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[1]LSET, Cadi AYYAD University, Marrakech, Morocco
[2]Biotechnologie de la Valorisation et la Protection des Agro-ressources Chimie Bio-organique et Macromoléculaire, Cadi Ayyad University, Marrakech, Morocco

Solar drying, hygroscopic equilibrium and biochemical quality of *Punica granatum Legrelliae*'s flowers

Hicham el Ferouali[1], Ahmed Zoukit[1], Naima Zehhar[2], Fatiha Benkhalti[2], Hafida Bouamama[2], Said Doubabi[1], Naji Abdenouri[1]*

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Summary

Punica granatum Legrelliae is a valuable medicinal plant that is widely planted in Morocco. The equilibrium moisture content was investigated. Peleg model was found the most suitable to describe the sorption phenomenon. The drying kinetic of *Punica granatum Legrelliae*'s flowers was investigated by using a convection solar dryer. Midilli-Kucuk model described well the drying curves' trend. The effective moisture diffusivity values were obtained. The Arrhenius relation, with an activation energy value of 92.91±2.51 kJ mol^{-1} expressed the temperature effect on the diffusion coefficient. Finally, the effect of drying these flowers at different temperatures on their quality was investigated. To assess the quality of the product after solar drying, the color, polyphenols content, antioxidant activity, and polyphenoloxidase and peroxidase activities were considered. The best drying temperature for the preservation of color and bioactive molecules with antioxidant property was 40 °C.

Keywords: Biochemical characterization; *Punica granatum Legrelliae*; quality; solar drying process; sorption; storage.

Introduction

Medicinal and aromatic plants have a crucial value in the pharmaceutical industry and traditional medicine. But, long-term storage of these products requires specific treatments to dehydrate, inactivate tissue enzymes and microorganisms and protect against further contaminations. Drying is the most used preservation operation in the storage of medicinal and aromatic plants and it is a part of the extraction process of high value substances. It aims to reduce the water content and minimizes there biochemical, chemical and microbiological deterioration. Direct sunlight drying is considered as one of the most common drying methods of aromatic and medicinal plants in developing countries. However, this drying technique highly affects the quality of dried product and exposes it to dust and other environmental contaminations. In industry, other techniques are usually used such as freeze-drying and microwave drying but they have always been recognized as expensive processes in terms of energy consumption (Karam et al., 2016). Therefore, the indirect solar drying is more adapted to developing countries; it is economic, fast and leads to a homogeneous and edible product. Thus, it can be strongly considered for the industrial exploitation.

Punica granatum Legrelliae (Punicaceae) is a flowering shrub without fruiting, native to the Mediterranean and Asia region and has been used extensively in the folk medicine. The flowers are a traditional antidiabetic medicine (Li et al., 2007), and are strongly astringent (Huang et al., 2005). The flowers are also used to treat chronic diarrhea (Zhang et al., 2011), and the passive bleeding. They contain polyphenols including gallic, ellagic acids and triterpenes (Zhang et al., 2011). They also contain a variety of secondary metabolites. The bright color of the flowers is due to anthocyanins.

Many studies have been conducted on the solar drying processes and water activity of various medicinal plants (Argyropoulos et al., 2011; Desmorieux and Decaen, 2005). However, few works have studied the drying process effect on the quality of the dried product. Furthermore, no studies have so far been reported on the physical and the hygroscopic behavior of *Punica granatum Legrelliae*'s flowers.

The sorption isotherms are a good way to describe how active water is bound to a wet product (Abdenouri et al., 2010). They are also an extremely valuable tool because it provides precious information about the hygroscopic equilibrium of the product. In other words, it is necessary to determine the optimum moisture content and the water activity that must be achieved during drying for better preservation of the dried product (Chirife and Iglesias, 2007).

Only experimental studies allow determining the drying kinetics of products. Therefore, it is interesting to study variations of moisture content for different controllable aerothermal parameters. The drying kinetics depends on the heat and mass transfers that occur within products. The mechanisms of these transfers are very complex and they lead to large physical, chemical and biological changes. Hence, the evolution of these parameters must be controlled in order to achieve the best quality (Değirmencioğlu et al., 2017; El Ferouali et al., 2017a; El Ferouali et al., 2017b).

In addition, the products' color evolution has to be examined during drying insofar color is one of the determinant parameters of dried products' quality and it sorely influences their commercial value. In fact, color change is a key parameter in the quality of several dried products such as kiwi (Orikasa et al., 2014) and tomato (Santos-Sánchez et al., 2012).

The main objectives of this study are:

- To determine the effect of temperature on the moisture desorption and adsorption isotherms of *Punica granatum Legrelliae*'s flowers, and to find the appropriate model that describes its sorption curves.
- To determine the optimal storage condition of the product and the isosteric heat of sorption.
- To study the drying kinetics of *Punica granatum Legrelliae*'s flowers for different controllable aerothermal parameters by using a convective solar dryer.
- To determine the effective moisture diffusivity for different temperatures and the corresponding activation energy.
- To study the effect of three drying temperatures (40 °C, 50 °C and 60 °C) on the color change and the biochemical parameters of *Punica granatum Legrelliae*'s flowers. The parameters taken into account are the total polyphenol content, polyphenoloxidase and peroxidase activities and antioxidant activity.

* Corresponding author

Nomenclature:

ΔH_d	Isosteric heat of sorption (kJ mol^{-1})
Δh_d	Net isosteric heat of sorption (kJ mol^{-1})
ΔH_{vap}	Heat of vaporization of pure water at 35 °C (43.53 kJ mol^{-1})
Ads.	Adsorption
a_w	Water activity
D_{eff}	Effective diffusivity (m^2 s^{-1})
Des.	Desorption
DM	Dry matter
D_v	Drying air flow rate (m^3 s^{-1})
E_a	Activation energy (kJ mol^{-1})
f	Dimensionless drying rate
H	Half thickness of the dried samples (m)
L^*, a^*, b^*	Color parameters
MBE	Mean bias error
M_d	Mass of dry matter (kg)
M_{eq}	Mass at the hygroscopic equilibrium (kg)
MRE	Mean relative error (%)
M_w	Mass of wet matter (kg)
N	Number of experimental points
r	Correlation coefficient
R	Universal gas constant (8.3145 J mol^{-1} K^{-1})
Rh	Relative humidity (%)
SD	Standard deviation
SEM	Standard error of moisture
T	Absolute temperature (K)
X	Moisture content at any time during drying (% d.b.)
X^*	Moisture ratio
X_0	Initial moisture content (% d.b.)
X_{eq}	Equilibrium moisture content (% d.b.)
X_f	Final moisture content (% d.b.)
θ	Temperature (°C)
χ^2	Reduced chi-square

Materials and methods

Sorption isotherms of *Punica granatum Legrelliae*'s flowers

The hygroscopic equilibrium was achieved by the static gravimetric technique, it consists on using six saturated salt solutions (KOH, $MgCl_2\ 6H_2O$, K_2CO_3, $NaNO_3$, KCl, $BaCl_2\ 2H_2O$). These salts provide a range of relative humidity of 5-90 % (Greenspan, 1977). The salts were prepared in six glass jars of 1 L each with an insulated lid. For each solution, the samples were suspended in the jars above salts and remained in a stabilized temperature and humidity environment. The samples were weighed every two days in order to determine their equilibrium moisture content X_{eq}. As soon as the masses had become stationary, the samples were weighed and placed in a drying oven whose temperature is fixed at 105 °C for 24 h. The difference of mass before and after drying at 105 °C (respectively M_{eq} and M_d) allows determining the product's moisture content X_{eq} at the hygroscopic equilibrium by Eq. (1).

$$X_{eq}(\%d.b) = 100 \times \frac{M_{eq} - M_d}{M_d} \quad (1)$$

The samples that were used for desorption were fresh and weighed between 0.093 and 0.102 g. The ones that were used for adsorption had been dried for 24 h in an oven at 105 °C before putting them on the glass jars; their weight were between 0.030 and 0.035 g. This process was performed at three different temperatures (30, 40 and 50 °C).

Description of the solar drying

The experimental apparatus consists of an indirect forced convection solar dryer, with a solar air collector, an electric auxiliary heater, a circulation fan and a drying chamber. The solar dryer was described in detail by El Ferouali et al. (2016). The same mass of fresh *Punica granatum Legrelliae*'s flowers (8.50 ± 0.01 g) was used for each drying experiment. Samples were uniformly spread forming a thin layer on the drying rack. In solar drying processes, the air temperature can vary with the magnitude of the solar radiation. The auxiliary heater was so used to control the air temperature. The variation of the weight of the product versus time was determined by a digital weighing apparatus (±0.01 g). Drying experiments were performed for three drying air temperatures (40, 50 and 60 ± 0.5 °C) with the air flow rate of 0.083 ± 0.001 m^3 s^{-1}.

Biochemical characterization protocol

Total polyphenols determination

100 mg of samples were ground in 2 ml of methanol at 80%. Then, the mixture was sonicated for 10 min in an ultrasonic bath containing distilled water. The homogenate was centrifuged at 15,000 × g during 10 min. Supernatant was tested by a differential assay in the presence and absence of polyvinylpolypyrrolidone (PVPP) according to Bridi et al. (2014). Samples were passed through three cycles of pretreatment in order to improve the ability of PVPP to absorb polyphenols. At first, 100 mg of PVPP was added to 1 ml of the supernatant, and the solution was stirred for 30 s using a vortex and then centrifuged at 10,000 × g for 5 min (one-cycle). After thus, 500 µl of the supernatant, obtained from the one-cycle procedure, was exposed to 50 mg of PVPP, and the obtained mixture was stirred and centrifuged in the same experimental conditions as mentioned above (second-cycle). Finally, 250 µl of the supernatant (obtained from the second cycle process) was treated by 25 mg of PVPP, and the obtained mixture was stirred and centrifuged again in the same experimental conditions as mentioned above (third-cycle). The total polyphenol concentration was determined using the Folin-Ciocalteu reagent according to the method adapted by Singleton and Rossi (1965). 1 ml of reagent was added to 75 µl of phenol extract, followed by the addition of 200 µl Na_2CO_3 (20%) and 225 µl of distilled water. The mixture was incubated in the dark for 30 min. The absorbance was determined at 765 nm. The obtained values were corrected by subtracting the value related to the absorbance with PVPP. The total polyphenol content was then calculated based on a calibration curve established from a standard range with known concentrations of gallic acid.

Measurement of polyphenoloxidase and peroxidase activities

50 mg of samples were ground in 1 ml of phosphate buffer (0.1 M, pH 6) containing the insoluble PVP (5%), and then centrifuged for 30 min at 12,000 × g. For the polyphenoloxidase activity, 100 µl of the obtained supernatant were added to 2 ml of catechol (10 mM), and then the absorbance was determined at 410 nm after 3 min. For the peroxidase activity, 100 µl of the supernatant were added to 1 ml of guaiacol (20 mM). The reaction was initiated by the addition of 0.5 ml of hydrogen peroxide (0.1%), and the absorbance was determined at 470 nm after 3 min.

Antioxidant activity

The determination of antioxidant activity was based on 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radical scavenging. Thus, 100 µl of different concentrations of each phenolic extract were mixed to 0.9 ml of a 0.004% methanol solution of DPPH. The negative control was prepared by mixing 100 µl methanol and 0.9 ml of methanol solution of DDPH. After 30 min of incubation in the dark, the absorbance was measured at 517 nm by using a spectrophotometer (Chen et al., 2013).

The results were expressed in IC 50 that is the amount of antioxidant necessary to decrease the initial concentration of DPPH by 50%. Radical DPPH was graphically determined by the linear regressions of the plotted graphs (inhibition percentages as a function of different concentrations of samples). The lower IC 50 values indicate a higher antioxidant activity.

Statistical analysis

All measurements were performed in triplicate and were reported as mean (± standard deviation). All data were analyzed using the SPSS 21.0 statistical package. An analysis of variance (ANOVA) followed by the Student Newman-Keuls post hoc test was used to compare differences in the means. The level of significance was defined as $P<0.05$.

Results and discussion

Desorption and adsorption isotherms

The hygroscopic equilibrium of *Punica granatum Legrelliae*'s flowers was reached in 11 days for desorption and 10 days for adsorption.

Figs. 1 and 2 show the effect of temperature on desorption and adsorption of *Punica granatum Legrelliae*'s flowers. X_{eq} increases by decreasing temperature at constant water activity. This result may be explained by the higher excitation state of water molecules at higher temperature thus decreasing the attractive forces between them. The sorption isotherms are type II of the IUPAC classification and exhibit a sigmoidal shape; this is consistent with the behavior of other medicinal and aromatic plants (Mujumdar, 2006). The hysteresis appears in Fig. 3. This phenomenon is explained by thermodynamical irreversible processes that occur during desorption or adsorption or both (Chirife and Iglesias, 2007).

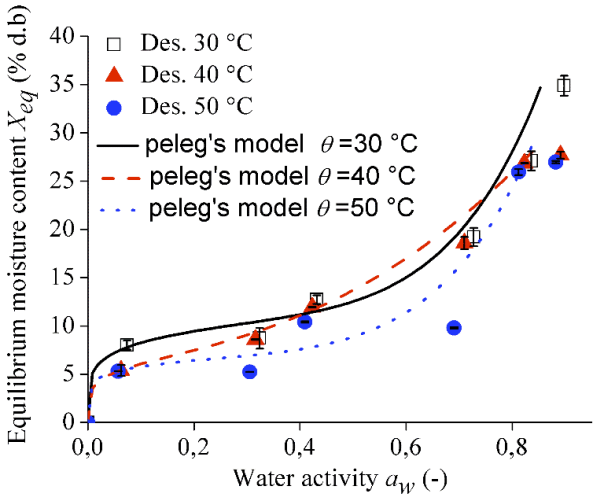

Fig. 1: Desorption isotherms of *Punica granatum Legrelliae*'s flowers at 30, 40 and 50 °C, SD_{max}=1.07.

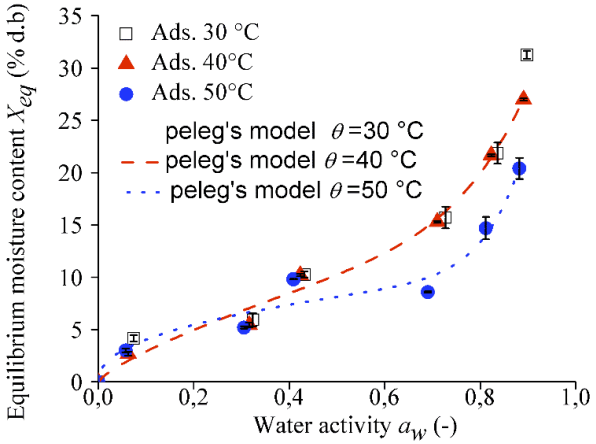

Fig. 2: Adsorption isotherms of *Punica granatum Legrelliae*'s flowers at 30, 40 and 50 °C, SD_{max}=1.08.

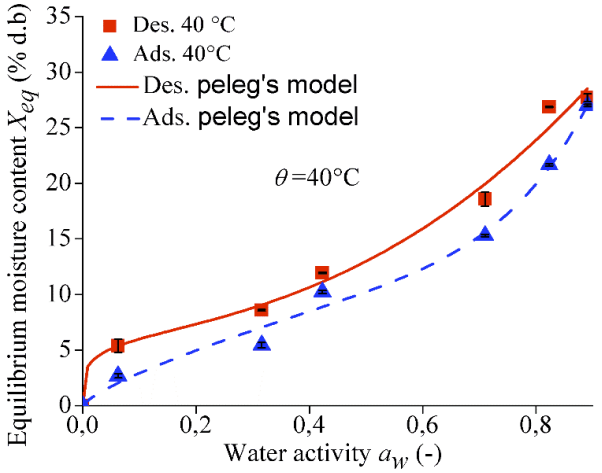

Fig. 3: Desorption and adsorption isotherms of *Punica granatum Legrelliae*'s flowers at 40°C, SD_{max}=0.64.

Modeling of sorption isotherms

In the present study, the relationship between X_{eq}, a_w at 30, 40 and 50 °C was predicted by applying mathematical models. The used models' equations (GAB, Modified Henderson, Modified Halsey, Modified Oswin and Peleg) are given by Basu et al. (2006), and the Enderby model is given by Popovski and Mitrevski (2004). Levenberg-Marquardt non linear optimization method was used to calculate the models' coefficients that describe the equilibrium curves and their statistical parameters. The best model, describing sorption isotherms of the product, has the highest value of the correlation coefficient r and smallest values of Standard Error of Moisture (SEM) and Mean Relative Error (MRE). These statistical parameters are defined respectively by Eqs. (2), (3) and (4):

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

Where, the experimental average moisture content is defined by:

$$SEM = \sqrt{\frac{\sum_{i=1}^{N}\left(Xeq_{i,pre} - Xeq_{i,exp}\right)^2}{d_f}} \quad (3)$$

$$MRE = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{Xeq_{i,pre} - Xeq_{i,exp}}{Xeq_{i,exp}}\right| \quad (4)$$

Where $Xeq_{i,exp}$ is the *ith* experimental moisture content, $Xeq_{i,pre}$ is the *ith* predicted moisture content, and d_f is the freedom degree of the regression model.

It can be seen from Tab. 1 that the Peleg model gives the best fitting to the experimental data with a correlation coefficient *r* of 0.9847 and 0.9916, *SEM* of 1.9771 and 1.1692, and *MRE* of 10.5050% and 12.1983% respectively for desorption and adsorption isotherms. The Peleg coefficients (A, B, C, D) are dependent on temperature and they are presented in Tab. 2.

Determination of the optimum conditions for the storage

All experimental data of desorption and adsorption at 30, 40 and 50 °C were gathered on the same graph (Fig. 4). The sorption isotherm may particularly be described by a 3rd degree polynomial. The polynomial fitting is presented in the same figure and its relative equation is expressed by Eq. (5).

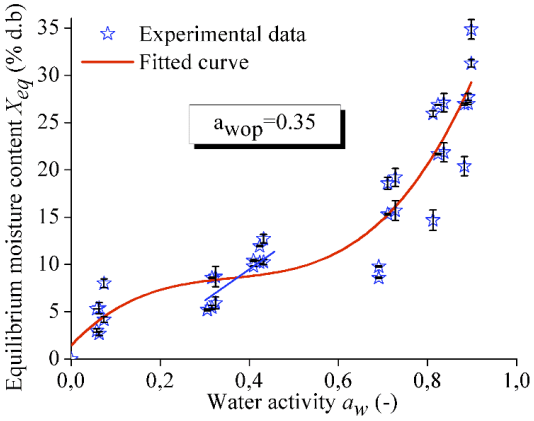

Fig. 4: Determination of the optimal water activity for storage of *Punica granatum Legrelliae*'s flowers, SD_{max}=1.08.

$$X_{eq} = 1.45549 + 49.0522\, a_w - 124.26595\, a_w^2 + 115.35468\, a_w^3 \quad (5)$$

This curve allowed to determine the value at which the second derivative of X_{eq} equals to zero (inflection point) and consequently the optimum value of water activity for storage. The found value for *Punica granatum Legrelliae*'s flowers (a_{wop}=0.35±0.005) is in agreement with the general stability domain of biological products that is between 0.2 and 0.4 (Le Meste et al., 2001). This result reveals that relative humidity for storage and conservation should be less than 35±0.5% in order to ensure better stability of the product.

Net isosteric heat

The net isosteric heat of sorption (Δh_d) or differential enthalpy stands for the binding energy of the water to the substrate. This energy must be added to the heat vaporization energy (Δh_{vap}) for dehydratation (Eq. (6)). The net isosteric heat of sorption was calculated from the experimental data using the Clausius Clapeyron equation given by Eq. (7) (Beristain et al., 1996):

$$\Delta H_d = \Delta h_d + \Delta h_{vap} \quad (6)$$

$$\left[\frac{d(\ln a_w)}{d(1/T)}\right]_{X_{eq}} = \frac{-\Delta h_d}{R} \quad (7)$$

This equation involves determining the isotherms at different temperatures in order to calculate the logarithmic variation of the water activity as a function of inverse temperature for fixed equilibrium moisture content. It is assumed that isosteric heat does not vary with the temperature. Hence, Δh_d is determined from the slope $-\Delta h_d/R$ as it is given in Eq. (8).

Tab. 1: Statistical parameters: *r*, *SEM*, and *MRE* of the six models fitted to the sorption isotherms.

	GAB	Modified Henderson	Peleg	Modified Halsey	Modified Oswin	Enderby
Des.						
r	0.9819	0.9661	**0.9847**	0.9745	0.9761	0.9629
SEM	1.7945	0.1026	**1.9771**	0.0787	2.3731	2.8614
***MRE* (%)**	12.0542	22.2729	**10.5050**	13.2845	16.3544	22.0315
Ads.						
r	0.9958	0.9729	**0.9916**	0.9766	0.9859	0.9960
SEM	1.0429	0.0873	**1.1692**	0.0803	1.4105	1.0122
***MRE* (%)**	17.8972	29.1219	**12.1983**	13.1607	12.9449	18.0610

Tab. 2: Peleg's coefficients for sorption isotherms of *Punica granatum Legrelliae's* flowers.

Model's expression	Temperatures					
		30 °C		40 °C	50 °C	
		Des.	Ads.	Des.	Ads.	Des.	Ads.
$X_{eq} = A(a_w)^C + B(a_w)^D$	***A***	15.6804	25.3289	16.9795	39.2313	41.5141	41.5141
	B	45.8227	9.6476	24.8467	8.0212	10.9518	10.9518
	C	0.6162	2.4406	0.7656	5.0284	11.2192	11.2192
	D	9.5455	0.2139	6.6552	0.1457	0.4330	0.4330

$$ln(a_w) = -\frac{\Delta h_d}{R}\frac{1}{T} + cst \quad (8)$$

Fig. 5 presents the isosteric heat of sorption of *Punica granatum Legrelliae*'s flowers at temperatures ranging between 30 °C and 50 °C. This curves show that the isosteric heat is higher for small values of the moisture content indicating the highest binding energy for water removal, and it decreased along with the increase of the X_{eq}.

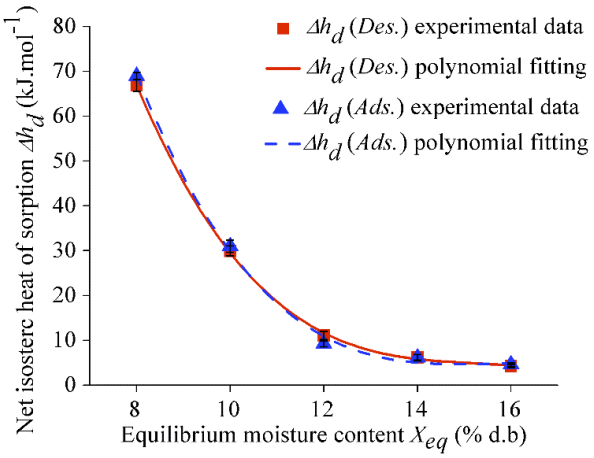

Fig. 5: Net isosteric heat of desorption and adsorption of *Punica granatum Legrelliae*'s flowers versus equilibrium moisture content, SD_{max}=1.37.

Drying kinetics of *Punica granatum Legrelliae*'s flowers

The experiments were performed at three air temperatures (40, 50 and 60 °C), under a drying air flow of 0.083 m^3·s^{-1} and at an ambient relative humidity varying from 41 to 46%. The moisture content of the product at each drying time is calculated by Eq. (9).

$$X(\%d.b) = 100 \times \frac{M_w - M_d}{M_d} \quad (9)$$

The initial moisture content of the product ranged from 304.8 to 325.0 (% d.b), and it was reduced to the final moisture content which varies from 4.8 to 28.6 (% d.b) (Tab. 3). X_{eq} were determined from the desorption isotherms.

An increase in the drying air temperature had led to a significant reduction in the drying time; from 310 min for a temperature of 40 °C to 70 min for a temperature of 60 °C (Fig. 6). It can be noticed the absence of phase 0, or the increasing drying rate period, and also the absence of phase 1, the constant drying rate period. There is only the presence of the falling drying rate period (phase 2) which is governed by the water diffusion in the material (Bimbenet et al., 1985).

Fig. 7 represents the characteristic drying curve; the variation of dimensionless drying rate *f* versus moisture ratio as given by Van

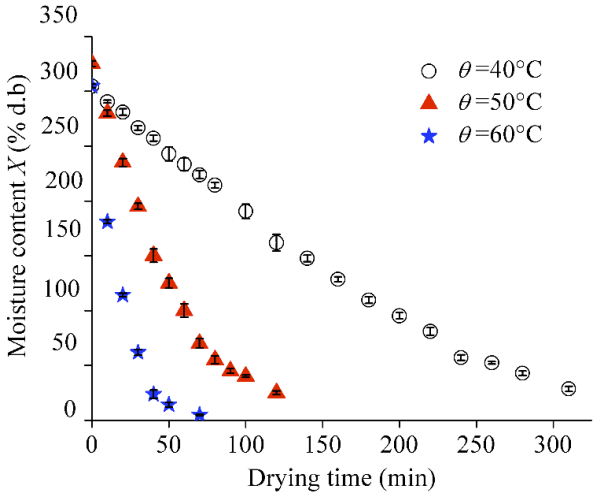

Fig. 6: Variation of moisture content as a function of time, SD_{max}=7.73.

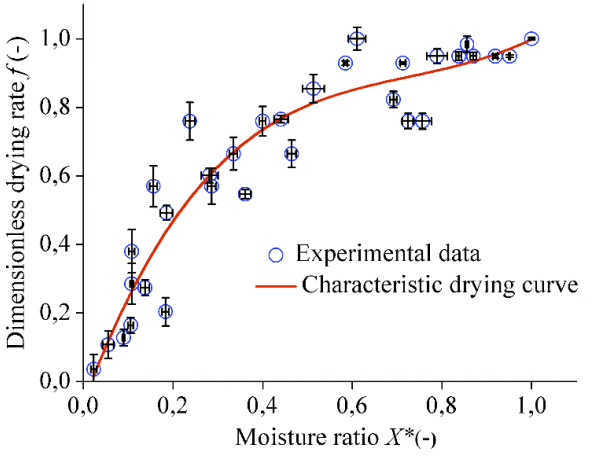

Fig. 7: Characteristic drying curve of *Punica granatum Legrelliae*'s flowers, for $X^*(-)$: SD_{max}=0.02, for $f(-)$: SD_{max}=0.06.

Meel's method (Van Meel, 1958). A polynomial model was found to be the best fitting of the dimensionless experimental data (Eq. (10)). The used criteria to evaluate goodness of fit are the correlation coefficient r= *0.96191* and the reduced chisquare χ^2= *0.0105*.

$$f = -0.06242 + 3.51118\,X^* - 4.84588\,X^{*2} + 2.77564\,X^{*3} - 0.38036\,X^{*4} \quad (10)$$

Modeling of the drying curves

Several mathematical models are used to describe the macroscopic behavior of the products. In this work, the most models describing drying kinetics were used: Newton, Page, Henderson and Pabis,

Tab. 3: Drying conditions during the experiments in the solar dryer.

Experiment	D_v ± 0.001 (m^3·s^{-1})	θ ± 0.5 (°C)	*Rh* (%)	X_0 ± 0,001 (%d.b)	X_{eq} ± 0,001 (%d.b)	X_f ± 0,001 (%d.b)	Time (min)
1	0.083	40	42	304.8	11.2	28.6	310
2	0.083	50	46	325.0	11.9	25.0	120
3	0.083	60	41	304.8	7.4	4.8	70

Logarithmic, Two term, Two term exponential, Wang and Singh, Diffusion approach, Verma et al. and Midilli-Kucuk. The models' expressions are given in literature (MENGES and ERTEKIN, 2006; YALDIZ et al., 2001). The moisture ratio and the dimensionless drying rate of *Punica granatum Legrelliae*'s flowers during the thin layer drying experiments were calculated respectively by using Eqs. (11) and (12):

$$X^* = \frac{X - X_{eq}}{X_0 - X_{eq}} \tag{11}$$

$$f = \frac{-\frac{dX}{dt}}{\left(-\frac{dX}{dt}\right)_{t=0}} \tag{12}$$

The appropriate model was selected according to the highest correlation coefficient (r), the lowest mean bias error (MBE) and the lowest reduced chisquare (χ^2). These parameters are given as following:

$$MBE = \frac{1}{N}\sum_{i=1}^{N}(X^*_{pre,i} - X^*_{exp,i}) \tag{13}$$

$$\chi^2 = \frac{\sum_{i=1}^{N}(X^*_{exp,i} - X^*_{pre,i})^2}{N_{ob} - n_c} \tag{14}$$

Where $X^*_{exp,i}$ stands for the experimental moisture ratio found in the measurements; $X^*_{pre,i}$ is the predicted moisture ratio for this measurement; N_{ob} is the number of observations; and n_c is the number of a model's constants.

Tab. 4: Statistical parameters r, χ^2, and MBE of the ten models applied to the drying curves.

Model	***r***	***χ²***	*MBE*
Newton	0.9910	0.00187	0.00042
Page	0.9983	0.00042	0.00343
Henderson and Pabis	0.9931	0.00158	0.00676
Logarithmic	0.9984	0.00048	$4.3122.10^{-8}$
Two term	0.9979	0.00083	0.00357
Two term exponentiel	0.9981	0.00046	0.0036
Wang and Singh	0.9974	0.00077	0.00207
Approximation of diffusion	0.9978	0.00060	0.00186
Verma et al.	0.9979	0.00056	0.00019
Midilli-Kucuk	**0.9990**	**0.00038**	**0,00018**

The statistical parameters of the ten studied models are summarized in Tab. 4. Midilli-Kucuk model was selected as the most convenient model to represent the drying behavior of *Punica granatum Legrelliae*'s flowers. The coefficients (a, k, n and b) of the chosen model at different temperatures are given in Tab. 5. Fig. 8 compares the experimental data with those predicted by Midilli-Kucuk model. The predicted data generally banded around the straight line. These observations highlighted the ability of this model to better simulate the change in water content in the solar drying *Punica granatum Legrelliae*'s flowers. Hence, this product presents a weak external resistance to heat and mass transfer (MIDILLI et al., 2002).

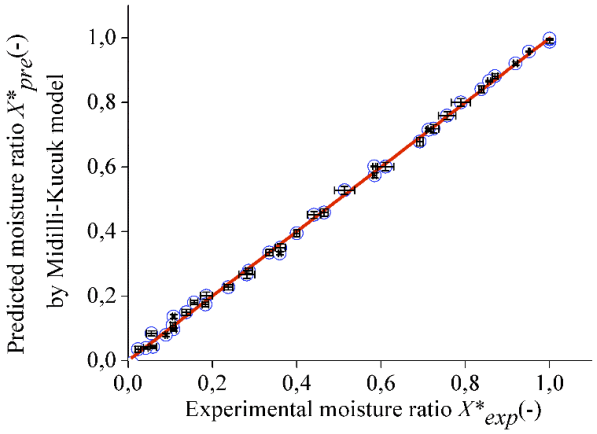

Fig. 8: Comparison of experimental moisture ratio with predicted moisture ratio from the Midilli-Kucuk model, for $X^*_{exp(-)}$: SD_{max}=0.02, for $X^*_{pre(-)}$: SD_{max}=0.01.

Effective moisture diffusivity and activation energy

Fick's second law can be used to describe the drying process on which diffusion is dominant. The solution of Fick's second law in slab geometry is given by Eq. (15) (CRANK, 1979), with the assumptions of moisture migration being by diffusion, shrinkage is negligible, and the temperature and the diffusion coefficient maintain almost the same value:

$$X^* = \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(\frac{-n^2\pi^2 D_{eff}\,t}{4H^2}\right) \tag{15}$$

For a sufficiently long drying time, all terms of the above series are negligible compared with the first term. Thus, Eq. (15) becomes:

$$ln(X^*) = ln(\frac{8}{\pi^2}) - \frac{\pi^2 D_{eff}\,t}{4H^2} \tag{16}$$

The effective moisture diffusivity D_{eff} was calculated using the slope of Eq. (16) (Eq. 17)), with H (the half thickness of the dried samples). It is found that $2H$=0.017±0.0019 cm:

Tab. 5: Midilli-Kucuk coefficients for *Punica granatum Legrelliae's* flowers.

Model's expression	**Coefficients**	**Temperatures**		
		40°C	**50°C**	**60°C**
$X^* = a\exp(-kt^n) + bt$	*a*	0.98732	0.99509	0.99692
	k	0.00161	0.00777	0.03864
	n	1.208	1.25159	1.11238
	b	$-4.73821.10^{-4}$	$-4.1336.10^{-5}$	$-2.86821.10^{-4}$

$$Slope = -\frac{\pi^2 D_{eff}}{4H^2} \quad (17)$$

The activation energy was calculated using Arrhenius type equations (Akpinar et al., 2003) (Eq. (18)):

$$E_a = -RTLn(\frac{D_{eff}}{D_0}) \quad (18)$$

Drying of *Punica granatum Legrelliae*'s flowers occurs only in the falling rate period, so liquid diffusion controls the process. Fig. 9 illustrated the effects of temperature on the effective diffusion coefficient of the product. Graphs were drawn between *ln(X*)* against the drying time according to Fick's diffusion model. The effective moisture diffusivities (D_{eff}) values are (2.480±0.06) × 10^{-11}, (7.794±0.2) × 10^{-11} and (2.111±0.19) × 10^{-10} m^2 s^{-1} respectively for 40, 50 and 60 °C. Hence, the increase in the drying air temperature increased the value of D_{eff}. In fact, when samples were dried at higher temperature, the activity of water molecules increased leading to higher moisture diffusivity (Xiao et al., 2010).

The values of the obtained D_{eff} lie within general range 10^{-8} to 10^{-12} $m^2 \cdot s^{-1}$ for drying of aromatic and medicinal plants (Zogzas et al., 1996). The activation energy was calculated from the slop of $ln(D_{eff})$ as function of *1/T* (Fig. 10); its value is 92.91±2.51 kJ mol^{-1}, this range corresponds to the activation energy of other food products in a general range reported by several researchers (Xiao et al., 2010; Zogzas et al., 1996).

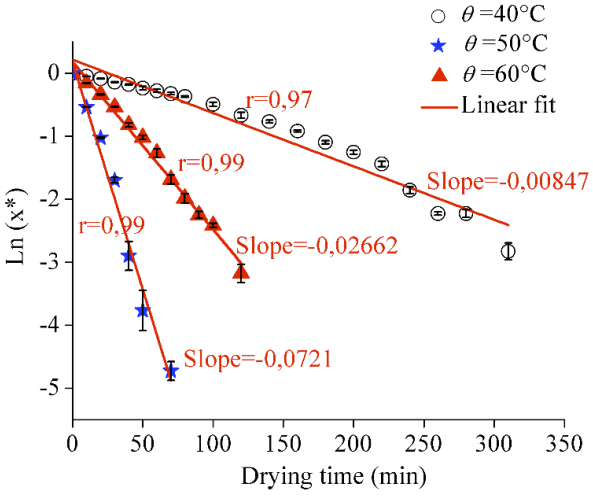

Fig. 9: Effects of temperature on the effective diffusion coefficient of *Punica granatum Legrelliae*'s flowers, SD_{max}=0.32.

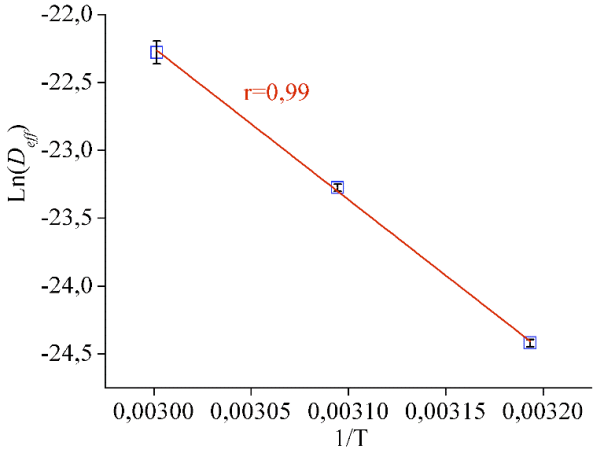

Fig. 10: $Ln(D_{eff})$ versus *1/T*, SD_{max}=0.08.

Effect of solar convective drying at different temperatures on the flowers' color

The CIE Lab color space was used for color analyses based on imaging process of samples. The *L**, *a** and *b** color parameters have been widely used to describe color changes during thermal processing of agricultural products. *L** represents lightness, ranging from 0 (black) to 100 (white), it indicates how dark/light are the samples. The parameter *a** ranges between -128 (green) and 127 (red), and *b** ranges between -128 (blue) and 127 (yellow). Fig. 11 shows the effect of convective solar drying at 40, 50 and 60 °C on *L**, *a** and *b** color parameters of *Punica granatum Legrelliae*'s flowers. The color of the fresh and dried flowers was determined. The fresh samples' color is red-orange, its (*L**, *a**, *b**) had an average value of almost (47.4±0.8944, 55±1.0801, 45.8±0.4472). The effect of temperature on the samples' color is that the (*L**, *a**, *b**) decreased by increasing temperature. In fact they decreased from an average of (41.8±1.3874, 54±1.2360, 34.8±1.7013) at 40 °C to an average of (27.6±0.8944, 40±1.5495, 25.2±1.9235) at 60 °C. Hence, by drying at higher temperature, the color became darker, and the red and yellow colors decreased.

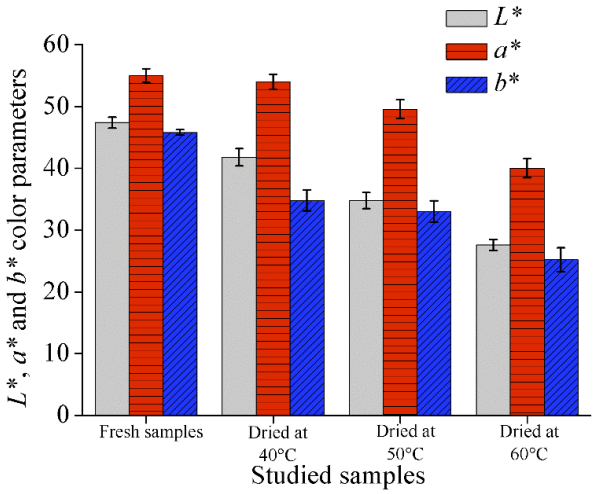

Fig. 11: Effect of convective solar drying at 40, 50 and 60 °C on *L**, *a** and *b** color parameters of *Punica granatum Legrelliae*'s flowers, SD_{max}=1.92.

Effect of drying on biochemical parameters

Effect on total polyphenol content

The highest total polyphenol content was assigned to the fresh sample (233.30±13.94 mg equivalent gallic acid/g DM) (Fig. 12). A very small decrease of total polyphenol content was noticed by increasing the drying temperature from 40 °C to 60 °C. In fact, their values at 40 °C, 50 °C and 60 °C are respectively 154.69±3.01, 150.40±1.95 and 146.98±3.08 mg equivalent gallic acid/g DM. Larrauri et al. (1997) also observed a decrease in the total polyphenol content in dried red grape pomace peels at high temperatures (100 °C, 140 °C) compared to dried samples at a lower temperature (60 °C). In fact, high temperatures affect the quality and quantity of these phenolic compounds due to their thermal decomposition. Other studies have suggested that the reduction in the polyphenol content is due to polymerizations of the antioxidant molecules caused by the high temperatures (Calín-Sánchez et al., 2013; Henríquez et al., 2014).

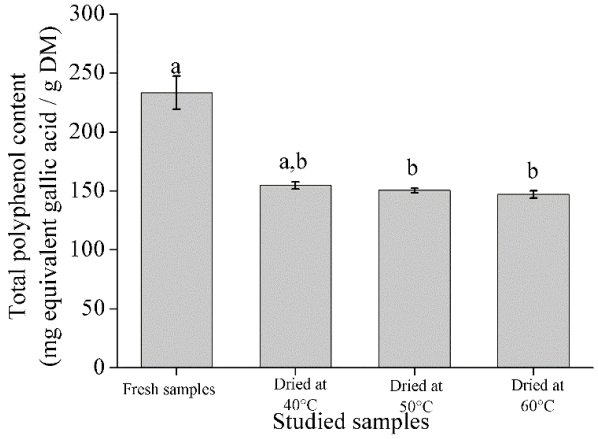

Fig. 12: Total polyphenol content (mg equivalent gallic acid / g DM) of *Punica granatum Legrelliae*'s flowers, SD_{max}=13.94.

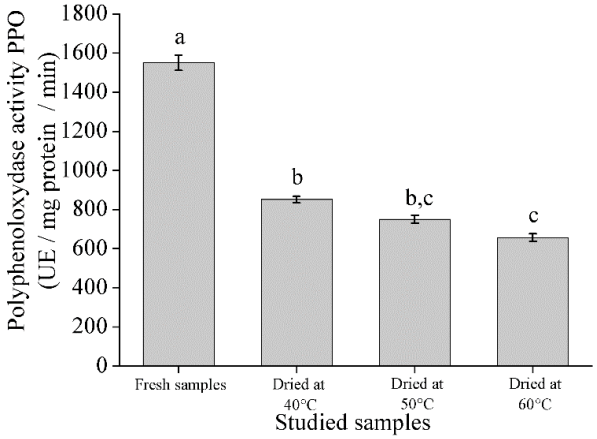

Fig. 13: Polyphenoloxydase activity (UE/mg protein/min) of *Punica granatum Legrelliae*'s flowers, SD_{max}=39.14.

Effect on polyphenoloxidase and peroxidase activities

Enzymatic browning is the result of the oxidation of o-diphenol to quinone by PPO in the presence of oxygen. According to Fig. 13, polyphenoloxidases activity is very high in fresh flowers (1550.14±39.14 UE/mg protein/min) compared to dried ones. The highest enzymatic activity (PPO) among the dried samples was recorded for dried samples at 40 °C and, it decreased by increasing temperature from 850.49±17.11 UE/mg protein/min (at 40 °C) to 656.12±19.87 UE/mg protein/min (at 60 °C).

The highest PO activity was recorded by dried samples at 40 °C (184.01±13.02 UE/mg protein/min) (Fig. 14). The obtained values of PO activity at 50 °C and 60 °C were lower; they are respectively 127.55±10.12 and 115.38±12.08 UE/mg protein/min. This reduction of polyphenoloxidase and peroxidase activities was also observed by Tan et al. (2015) after convective drying of mulberry leaves at 50 °C and 100 °C. According to Baltacioğlu et al. (2015); PPO is very active at 40 °C, but this activity decreases after heat treatment between 50 °C and 70 °C. In general, inactivation or reduction of PPO and PO during drying is due to the denaturation of enzymes by heat, as well as to the reduction of water activity of the plant material during drying. The inactivation of these enzymes thus leads to the inhibition and the degradation of the phenolic compounds (Tan et al., 2015). Finally, the high PPO and PO activities at 40 °C indicate that this temperature is the optimum one for the enzyme.

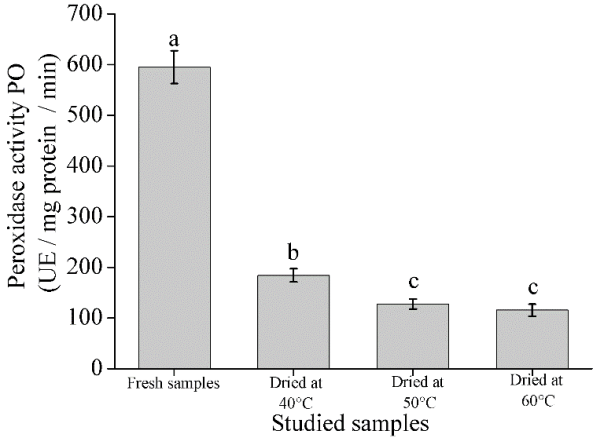

Fig. 14: Peroxidase activity (UE/mg protein/min) of *Punica granatum Legrelliae*'s flowers, SD_{max}=32.71.

Effect on antioxidant activity

According to DPPH radical scavenging ability, fresh samples had a strong antioxidant activity compared to the dried samples with an IC50 of 869.86±10.14 µg/g DM (Fig. 15). Convective dried samples at 40 °C recorded the highest antioxidant activity, with an IC 50 of 1190.54±11.13 µg/g DM. Dried samples at 50 °C and 60 °C had lower activity, with respectively IC 50 of 1638.84±17.98 and 1696.63±56.11 µg/g DM. Calín-Sánchez et al. (2013) reported that convective drying of pomegranate arils and rind resulted in a reduction in antioxidant activity from 45.1 mg eq Trolox/g DM for fresh samples to 24.5 mg eq Trolox/g DM for dried ones at 60 °C. Otherwise, according to Wojdyło et al. (2016), jujube fruit showed better antioxidant activity when they are dried at low temperature (ranging from 23.9 mmol Trolox/100 g DM at 50 °C up to 9.6 mmol Trolox/100 g DM at 70 °C). Similarly, Rodríguez et al. (2013) observed a significant decrease in antioxidant capacity of thyme by the increase of drying temperature from 40 °C to 60 °C. Hence, drying at high temperatures destroys some phenolic compounds and leads to the loss of the antioxidant activity. This could be explained by the degradation of phenolic monoterpenes and volatile aromatic compounds that significantly contribute to enhance the antioxidant capacity (Rodriguez et al., 2013). It thus appears that drying at 40 °C is more preservative of the antioxidant activity for the studied samples.

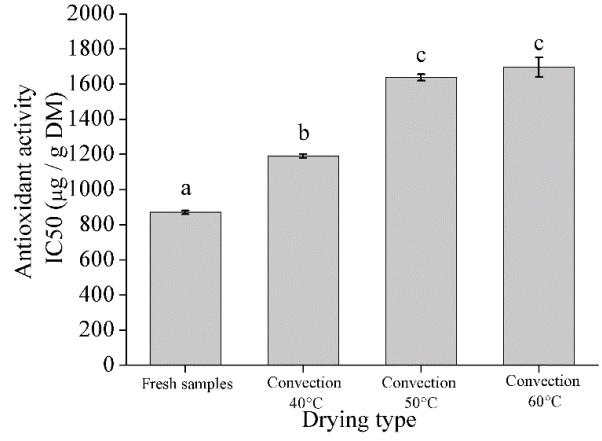

Fig. 15: Antioxidant activity IC50 (µg/g DM) of *Punica granatum Legrelliae*'s flowers, SD_{max}=56.11.

Conclusions

The present paper highlights links between the hygroscopic behavior, the solar drying characterization and the dried *Punica granatum Legrelliae's* flowers' quality. The quality of the dried product was spotted in terms of its biochemical composition of polyphenols, antioxidant activity, polyphenoloxydase and peroxydase activities, and also regarding the color change. The modeling and the hygroscopic characteristics were determined for desorption and adsorption of *Punica granatum Legrelliae*'s flowers. Evaluation of sorption isotherm provided valuable information for drying and storing this seasonal plant. These isotherms presented a sigmoidal shape of type II in the IUPAC classification and among the six models chosen to fit the sorption curves, the Peleg model provided the best description of the sorption isotherms. A polynomial fitting of the experimental sorption isotherms data led to disclose the optimal relative humidity for the storage and conservation, it should be less than 35±0.5% for better stability of the dried product. The net isosteric heat of sorption was evaluated, it is in the range of 70 kJ mol^{-1} for small values of the moisture content (X_{eq}=8 % d.b.), and it decreased along with the increase of the *Xeq*; this thermodynamic quantity estimates the required energy for dehydration processes. According to the drying kinetics study, among the three drying periods, only the falling rate period exists. Furthermore, the results of regression analysis showed that Midilli-Kucuk drying model predicts the drying kinetics of *Punica granatum Legrelliae*'s flowers, which means that heat and mass transfer are more limited in intern than in extern of the product.

The effective moisture diffusivity values were obtained from the Fick's diffusion model, and the increase in air temperature raised the value of D_{eff} from (2.480±0.06) × 10^{-11} m^2 s^{-1} at 40 °C to (2.111±0.19) × 10^{-10} m^2 s^{-1} at 60 °C. The Arrhenius relation, with an activation energy value of 92.91±2.51 kJ mol^{-1}, expressed the effect of temperature on the diffusion coefficient.

The effect of forced convection drying at 40, 50 and 60 °C on the main quality criteria of *Punica granatum Legrelliae*'s flowers was studied. Accordingly, the solar drying at 40 °C is of great importance because it relatively preserved the bright color of fresh samples, as well as active compounds because this temperature kept the polyphenol content high (154.69±3.01 mg equivalent gallic acid/g DM). Moreover, dried samples at this temperature were endowed with the highest antioxidant activity with an IC 50 of 1190.54± 11.13 µg/g DM. This drying temperature was also optimal for the enzyme since polyphenoloxidase and peroxidase activities recorded the highest values (850.49±17.11 and 184.01±13.02 UE/mg protein/ min, respectively).

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Address of the author:
H. el Ferouali, A. Zoukit, S. Doubabi, N. Abdenouri*: LSET, Cadi AYYAD University, Marrakech 4000 Morocco
*E-mail: n.abdenouri@uca.ma
N. Zehhar, F. Benkhalti, H. Bouamama: Biotechnologie de la Valorisation et la Protection des Agro-ressources Chimie Bio-organique et Macromoléculaire, Cadi Ayyad University, Marrakech 4000 Morocco