

# Experimental determination and mathematical fitting of sorption isotherms for Lemon Balm (*Melissa officinalis* L.)

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**Abstract:** Knowledge of the equilibrium moisture content (EMC) is important for modelling and planning of drying and, to select the conditions for storage of biological products. Equations for modeling water sorption isotherms have special importance in many aspects of product preservation by dehydration. In this work, desorption and absorption isotherms for *Melissa officinalis* L. (Lemon Balm) were determined at four different temperatures (25, 40, 50 and 60°C) by using the method recommended by the project COST 90. This method is based on maintaining a known mass of sample to an atmosphere generated by the use of saturated saline solutions until achieving the balance. The saline solutions were prepared according to DIN 50008 for a range of relative humidity between 10 and 85%. Samples of 0.5 grams of whole leaves of *Melissa officinalis* L. variety Citronella were placed in perforated stainless steel bins, positioned inside of tightly sealed glass containers. The weight of the samples was registered until the samples achieved balance. Experimental data were fitted using the following mathematical models: BET, GAB, Halsey, Lagmuir, Oswin, Peleg, Henderson and Chung & Pfof. Using nonlinear regression, the experimental data was fitted to the considered models. The chi-square test and the coefficient of determination were used to evaluate the fit. Halsey's model was found to be the most suitable for describing the desorption curves at the temperatures of 25°C and 40°C and BET's model was most suitable for describing the data at the temperatures of 50°C and 60°C.

**Keywords:** *Melissa officinalis* L., desorption isotherms, water activity, Equilibrium moisture content EMC

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## 1 Introduction

Lemon Balm (*Melissa officinalis* L.) is native to the countries bordering the Mediterranean Sea; however, it also grows from the Alps to the Pyrenees. In the natural forms, leaves are ovate and serrate. The leaves have fine hairs on both sides and emit a lemony scent when they are crushed. Traditionally, the leaves are important due to the plant's medicinal properties. Its essential oil is required mainly in the pharmaceutical, product and cosmetic industries. The properties of the plant extracts include sedative, relaxing, antibacterial, antiviral, and antispasmodic effects (Abuhamdah and Chazot, 2008; Heeger, 1989). The main components of the essential oil

are citral, citronellal and linalool. By means of gas chromatography studies of the essential oil, 70 components are known (Abuhamdah and Chazot, 2008; Heeger, 1989; Bomme, 2001). Dry leaves of lemon balm contain between 0.05 and 0.12% vol. Essential oil (Bomme, 2001). As a result of low essential oil content, lemon Balm oil has a very high price level.

The sorption isotherm relates the water activity to the water content of the mixture of water and material at a certain temperature and pressure. The water activity is defined as the ratio of the partial vapor pressure in equilibrium with the water in the product material and the vapor pressure in equilibrium with pure water at the same temperature. Therefore, it characterizes the state of the water in products. This means that the sorption isotherm gives an impression of how strong and in which way water is bound by the material constituents (Quirijns, 2006).

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The effect of temperature on the sorption isotherms is of great importance given that medicinal plants are exposed to a range of temperatures during storage and processing, and water activity changes with temperature. In describing the moisture sorption isotherm, the temperature has to be specified and held constant because temperature affects the mobility of water molecules and the dynamic equilibrium between the vapor and the adsorbed phases. Water activity increases as temperature increases for a constant moisture content (Barbosa-Canovas *et al.*, 2007).

The sorption isotherm curves can be generated from an absorption or desorption process. When solid products are exposed to conditions where vapor pressure of water is higher than vapor pressure of water in the solids, adsorption occurs and when the lower vapor pressure of water in surrounding product solids becomes the driving force for desorption. At equal vapor pressure, the amount of adsorption and desorption for the same product may differ, which is known as sorption hysteresis. One of the main causes of this phenomenon is that the capillaries can empty differently upon desorption; then narrow ends of surface pores will trap and hold water internally below the water activity where it should have been released during adsorption; the narrow end prevents the body from filling (Barbosa-Canovas *et al.*, 2007).

The knowledge of the Equilibrium moisture content (EMC) is important for modeling and planning of the drying process and to select the conditions for storage of the product. Equations for modeling water sorption isotherms are of special interest for many aspects of product preservation by dehydration. Knowledge of the thermodynamic properties associated with sorption behavior of water in products is important to dehydration in several respects, especially in the design and optimization of the process.

Numerous mathematical equations can be found in literature that describes water sorption isotherm of product materials. Each of the proposed, empirical, semi-empirical or theoretical, has had some success in reproducing equilibrium moisture content data of a given type of product and in a given range of water activity, these mathematical models differ from each other in the

quantity of related parameters (Park *et al.*, 2002), (Roman and Hensel, 2010).

## 2 Materials and methods

Lemon Balm (*Melissa officinalis* L.) was used for the determination of sorption isotherms. The Lemon Balm was planted in Witzenhausen, Germany (51°20'45.76" N, 9°51'52.08"E) the samples were harvested little before the flowering and only the leaves were taken randomly to complete the selected size of the sample. For the measurement of the weight of the samples a precision analytic balance with resolution of 0,0001 g was used. To obtain the required temperature conditions for each test a forced ventilation oven was considered. The required humidity conditions were obtained by using saline solutions that generated different humidity conditions depending on the temperature. During the test, the samples were placed inside glass bottles that contain the solutions, in order to maintain the product at constant conditions of humidity and temperature. The bottles were transparent, with one liter capacity and a hermetic seal. The samples were placed inside the bottles by using a perforated stainless steel container that allowed gas exchange.

To determine the isotherms, the methodology recommended by the European project COST 90 (Spiess and Wolf, 1983) was applied. This methodology is based on the gravimetric method that uses saline solutions. The saline solutions were prepared according to the norm DIN 50008 (DIN, 1982), considering humidity ranges between 10 and 80% as shown in Table 1. In this study, isotherms at 25, 40, 50 and 60°C were obtained. Figure 1 shows the considered methodology to determine the sorption isotherms.

**Table 1** Relative humidity (%) obtained by the salt solution in a closed vessel at different temperatures (DIN 50008-part1)

Salt	25°C	40°C	50°C	60°C
LiCl	12	11	11	11
CH <sub>3</sub> COOK	22	20	-	-
MgCl <sub>2</sub>	33	32	31	30
K <sub>2</sub> CO <sub>3</sub>	43	40	38	36
Mg(NO <sub>3</sub> ) <sub>2</sub>	53	48	46	43
NaNO <sub>2</sub>	64	61	60	58
NaCl	75	75	75	75
KCl	85	83	81	80

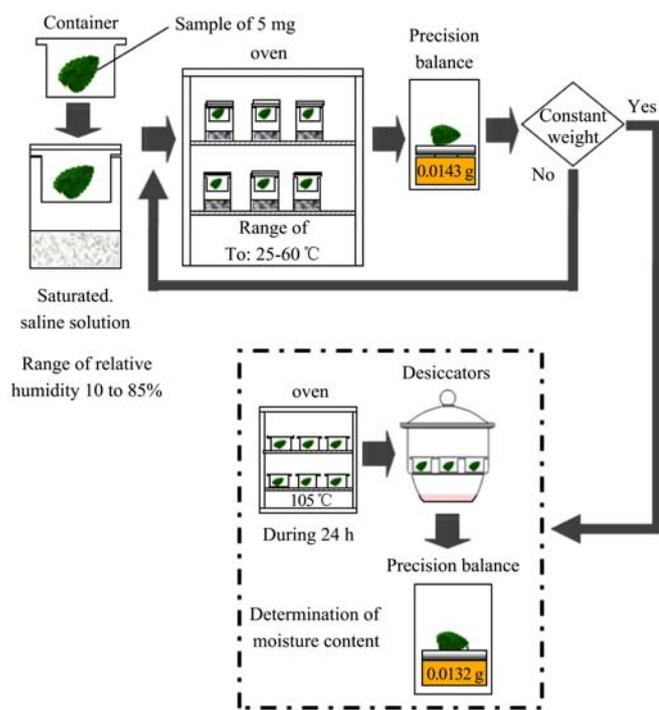


Figure 1 Set-up and methodology for determining the sorption isotherms

The samples at constant relative humidity and temperature conditions were weighed every three days until there was no weight difference (it was assumed no more than 0.0001 g). At this point the equilibrium between the product and surroundings is reached. After that, the moisture content of the sample was determined using the oven method, in which the temperature was maintained at 105°C during 24 h (AOAC, 1990). At last, the sample was maintained inside desiccators during 30 min before weighing it. The amount of equilibrium moisture content *EMC* in a product is determined considering dry or wet basis. On wet basis it can be calculated as follows using the following Equation (1):

$$EMC_{w.b} = \frac{m_w}{m_w + m_{DM}} \cdot 100 \quad (1)$$

The moisture content on dry basis (*x*) which is defined as mass of water per dry mass was also calculated using the following mathematical Equation (2):

$$x = \frac{m_w}{m_{DM}} \quad (2)$$

where, *m<sub>w</sub>*: is weight of water contained in the product; *m<sub>DM</sub>*: dry matter weight of the product.

The values obtained in the experiment were statistically evaluated using the BET, GAB, Halsey,

Oswin, Peleg, Henderson & Chung Pfof models. The non-linear regression and the Marquart method were used. To monitor the quality of statistical analysis with the proposed models, the Chi-square test  $\chi^2$  and determination coefficient  $R^2$  were used (Equations (3) and Equation (4)).

$$\chi^2 = \frac{\sum_{i=1}^n (O_i - E_i)^2}{E_i} \quad (3)$$

where, *O<sub>i</sub>* is the observed frequency; *E<sub>i</sub>* expected frequency and *n* number of observations

$$R^2 = \frac{SS_R}{SS_T} = 1 - \frac{SS_E}{SS_T} \quad (4)$$

where, *SS<sub>R</sub>* is the regression sum of squares; *SS<sub>T</sub>* is the total sum of squares and *SS<sub>E</sub>* is the sum of squared errors. The values of the lowest  $\chi^2$  or those that tend to zero and the highest  $R^2$  or those that tend to 1, are considered optimal, and are used as criteria to determine the best model (Ross, 2005). The models used in this study for the setting of isotherms obtained experimentally appear in Table 2.

Table 2 Mathematical models used in fitting of isotherms for Lemon Balm

Model	Formula	Reference
BET lineal	$X_{eq} = \frac{(a_w X_m C)}{(1 - a_w)(1 + (C - 1)a_w)}$	Kneulle, 1975; Bell, 1984
GAB	$X_{eq} = \frac{a_w k X_m}{(1 - k a_w)(1 - k a_w + C k a_w)}$	Timmerman and Chirife, 2001
Halsey	$X_{eq} = X_m \left[ \frac{A}{\log a_w} \right]^{\frac{1}{n}}$	Halsey, 1985; Silva, 2007
Henderson	$X_{eq} = \left[ \frac{-\log(1 - a_w)}{k(T + C)} \right]^{\frac{1}{2}}$	Timmerman, 2001
Langmuir	$X_{eq} = \frac{X_m C a_w}{1 + C a_w}$	Timmerman, 2001
Oswin	$X_{eq} = A \left[ \frac{a_w}{1 - a_w} \right]^B$	Barbosa-Canovas and Juliano, 2007
Peleg	$X_{eq} = k_1 a_w^{n_1} + k_2 a_w^{n_2}$	Barbosa-Canovas et al, 2007
Chung & Pfof	$X_{eq} = E - D \ln((C - T) \ln a_w)$	Spieß and Wolf, 1983

### 3 Results

Figure 2 and Figure 3 show the experimental data obtained after desorption performed on *Melissa officinalis* L. at 25, 40, 50, and 60°C and adsorption at 40°C and

60°C for eight relative humidities. It can be observed that sorption isotherms are temperature dependent. A higher temperature will decrease the binding energy between molecules, because of an increased state of excitation of the molecules, their mutual distances increase and the attractive forces between them decrease. They become less stable and break away from the water binding site of the food materials.

The results reveal the temperature dependence of the sorptive behavior, with an increase in temperature decreasing the sorption capacity. This is consistent with the thermodynamics of sorption (Hossain *et al.*, 2001). The EMC increases with decreasing temperature the constant relative humidity. The sorption isotherms present the characteristic S-shaped curve (Type II), typical of sorption isotherms for many hygroscopic products.

Mathematical models evaluation

The results of nonlinear regression analysis for fitting desorption and adsorption models to experimental data and the estimated constants for all models analyzed in this research, the coefficient determination  $R^2$  and Chi-square test  $\chi^2$  the all models data are presented in

Table 3.

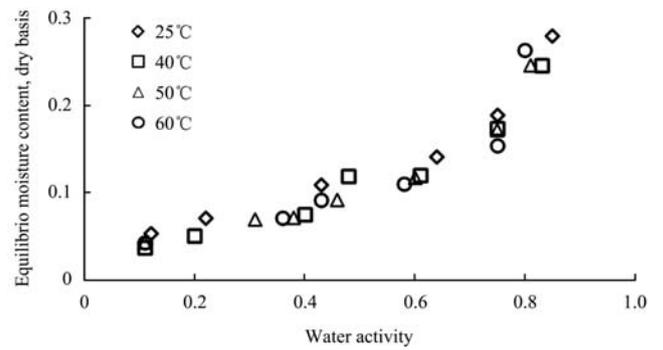


Figure 2 Experimental desorption isotherms of Lemon Balm for 25, 40, 50 and 60°C considered relative humidity between 10 and 80%

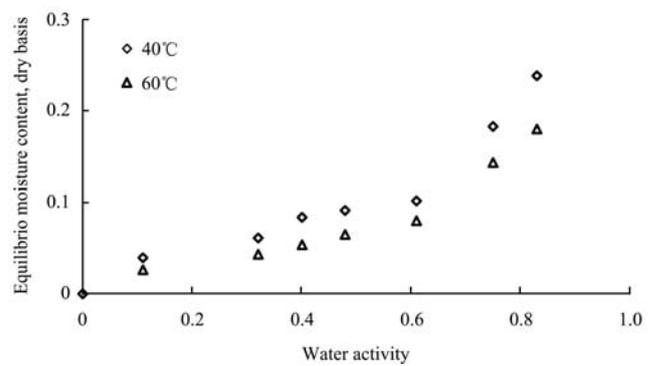


Figure 3 Experimental adsorption isotherms of Lemon Balm for 40°C and 60°C considered relative humidity between 10 and 80%

Table 3 Estimated parameter values and criteria for comparing the models in desorption

Model	Adsorption			Desorption				
	Constant	40°C	60°C	Constant	25°C	40°C	50°C	60°C
BET	$X_m$	0.0428	0.0355	$X_m$	0.0444	0.0434	0.046	0.048
	$C$	142.68	23.15	$C$	3.12	3.35	79.54	30.79
	$\text{Chi}^2$	0.0007	0.0001	$\text{Chi}^2$	0.0019	0.0015	0.0003	0.0021
	$R^2$	0.9809	0.9975	$R^2$	0.9646	0.9561	0.9913	0.9337
GAB	$X_m$	0.0318	0.0041	$X_m$	0.0711	-	-	0.0752
	$C$	-3.8356	0.0206	$C$	2.6742	-	-	1.4932
	$k$	1.0444	-3.7205	$k$	0.9062	-	-	0.9042
	$\text{Chi}^2$	0.0079	0.0041	$\text{Chi}^2$	0.0039	-	-	0.0054
	$R^2$	0.8697	0.9014	$R^2$	0.9547	-	-	0.9061
Halsey	$X_m$	0.1558	0.1371	$X_m$	0.1692	0.1618	0.1601	0.1608
	$A$	0.1471	0.1306	$A$	0.1561	0.1496	0.1524	0.1553
	$n$	1.3719	1.2697	$n$	1.1663	1.517	1.3184	1.2113
	$\text{Chi}^2$	0.0004	0.0001	$\text{Chi}^2$	0.0002	0.0007	0.0004	0.0024
	$R^2$	0.9932	0.9984	$R^2$	0.9947	0.9774	0.9867	0.9237
Henderson	$k$	0.5034	0.5967	$k$	0.4547	-0.372	0.9182	-
	$n$	1.9551	1.8193	$n$	1.3841	1.4157	2.4609	-
	$C$	1.2071	1.1716	$C$	-13.18	-55.24	-3.17	-
	$\text{Chi}^2$	0.0055	0.0027	$\text{Chi}^2$	0.0018	0.0018	0.0088	-
	$R^2$	0.9067	0.9277	$R^2$	0.9498	0.9546	0.7664	-

Model	Adsorption			Desorption				
	Constant	40°C	60°C	Constant	25°C	40°C	50°C	60°C
Lagmuir	$X_m$	0.393	0.3113	$X_m$	1.3778	1.5627	12.6211	-
	$C$	0.9456	0.919	$C$	0.2266	0.1787	0.0182	-
	$\chi^2$	0.0089	0.0049	$\chi^2$	0.0051	0.0031	0.0050	-
	$R^2$	0.8435	0.866	$R^2$	0.8580	0.8985	0.8378	-
Oswin	$A$	0.0955	0.0742	$A$	0.1184	0.1083	0.0994	0.0971
	$B$	0.5709	0.6045	$B$	0.4740	0.4965	0.5809	0.6295
	$\chi^2$	0.0007	0.0001	$\chi^2$	0.0006	0.0007	0.0009	0.0030
	$R^2$	0.9892	0.9964	$R^2$	0.9840	0.976	0.9719	0.9047
Peleg	$k_1$	0.1451	-0.218	$k_1$	0.1437	0.1376	0.1449	0.1532
	$n_1$	1.4654	1.1812	$n_1$	1.2009	1.157	1.4335	1.5458
	$k_2$	0.1451	0.4561	$k_2$	0.1437	0.1376	0.1449	0.1532
	$n_2$	1.5518	1.3857	$n_2$	0.9854	1.1646	1.4041	1.5194
	$\chi^2$	0.0028	0.0012	$\chi^2$	0.0042	0.0022	0.0032	0.0056
	$R^2$	0.9551	0.9719	$R^2$	0.8827	0.9287	0.8974	0.8259
Chung & Pfof	$E$	0.5105	-	$E$	0.4993	0.5153	0.5347	0.5585
	$D$	0.0808	-	$D$	0.0821	0.0792	0.0820	0.0846
	$C$	-168.62	-	$C$	-102.05	-170.41	-197.01	-212.8585
	$\chi^2$	0.0025	-	$\chi^2$	0.0021	0.0016	0.0029	0.0054
	$R^2$	0.9572	-	$R^2$	0.9414	0.9483	0.9040	0.8266

Figures 4 and 5 show the best fitted models for different considered temperatures. In Table 3 can be observed that the BET, Oswin and Halsey models are those with the lowest Chi-square ( $\chi^2$ ) values and values  $R^2$  near one.

The best fit was obtained using Halsey's model and, was the most suitable model for the temperatures of 25°C and 40°C with each  $\chi^2$  values of 0.0002 and 0.0007 and  $R^2$  from 0.9947 to 0.9774. For temperatures of 50°C and 60°C is the best fit was obtained using BET's model with  $\chi^2$  of 0.0003 and 0.0021 and  $R^2$  of 0.9337 and 0.9913.

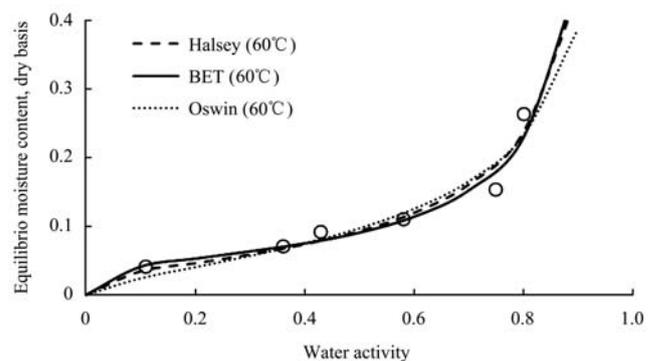
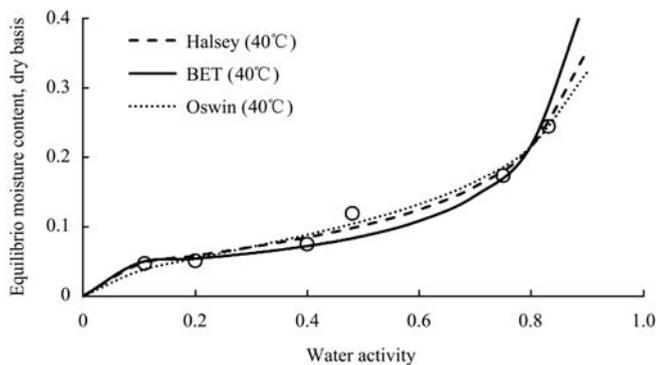
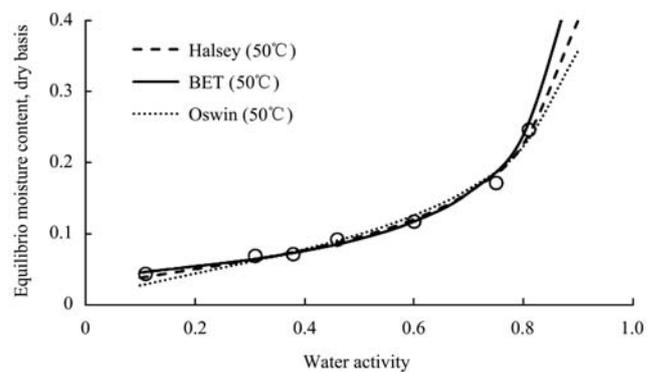
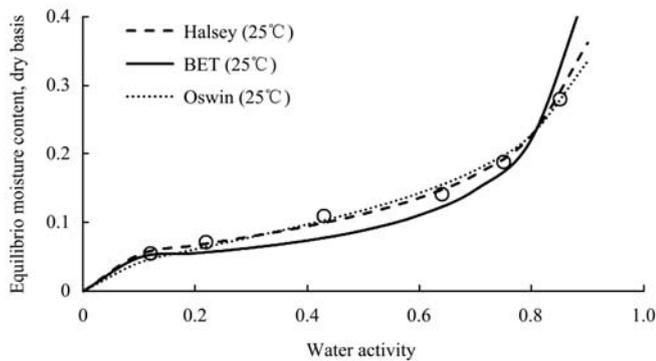


Figure 4 The best fitting desorption isotherm models for 25°C and 40°C for Lemon Balm

Figure 5 The best fitting desorption isotherm models for 50°C and 60°C for Lemon Balm

From Table 3, it can be observed the best fit models for adsorption at 40°C and 60°C were Halsey, Oswin and BET. The best fit was obtained by using Halsey's model that is suitable for temperatures of 40°C with  $\chi^2$  values of 0.0004 and  $R^2$  from 0.9932 and for temperature of 60°C with  $\chi^2$  values of 0.0001 and  $R^2$  from 0.9987.

Water vapor sorption hysteresis refers to the different paths of the adsorption and desorption isotherms for the same material under isothermal conditions. From the analysis of the curves it follows that a much lower vapor pressure is required to attain a certain amount of water by desorption than by adsorption. Moisture sorption hysteresis has important theoretical and practical implications. The theoretical implications range from the general aspects of the irreversibility of the sorption processes to the question of the validity of thermodynamic functions derived from such a system. The practical implications deal with the effects of hysteresis on chemical and microbiological deterioration particularly of biotechnological and food products during thermal processing and storage.

Most frequently, the hysteresis is classified on the basis of the structure of the sorbent, distinguishing hysteresis on porous, non-porous, and non-rigid solids. The first category belongs to the theories based on capillary condensation; the second one includes interpretation based on partial chemisorption or phase changes, while the third one deals with changes in structure. Figure 6 shows the curves of adsorption and desorption under the temperatures of 40 and 60 degrees. These graphs allow us to observe the effect of temperature on the hysteresis. Since raising the temperature from 40°C to 60°C, there is an increased distance between the adsorption and desorption curves.

During adsorption, the capillary begins to fill as a result of the rising in water activity, while the pore is still empty. For desorption, the pore is initially full of liquid at saturation. This liquid can escape only when the pressure of the surrounding air becomes lower than the vapor pressure of liquid inside the capillary. As the system of pores has generally a large range of capillary diameters, it results in that differences between adsorption and desorption are observed (Rockland and

Beuchat, 1987; Barbosa-Canovas and Juliano, 2007).

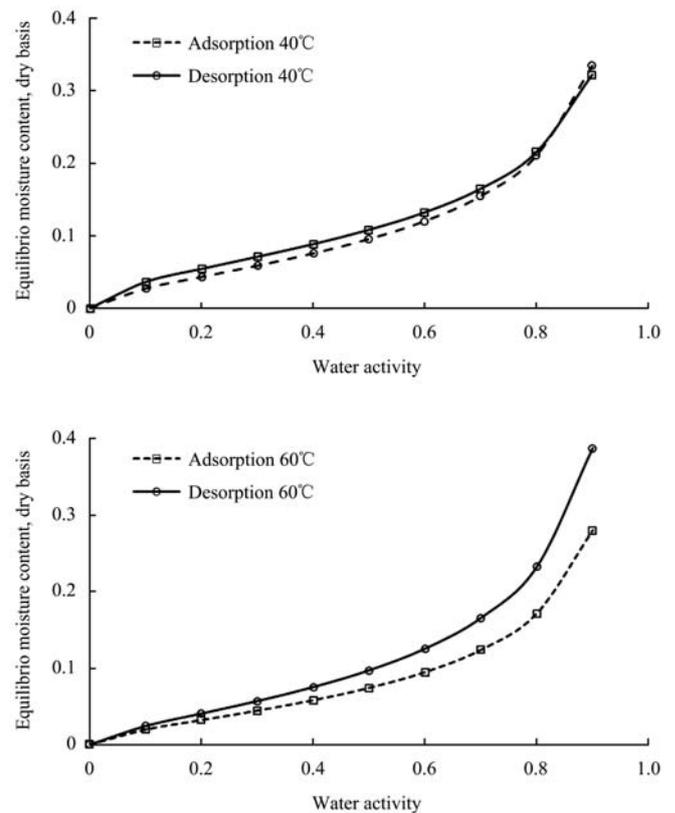


Figure 6 Sorption hysteresis measured for 40°C and 60°C

#### 4 Conclusion

The desorption curves of Lemon Balm (*Melissa officinalis* L.) leaves were determined at four temperatures (25, 40, 50 and 60°C). The experimental data isotherms of sorption were fitted with eight mathematical models. Halsey, BET and Oswin models describe better the behavior of sorption data under the studied conditions.

On the base of the obtained results, it can be concluded that the Equilibrium Moisture Content of Lemon Balm is proportional to the activity of water or relative humidity of the air and it falls with the increase of the temperature, for the same relative humidity of the air that is the prospective behavior.

Considering the coefficient of determination  $R^2$  and Chi-square test  $\chi^2$  the Halsey model is the one that better describes the phenomenon of hygroscopicity of the Lemon Balm for the temperatures of 25°C and 40°C and the pattern of BET describes better for the temperatures of 50°C and 60°C, compared with other studied models.

## Nomenclature

$C_1, k, A, E$ and $D$	equation coefficients
$SS_R$	Regression sum of squares
$SS_T$	Total sum of squares
$SS_E$	Sum squared errors
$T$	Temperature, °C

$R^2$	Determination coefficient
$EMC$	Equilibrium Moisture Content
$m_w$	Weight water
$m_{DM}$	Dry matter weight
$O_i$	Observed frequency

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