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Adsorption measurements and study of temperature and humidity influences on the dandelion leaves' powder

Haytem Moussaoui , Hamza Lamsyehe, Mounir Kouhila, Younes Bahammou, Zakaria Tagnamas, Ali Idlimam*, Abdelkader Lamharrar

Team of Solar Energy and Medicinal Plants, Teacher's Training College, Cadi Ayyad University, BP 2400 Marrakesh, Morocco

** Corresponding author:*
al.idlimam@uca.ma

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Abstract

Medicinal plants are photosynthetic organisms that have potential biological activities thanks to their phytochemical compounds. However, the potential of these activities inhabits due to several factors such as temperature and humidity. This paper presents the results of several experimental studies on moisture adsorption phenomena using experimental design methodology and the gravimetric static method as keys to study the impact of temperature and humidity on the powder of the Taraxacum Officinale leaves as well as modeling the moisture adsorption at different temperatures. Additionally, empirical models are fitted in order to regress the isotherms data and represent the relationship between the equilibrium moisture content of the product and water activity. The analysis of the interaction between these factors is based on experiments, statistical calculations, and the analysis of variance method which allow to verify the fact that the humidity affects the powder stability more than the temperature or their interactions

Keywords: Adsorption isotherms, optimal water activity, Peleg model, Response Surface Methodology, temperature, humidity.

1. Introduction

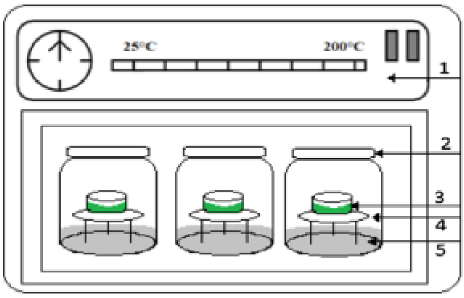
Taraxacum Officinale is a medicinal plant that belongs to a vast family of Asteraceae. This family is represented by more than 2500 species. This plant has been used widely as an effective medicine to cure a large number of illnesses [1]. They are utilized to treat dyspepsia, bile stimulation, bruises, eczema, rheumatism and muscle aches [2]. Moreover, the dandelion powder is used as a special food ingredient notably in soup, green salads, teas and wine.

Medicinal plants are complex chemical mixtures of organic and non-organic elements. They are characterized by various types of biological activities [3]. Therefore, the determination of the plant's hygroscopic stability within the environment is hardly predictable. This is actually attributed to the fact that the product goes through very complicated mass and heat transfer mechanisms [4]. The hygroscopic behavior of any product is bound to its water activity. This later is deemed of as a crucial criterion that allows to analyze the chemical, physical and microbiological properties of the product. It is taken for granted that the water activity value tends to reach the zero value when the binding forces between the water molecules and the solid matrix are intense [5]. As an effect, the microorganisms are deteriorated and the degree of oxidation tends to have a maximum value. On the other hand, if the water activity reaches the free state, its value tends to drift towards one that gives room to the proliferation of microorganisms as well as the enzymatic activities of the product [6]. The variation of water activity is mainly affected by temperature and humidity factors. A real gas equilibrium is created in the case of contact with the solid and the gas on the surface of the product. If a dry product is to be kept and preserved, it is necessary to know the water content of the product needed for its stability [7]. In the hygroscopic field, there is a specific relationship between the moisture content of the product and the relative humidity of the surrounding environment. Therefore, determining the appropriate water content to conserve the product at a certain temperature requires the knowledge of the adequate relative humidity of the surrounding air [8]. This work aims to develop and validate an experimental model for the powder's dandelion leaves by identifying the moisture sorption isotherms curves and the adsorption activity optimal water. These data constitute an important source of information for establishing stability and determining a typical storage conditions for medicinal and aromatic herbs [9]. The use of a suitable model for the analysis of the adsorption data is an essential step in optimizing and improving storage operations [10]. Furthermore, the temperature and the humidity are the two main factors that affect the quality of the product in the storage process [11]. Studying the effect of temperature and humidity is carried out by using various methods: the dynamic column method, the static volumetric method, and the static gravimetric method [12]. The static gravimetric method proves to be the most convenient technique in the present study. This technique consists in calculating the variations in mass that might take place in the powder throughout frequent measurements. What's more, the salt solution method is utilized as it is recommended by COST 90 procedure [13]. Thanks to response surface methodology, the relationships between temperature and humidity variables and the equilibrium moisture content response are explored. Indeed, the RSM method was introduced by E.P. George Box and K.B. Wilson in 1951 [14]. One of its major features is to use a sequence of designed experiments so as to get an optimal response.

2. Materials and methods

2.2. Materials

This study is wholly dependent on the powder of the dandelion's leaves. The plant is collected locally in Settat region, Morocco. Additionally, the implementation of these experiments necessitates the use of six watertight jars, a sample holder for each jar, six saturated salt solutions (KOH, ($MgCl_2$, $6H_2O$), K_2CO_3, $NaNO_3$, KCL, and ($BaCL_2$, $2H_2O$)) with a relative humidity rages (5–90%) [15], as it is displayed in figure 1, in addition to an adjustable temperature laboratory oven. Finally, an electronic balance precisely the one characterized by 0.0001g value is also used.



1: Adjustable temperature oven
2: Watertight jar
3:Sample (powder of dandelion)
4:Sample-holder
5:Saturated salt solution

Figure 1. Experimental apparatus for the sorption isotherms measurement

2.2. Experimental Procedure.

Implementing this experiment involves preparing the powder as a prerequisite. After having collected the plant, we opted for just the leaves to wash them and later dry them at the room temperature [6]. The next step is to grind the leaves so that we can have the powder as it is shown in figure 2. At this stage, the sample masses of the powder are at first measured and then put into the jars in order to achieve the hygroscopic equilibrium, where the sample mass is referred to as (Mh). Later, the powder should be dried at 105°C for 24 hours. Finally, it is worth noting that to determine the moisture content Xeq at the hygroscopic equilibrium, the mass samples are to be measured (Ms) and then calculated in accordance with the following equation 1 [5]:

$$EMC = X_{eq} = \frac{M_h - M_s}{M_s} \qquad (1)$$

a b

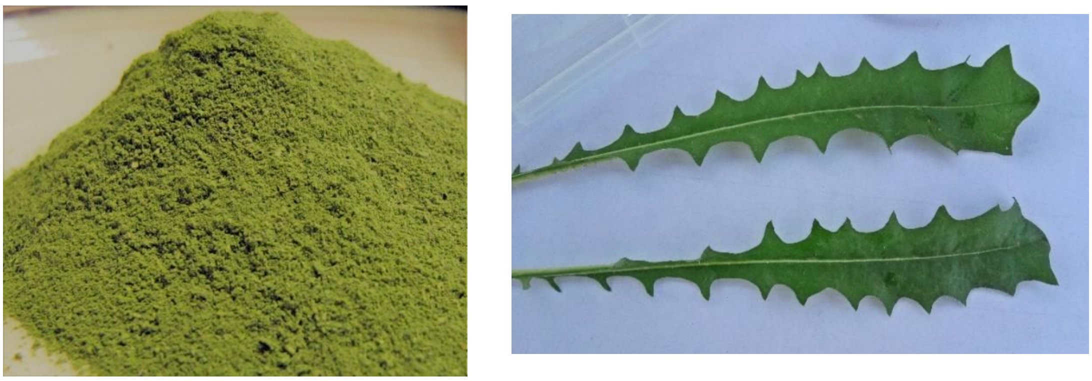


Figure 2. Dandelion (a) leaves powder; (b) leaves

2.3. Modeling the sorption isotherms curves

The sorption curves depend on the hygroscopic behavior of the powder of Taraxacum Officinale leaves and how the equilibrium is achieved. Several empirical mathematical models exist in the literature to describe the graphical relationship between the equilibrium moisture content and the water activity at a specific temperature [16]. In the case of the present study, we used three models that had better describe the sorption isotherms. These models are shown in table 1:

The correlation coefficient (r) is one of the first criterion for predicting the best equation that describes the sorption isotherms. In addition to the correlation coefficient (r), the standard error of estimate (SEE) is used for the same purpose [17, 6]. These statistical parameters are calculated as follows:

$$r = \sqrt{\frac{\sum_{i=1}^{N}\left(Xeq_{i,pre} - \overline{Xeq}_{i,\exp}\right)^2}{\sum_{i=1}^{N}\left(Xeq_{i,\exp} - \overline{Xeq}_{i,\exp}\right)^2}} \quad (5)$$

$$ESS = \sqrt{\frac{\sum_{i=1}^{N}\left(Xeq_{i,\exp} - Xeq_{i,pre}\right)^2}{d_f}} \quad (6)$$

Where N is the number of data points; $X_{eqi,exp}$ is the experimental moisture content (%d.b); $X_{eqi,pre}$ is the predicted moisture content (%d.b).

Table 1. Mathematical models

Model	Equation	Parameters	Eq. No
GAB [5]	$MC = \frac{M_0 CKa_w}{\left[(1-Ka_w)+(1-Ka_w+CKa_w)\right]}$	M_0, C, K	2
Peleg [6]	$MC = k_1 a_w^{n1} + k_2 a_w^{n2}$	k_1, k_2, n_1, n_2	3
Modified Oswin [17]	$MC = (A + B\theta)\left[\frac{a_w}{1-a_w}\right]^C$	A, B, C	4

2.4. Experimental design

In order to study the impact of temperature and humidity factors on the equilibrium moisture content of the powder of Dandelion, Response Surface design was constructed using the JMP from SAS version 10. This later is widely used in experiments involving several factors to analyze their effect on a response. In this study, the influence of these factors: the temperature (T) as a quantitative factor, the relative humidity of air in equilibrium with a sample is called the equilibrium relative humidity (ERH). According to equation 7, we can note that water activity (aw) is equivalent to the equilibrium relative humidity (ERH). Therefore, it is considered to be a quantitative factor on response equilibrium moisture content (Xeq) which was investigated. This scientific investigation requires undertaking ten trial experiments. Table 3 represents the domain of the factors mentioned earlier as well as their levels. In other circumstances, a complete description of the process behavior might require a quadratic model. This phase is referred to as the determination of the domain of the study. The following equation (8) is very useful in describing the overall interaction between various experimental variables. To analyze and optimize data resulted from the experiment, several methods were used most notably the analysis of variation (ANOVA) and the response surface methodology (RMS).

$$ERH = a_w \times 100\% \quad (7)$$

$$Y(\%) = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2 + a_{11}X_1^2 + a_{22}X_2^2 \quad (8)$$

Where Y is the response, a0 is a constant coefficient, a1and a2 are factors coefficients, a12, a22 and a11 designate variables interaction effects: X1 and X2 corresponding to temperature T and water activity (aw) respectively. This relationship describes how the experimental variables influence the experimental response.

3. Results and discussion

3.1. Adsorption isotherms

Experimental data of the equilibrium adsorption moisture content of the dandelion leaves' powder for three temperatures (30, 40 and 50 ° C) are shown in Figure 3. As it is displayed in this figure, the value of the equilibrium moisture content increases with the increase of the water activity. Additionally, the EMC decreases with increasing temperature. This can be explained by the fact that the excitation of water molecules increases by increasing temperature; thus decreasing the attracting forces between them. The adsorption equilibrium helps determine the storage conditions for preserving the quality of the powder sample [8]. The moisture adsorption isotherms have a sigmoidal shape at the three temperatures (30, 40 and 50 °C). This could be explained by the dandelion leaves' powder has a Physisorption of the moisture on its macro porous surface. This a behavior similar to most agri-food products summarized in table 6.

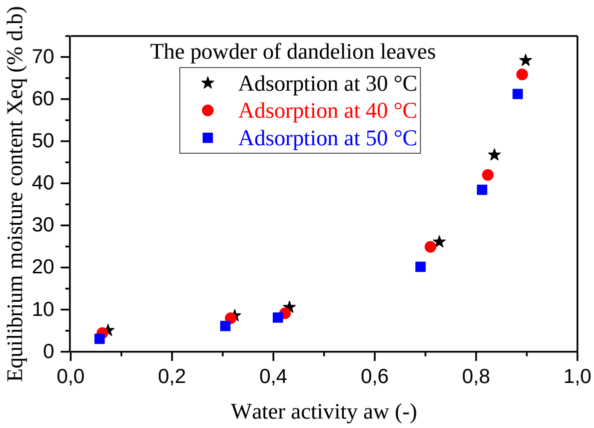


Figure 3. Adsorption isotherms of dandelion leaves' powder

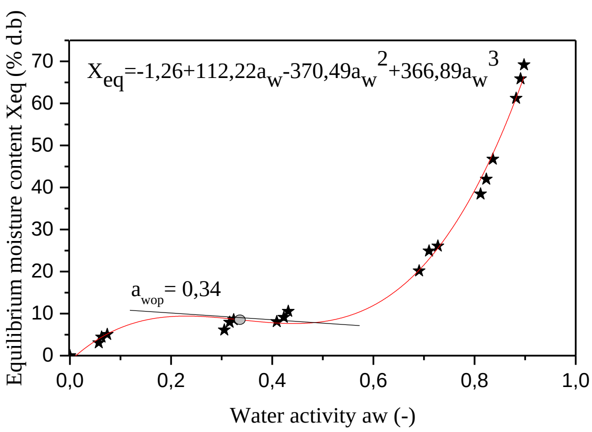


Figure 4. Determination of the optimal water activity for conservation of dandelion leaves' powder

Figure 4 shows the experimental equilibrium moisture content in adsorption at three temperatures. It also displays a polynomial model of degree three that allows predicting the value of EMC at different temperatures ranged from 30-50 °C as given by the equation 9. Moreover, using the second derivative for this polynomial, the value of optimal water activity, as well as the optimal EMC, are determined. In our case, the value of the water activity equals awop=0.34 and the optimal equilibrium moisture content equals EMCop=8.83. According to Machhour et al. (2012) [18], the optimal water activity of food is ranged from 0.3–0.4.

$$Xeq=-1.26+112.22a_w-370.49a_w^2+366.89a_w^3 \quad (9)$$

3.2. Adsorption modeling

To model these isotherms, many empirical correlations exist in the scientific literature. To better account for the influence of temperature on the hygroscopic equilibrium, and better predict the water content, we use the GAB, the Pele, and the Modified Oswin models. Indeed, the choice of these models is justified by the fact that it has the advantage of describing the set of sorption isotherms for a wider range of temperature and relative humidity of the medium surrounding the product [16].

Table 2. Results of fitting of adsorption isotherms of dandelion leaves' powder

Models and parameters	Adsorption		
GAB	30 °C	40 °C	50 °C
M_0	8	7.87	7.68
K	0.99	0.99	0.99
C	7.85	5.66	2.74
r	0.99	0.99	0.99
SEE	1.88	1.68	1.42
Peleg			
K_1	115.37	111.95	116.15
K_2	6.81	6.55	6.87
N_1	14.15	13.29	12.67
N_2	0.41	0.42	0.54
r	0.99	0.99	0.99
SEE	0.62	1.67	0.85
Modified Oswin			
A	11.16	10.42	9.14
B	-0.07	-0.05	-0.03
C	0.76	0.78	0.86
r	0.99	0.99	0.99
SEE	2.24	1.88	1.53

Table 2 presents the statistical parameters and the parameters of the models used in the study. The correlation coefficients are all high for different temperatures. A decrease in the parameters M0 and C of the GAB model is observed with the increase in temperature. Where M0 designates the value of the water content corresponding to the saturation of the monolayer [19]. After analyzing the statistical parameters, the Peleg Model is selected as a best suitable one to model the moisture adsorption isotherms at the three temperatures because it presents a higher correlation coefficients r (0.99, 0.99, 0.99) and a lower standard error of estimate (SEE) (0.62, 1.67, 0.85) at the temperature (30 °C, 40°C, 50°C) respectively.

3.3. Response Surface design

3.3.1. Domain and level of factors

Table 3. Factors values

Quantitative factors	Level	
Temperature	1	50
	-1	30
Water activity	1	0.05
	-1	0.89

Table 3 represents the different levels and domains of each factor. We have attributed number 1 to the possible highest temperature in this system, which is 50 degrees Celsius and -1 to the lowest temperature which is 30 degrees.
The number 1 has also been allocated to the water level of 0.05 and the following -1 to the level of 0.89.
In this regard, the study we will be conducted relying on the temperatures of 30 and 50 degrees Celsius and the water levels of 0.05 and 0.89.

3.3.2. Experimental design and results

Table 4. Experiment values

Experiment	Real and coded values				Responses		
	T (°C)	X_1	a_w	X_2	Y_{exp}	Y_{mod}	Residue
1	40	0	0,05	-1	4,41	4,28	0,13
2	50	1	0,05	-1	3,05	3,49	-0,44
3	30	-1	0,05	-1	5,04	4,74	0,30
4	40	0	0,89	1	65,85	65,53	0,32
5	30	-1	0,89	1	69,19	68,98	0,21
6	50	1	0,89	1	61,22	61,75	-0,53
7	50	1	0,47	0	10,25	9,29	0,96
8	30	-1	0,47	0	13,02	13,53	-0,51
9	40	0	0,47	0	12,25	11,57	0,68
10	40	0	0,47	0	10,44	11,57	-1,13

Tables 4 reveals the various experiments conducted by JMP from SAS. For each experiment, we set a particular temperature and a particular relative humidity or water activity. As such, we were able to calculate the equilibrium moisture content using equation 1. Then, we use it as an experimental response. Finally, the residue column in the table shows the difference between the responses given by the model and the responses calculated by the experimental data.

3.3.3. Determination of the regression model and its validation

$$EMC=Xeq=11.57-2.12\left[\frac{(T-40)}{10}\right]+30.62\left[\frac{(aw-0.47)}{0.42}\right]+\left[\frac{(T-40)}{10}\right]\left[\left[\frac{(aw-0.47)}{0.42}\right](-1.49)\right]$$
$$+\left[\frac{(T-40)}{10}\right]\left[\left[\frac{(T-40)}{10}\right](-1.16)\right]+\left[\frac{(aw-0.47)}{0.42}\right]\left[\left[\frac{(aw-0.47)}{0.42}\right](23.33)\right] \quad (10)$$

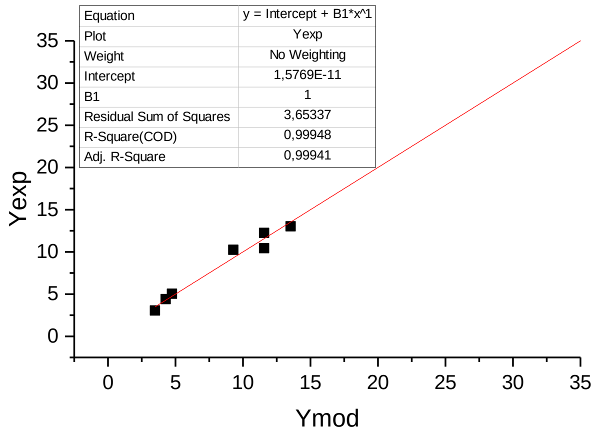


Figure 5. Validation test of the regression model

The predicted model elaborated by the JMP software in equation 10 shows the values of several coefficients of factors. This empirical model summarizes the relationships between the equilibrium moisture content, the temperature, the water activity, and their interactions. What's more, the established model is valid for a temperature ranged from 30 to 50 °C, and a water activity ranged from 0.05 to 0.89.

Figure 5 displays the relationship between the experimental responses and the predicted responses Yexp=f (Ymod). It also shows that the experimental values closely fit the values predicted by the empirical model as it is represented in the straight line in the graph. The statistical measures (R-square and adj.R-square) summarised in figure 5 indicate a good fit of the data to the equation 10.

3.3.4. Model coefficients and statistical evaluation

Table 5. ANOVA of model coefficients.

Term	Estimate	SEE	T Ratio	P values
aw	30,62	0,39	78,5	<,0001*
aw*aw	23,3	0,62	37,29	<,0001*
T	-2,12	0,39	-5,44	0,0056*
T*aw	-1,49	0,48	-3,13	0,0352*
T*T	-0,16	0,62	-0,26	0,8058

The table 5 displays the ANOVA parameters of the model coefficients, which are the standard error of estimate (SEE), the T ratio, and the p values. According to the data provided by this table, the water activity coefficients have positive values. This means that as long as the value of water activity rises the EMC rises while the temperature coefficients and their interaction (temperature*water activity) are characterized by negative values. In others words, the EMC rises when the temperature drops. In addition, all the coefficients of the model have a SEE that is less than 0.7 and a p-value

less than 5% except for the term (T*T). These results mean that the terms that aims at modeling the factors' impact are found to be significant [20]. The figure 6 is a column representation that denotes the polynomial coefficient values. The values of a2 and a22 which respectively correspond to aw and aw*aw are far higher than a1, a11 and a12 which in turn correspond to the values of T, T*aw and T*T.

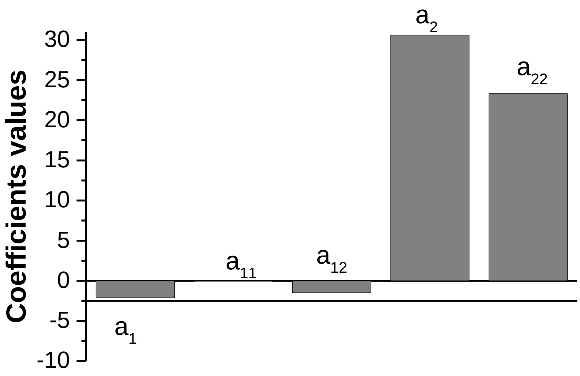


Figure 6. The column representation of model coefficients values.

3.3.5. Surface Profiler

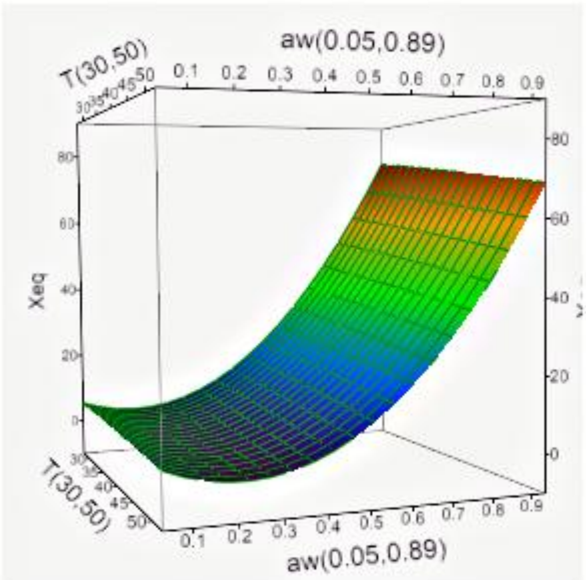


Figure 7. Surface Profiler of moisture adsorption of dandelion leaves' powder

The effect of the temperature (T), water activity (aw) as well as their interactions on the equilibrium moisture content (Xeq) is shown in the figure 7 as a surface profiler elaborated by the software JMP from SAS. We can note from the figure that the equilibrium water content reaches the maximum when the water activity is at the maximum. It is also evident that the function that relates the (Xeq) and (aw) has a sigmoid shape. On the other side, the relation between the EMC and the temperature (T) has a rather decreasing linear function as it is demonstrated in figure 7. In addition, we can observe that humidity has a higher impact than that of the temperature. Similar findings have been previously proven by several research such as the powder milk by Naji et al. (2010) [21].

4. Conclusion

The aim behind this study is to model and analyze the impact of the temperature as well as the humidity on the powder of Taraxacum Officinale's leaves. In this respect, it has been investigated that the function that links the equilibrium

moisture content (EMC) and water activity (aw) has a sigmoid shape. By analyzing the statistical parameters, it has been found that the Peleg model is definitely a convenient model to represent the moisture adsorption isotherms regression. According the optimal water activity technique, the powder of dandelion's leaves has a stable hygroscopic state when its water activity reaches 0.34 and its EMC equals 8.83. On the other hand, the equilibrium moisture content (EMC) and the temperature (T) relation has a nearly linear function. Moreover, it has been found out that the impact of humidity on the equilibrium moisture content (EMC) of the powder is higher than that of the temperature (T). Furthermore, it is of extreme significance that the empirical model, which has been elaborated relying on the Response Surface design, is validated with a coefficient of correlation R = 0.99.

References

[1] K. Hostettman, A. Marston, K. Ndjoko, J-L. Wolfender, *Curr. Org. Chem.*, 4 (2000) 973-1010.

[2] T. Michael, N.D. Murray, J.E. Pizzorno, M.T. Murray, Textbook of Natural Medicine, 4th ed., Churchill Livingstone, London, 2013.

[3] P. Guilan, C. Xiaoguang, W. Wenfu, J. Xiujuan, *J. Food Eng.*, 80 (2007) 562–567.

[4] L. Ait Mohamed, M. Kouhila, A. Jamali, S. Lahsasni, M. Mahrouz, *J. Food Eng.*, 67 (2005) 491–498. https://doi.org/10.1016/j.jfoodeng.2004.05.016.

[5] H. Moussaoui, Y. Bahammou, A. Idlimam, A. Lamharrar, N. Abdenouri, *Food Bioprod. Process.*, 114 (2019) 12-22. https://doi.org/10.1016/j.fbp.2018.11.002.

[6] L. lahnine, M. Ouhammou, A. Idlimam, M. Mahrouz, A. Lamharrar, H. Hanine, M. Bouchdoug, M. Kouhila, Mor. J. Chem., 4 (2016) 128-139.

[7] Al-Muhtaseb, A., McMinn, W., Magee, *T. Trans. IChemE*, 80 (2002) 118–128.

[8] R. Moreira, F. Chenlo, J. Sineiro, S. Arufe, S. Sexto, *J. Food Process. Preserv.*, 41 (2016) e12997.

[9] A. H. Al-Muhtaseb, M. A. Hararah, E. K. Megahey, W. A. M. McMinn, T. R. A. Magee, *LWT-Food Sci. Technol.*, 43(7) (2010) 1042–1019.

[10] O.J Oyeladea, T.Y. Tunde-Akintundeb, J.C. Igbekac, M.O. Okeb, O.Y. Rajid, *J. Stored Prod. Res.*, 44 (2008) 179–185.

[11] E.Ö., Evranuz, *Int. J. Food Sci. Technol.*, 28 (1993) 193-199.

[12] P. Jingjing, S.Z. Jianshun, *Build. Environ.*, 48 (2012) 66-76.

[13] W. Wolf, W.E.L Spiess, G. Jung, D. Simatos, J.L. Mullon, Properties of Water in Foods, Springer, Netherlands, 1985.

[14] G. E. P. Box, K. B. Wilson, *J. R. Stat. Soc.*, 1 (1951) 1-45.

[15] L. Greenspan, *J. Res. Natl. Stand. Sec. A.*, 81 (1977) 89–96.

[16] P. Ritika, K. Kaushik, *J. Food Process. Preserv.*, 40 (2015) 999-1009.

[17] A. Jamali, M. Kouhila, L. AIT Mohamed, J. Jaouhari, A. Idlimam, N. Abdenouri, *J. Food Eng.*, 72 (2004) 77–84.

[18] H. Machhour, A. Idlimam, M. Mahrouz, I. El Hadrami, M. Kouhila, *J. Mat. Environ. Sci.*, 3 (2012) 232–247.

[19] G. Fahrettin, M. Medeni, K. Ahmet, *J. Food Process. Preserv.*, 22 (1998) 345-357.

[20] L. L'Hocine, M. Pitre, *Food Chem.*, 194 (2016) 780–786.

[21] A. Naji, A. Idlimam, M. Kouhila, *Chem. Eng. Commun.*, 197 (2010) 1109–1125.