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Comparative moisture sorption isotherms, modelling and isosteric heat of sorption of controlled and irradiated Moroccan rosemary leaves

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ABSTRACT

In this paper, we studied and compared water sorption isotherms of irradiated and non-irradiated (controlled) rosemary leaves at three temperatures: 30, 40 and 50 °C, using the standard static gravimetric method. This method consists on the use of different salts solutions, over a range of water activity from 0.05 to 0.9.

The sorption isotherms of all samples were conceived to be typical type II sigmoid. These isotherms have been fitted using four different sorption equations (modified Oswin, Enderby, Peleg, and LESPAM), Enderby model was proved to be the most suitable for describing the sorption curves for controlled and irradiated rosemary leaves.

The experimental data curves allows us to calculate the value of the optimal water activity as for the conservation of controlled and irradiated rosemary leaves.

Respectively, the net isosteric heat of sorption of our samples was computed from the predicted sorption data by applying the integrated form of the Clausius–Clapeyron equation.

1. Introduction

Rosmarinus officinalis, member of the family Lamiaceae, is a flowering plant that grows in Mediterranean countries, southern Europe and in the littoral region through Minor Asia areas wildly (Pintore et al., 2002). Rosemary is known to contain an important amount of tannins, it is used as a flavor enhancer, as a beverage, it is also used in cosmetics and in traditional medicine thanks to its choleretic, hepatoprotective and antitumorigenic activity (Variyar et al., 1998).

One of the common methods of medicinal plants preservation is irradiation. This technique is a safe process that exposes food to a predetermined dose of radiation according to the food type in question. In our case; we irradiate samples of rosemary leaves at low dose (Machhour et al., 2011), and we study and compare moisture sorption isotherms, the water activity, and the isosteric heat of sorption of controlled and irradiated rosemary leaves.

Moisture sorption isotherms describe how actively water is bound to a solid (Naji et al., 2010), and they also are used in order to predict the storage stability of food products (Labuza et al., 1985). So, in a fixed humid environment, materials could lose or absorb moisture on the basis of the equilibrium state because of the balance in vapor pressure (Lahsasni et al., 2004).

Moisture sorption isotherms present the thermodynamic data related to the material being studied, which are necessary to design calculations belonging to the drying process and the prevision of the final moisture content for the product at the end of drying (Naji et al., 2010). The moisture adsorption data can be analyzed to provide a theoretical interpretation for food microstructure and physical interaction between water molecules and the solid matter of a foodstuff (Rizvi, 1986).

Many different methods can be used to determine the sorption properties including: static volumetric method, dynamic column method and gravimetric method (Peia and Zhang, 2012).

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Nomenclature:

EMC or X_{eq}	Equilibrium Moisture Content (kg water/(kg d.b.))
M_s	Mass of dry matter (kg)
M_h	Mass of wet matter (kg)
$X_{eqi,exp}$	Experiment EMC (% d.b)
$X_{eqi.pre}$	The predicted EMC (% d.b)
A,B,C,D	Model coefficients
LESPAM	Laboratory of Solar Energy and Medicinal Plants
T	Temperature
a_w	Water activity
$a_{w(op)}$	Water activity optimal
MRE	Mean relative error
r	Correlation coefficient
N	Number of data points
P	Partial pressure of water in the food (atm)
P_0	Vapor pressure of pure water at the same temperature (atm)
d.b	Dry weight basis
Ads	Adsorption
Des	Desorption
CR	Controlled rosemary
IR	Irradiated rosemary
Pred	Predicted
Δh_d	Isosteric heat of sorption (kJ mol^{-1})
Fig.	Figure
Eq.	Equation

In our case, we used the standard static gravimetric method. In this respect; the samples were placed in containers in an airtight environment under a fixed temperature. In these containers, we put salt solutions, in order to maintain an environment with constant humidity.

The gravimetric method is cheap and simple, but it requires several weeks to reach an equilibrium state.

2. Materials and methods

2.1. Materials

R. officinalis samples consist of both dried (traditional drying at room temperature) and moist leaves, obtained from the province of Errachidia in the south east of Morocco and used without any sorting or cleaning treatment.

Some of rosemary's samples studied were treated by gamma irradiation at low dose; >1 kGy.

Our study focuses on investigating and comparing the sorption isotherms of irradiated and non-irradiated (controlled) rosemary leaves. In this regard, the sorption method adopted was the standard static gravimetric technique, it consists on using six saturated salt solutions: KOH, ($MgCl_2{\cdot}6H_2O$), K_2CO_3, $NaNO_3$, KCl, and ($BaCl_2{\cdot}2H_2O$). The mass transfer between the product and the ambient atmosphere is guaranteed by natural diffusion of the water vapor and the water activity of the product.

2.2. Experimental procedure

These salts were prepared and introduced in six glasses of 1L each with an insulated lid.

About 0.3 ± 0.001 g of the leaves were placed in each glass containing the saturated salt solution. The controlled and irradiated rosemary leaves samples were weighted every two days until they reached a constant weight. The final moisture content of each sample was determined by using drying oven at 105 °C for 24 h, until we get a constant sample mass over time. The difference of mass before (M_h) and after drying (M_s) at 105 °C which gives the product moisture content X_{eq} at hygroscopic equilibrium Eq. (1);

$$\text{EMC} = X_{eq} = \frac{M_h - M_s}{M_s} \tag{1}$$

This procedure was repeated at three different temperatures (30, 40 and 50 °C) in order to obtain the sorption isotherm.

The time required for equilibrium was 12 days for desorption and 14 days for adsorption.

2.3. Mathematical description of sorption isotherms

The experimental sorption curves were studied using four equations: modified Oswin (Oswin, 1946), Enderby (Popovski and Mitrevski, 2004), Peleg (Peleg, 1993) and LESPAM (Idlimam et al., 2008).

$$\text{Modified Oswin:}\quad X_{eq} = (A + (B \times T))\left(\frac{a_w}{1 - a_w}\right)^C \tag{2}$$

$$\text{Enderby}:\quad X_{eq} = \left[\frac{A}{(1 - Ba_w)} + \frac{C}{(1 - Da_w)}\right] a_w \tag{3}$$

$$\text{Peleg}:\quad X_{eq} = A(a_w)^C + B(a_w)^D$$

$$\text{LESPAM}:\quad X_{eq} = A \times \exp\left(\frac{Ba_w}{T}\right) + C$$

The models are presented in terms of moisture content; X_{eq}, dry basis (kg/kg d.b.), water activity a_w, temperature T (°C) and A, B, C, D as model constants.

In order to select the most suitable model for describing the relationship between the equilibrium moisture content, the water activity, and the temperature, two criteria are used; the coefficient of correlation (r) (Leonard and Labuza, 1994) and the statistical parameter mean relative error as a percentage (MRE). The adequate model should present the smallest MRE and the highest coefficient of correlation (Machhour et al., 2008).

Levenberg–Marquardt nonlinear optimization method using appropriate software is used to calculate the model coefficients that describe the equilibrium curves and their statistical parameters: mean relative error (MRE) and the correlation coefficient (r).

Correlation coefficient:

$$r = \sqrt{\frac{\sum_{i=1}^{N}\left(X{eq}_{i,\,pred} - \overline{X{eq}}_{i,exp}\right)^2}{\sum_{i=1}^{N}\left(X{eq}_{i,\,exp} - \overline{X{eq}}_{i,exp}\right)^2}} \tag{6}$$

Mean Relative Error:

$$\text{MRE} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{X{eq}_{i,exp} - X{eq}_{i,pred}}{X{eq}_{i,exp}}\right| \tag{7}$$

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)

It is generally considered that MRE below 10% indicate an adequate fit for practical purposes (Aguerre et al., 1989).