isosteric heats of desorption and adsorption (Eq. (10)) of *Allium roseum* leaves and the corresponding statistical parameters (r, S) are recapitulated in Table 4.

Table 4. Estimated parameters values of the equation used for fitting isosteric heats of desorption and adsorption (Eq. (9)) of *Allium roseum* leaves and the corresponding statistical parameters (r, S).

Parameters		Desorption	Adsorption
Model coefficients	a	4.121	0.657
	b	-1.402	0.031
	c	158.097	56.216
	d	-30.417	-43.104
Statistical coefficients	r	0.999	0.999
	S	0.162	0.003

4. Conclusions

Allium roseum leaves were found to be rich in polyphenols and flavonoids and had high antioxidant activity. This antioxidant activity suggests the potential use of this category of plants as conservator and antioxidant additives in foods.

Standard gravimetric method can be used successfully for the sorption isotherms experimental determination of *Allium roseum* leaves. The decrease in temperature and the increase in water activity significantly augment the equilibrium water content. A significant difference between desorption and adsorption (hysteresis effect) was found at lower temperature (20°C) and it disappeared at higher temperature. GAB and Peleg models proved to be satisfactory for the prediction of the experimental data obtained. The net isosteric heat of sorption can be calculated using the Clausius-Clapeyron equation. Exponential equations were found to describe the dependence of the net isosteric heat of sorption on the equilibrium moisture content.

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Nomenclature

A, B, C, D models parameters sorption isotherms
a, b, c, d models parameters for sorption isosteric heats

a_w	water activity
d.b.	dry basis
Ea	activation energy, kJ/mol
K	constant
L_v	pure water vaporization heat, kJ/mol
MH	humid mass, kg
MS	dried mass, kg
Q_{st}	sorption isosteric heat, kJ/mol
q_{st}	sorption net isosteric heat, kJ/mol
R	universal gas constant, kJ/mol K
r	correlation coefficient
S	standard error
T	temperature, K
X	moisture content, kg water/kg d.b.

Subscripts

cal	calculated
eq	equilibrium
exp	experimental
st	isosteric