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Mathematical modeling of drying kinetics of *Morchella esculenta* mushroom, Bulgaria

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Drying kinetics of *Morchella esculenta* mushroom slices (2 mm) in a fan oven was studied at air temperatures of 35°C, 45°C and 55°C. Drying of *Morchella esculenta* mushroom slices occurred in two falling rate periods for each of the pointed temperatures. In order to select a suitable drying curve, eleven thin layer-drying models were fitted to the experimental moisture ratio data. All the models were compared using statistical parameters: coefficient of determination (R^2), sum square error (*SSE*), root mean square error (*RMSE*), reduced chi-square (χ^2) and mean bias error (*MBE*). The best one among the mathematical models investigated was resolved describing the drying behaviour of *Morchella esculenta* mushroom slices with high (R^2) values and low *SSE*, *RMSE*, χ^2 values. The effective moisture diffusivity (*Deff*) of *Morchella esculenta* mushroom increased as the drying air temperature increased. The moisture diffusivity in *Morchella esculenta* mushroom was found to increase from 6.17 to 12.98 × 10^{-9} m^2s^{-1} during the initial stage of drying, and from 16.11 to 24.63 × 10^{-9} m^2s^{-1} during the later stage of drying. Activation energy (kJ mol^{-1}) for the moisture diffusivity was 31.26 kJ mol^{-1} during the first period, respectively 17.75 kJ mol^{-1} during the second one, to detach and move the water during the drying process.

Keywords: Moisture diffusivity, Mathematical model, *Morchella esculenta* mushrooms

INTRODUCTION

Mushrooms are highly perishable in nature, with extremely short shelf-life as they contain moisture in the range of 87 to 95 % wet basis (w.b.). Quality deterioration takes place if fresh mushrooms are not immediately processed. Therefore, their processing to the forms of more stable products is important. Long term preservation methods such as canning, pickling and drying are most commonly used methods of preservation of mushrooms to make the product available throughout the year. Drying reduces bulk quantity, thus facilitating transportation, handling and storage. Although sun-drying is economical, mechanical drying speeds up the process, prevents losses, ensures use of safer drying temperatures and produces superior product compared to sun drying. Dehydrated mushrooms are used as an important ingredient in several food formulations including instant soups, pasta salads, snack seasonings, stuffing, casseroles, and meat and rice dishes [1, 2]. The drying kinetics of food is a complex phenomenon and requires simple representations to predict the drying behaviour and to optimise the drying parameters. Thus, layer drying equations were used for drying time prediction and for generalisation of drying curves [3, 4]. Limited research in drying characteristics of mushrooms was carried out and data was reported on moisture loss and drying rates [5].

However, systematic studies on the drying kinetics of *Morchella esculenta* mushrooms are lacking. The objectives of the present study were: *i*) to study the drying kinetics of *Morchella esculenta* mushroom in a fluidized bed dryer, *ii*) to evaluate a suitable thin layer drying model, and *iii*) to determine the moisture diffusivity and activation energy during drying of *Morchella esculenta* mushroom.

EXPERIMENTAL

Samples

Morchella esculenta (L.) Pers. (morel) (Fig. 1) is a well known and extraordinary mushroom species. The head is distinctly conical in shape. The surface of head comprises a honeycomb of sharp ridges and deep pits and is rich brown in colour. The texture is sponge-like. The head and stem is generally hollow. It grows generally on chalky soil in grassy woodlands, field margins ad roadside verges. *Morchella esculenta* is picked up every year if the weather condition is suitable for growth in Bulgaria. It is collected especially in April and May, and marketed in abroad either fresh or dried.

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Fig.1. *Morchella esculenta*

Mushroom samples were collected in 2018 from the Batak Mountain, Bulgaria personally by the authors. Fresh stipe of mushroom were removed, samples were stored at 4°C within 12 h before drying. Prior to dehydration, mushrooms were thoroughly washed to remove the dirt and graded by size (2 mm in diameter) to eliminate the variations in respect to the exposed surface area.

Slices of desired thickness were obtained by carefully cutting mushrooms vertically by using a vegetable slicer and the slices from middle portions of mushroom were used for drying experiments without any pretreatments. Besides, prior to initial moisture contents of the mushroom (*Morchella esculenta*) were determined by AOAC standard (1984) to 89.41 %.

Mathematical modeling

Analysis of process and modeling. The moisture ratio of the samples during drying was expressed by the following equation:

$$MR = \frac{M_t - M_e}{M_o - M_e}, \quad (1)$$

where: MR is the dimensionless moisture ratio, M_t is the moisture content at time t, and M_o and M_e are the initial and equilibrium moisture contents, respectively, on dry basis.

As the M_e is very small compared to M_o and M_t values, the M_e can be neglected and MR can be expressed [6, 7].

$$MR = \frac{M}{M_o} \quad (2)$$

To select a suitable model for describing the drying process of *Morchella esculenta*, drying curves were fitted with eleven thin-layer drying equations (Table 1). Non-linear regression analysis was performed using MATLAB software package. The coefficient of determination R^2 was one of the main criteria for selecting the best equation. In addition to the coefficient of determination, the goodness of fit was determined by other statistical parameters such as sum square error (*SSE*), total sum of squares (*SST*), reduced chi-square (χ^2), mean square error (*MSE*), root mean square error (*RMSE*) and mean bias error (*MBE*). For goodness fitting, R^2 value should be higher and χ^2 and *RMSE* values should be lower [22]. These parameters are calculated as follows:

Table 1. Mathematical models for the drying curves

№	Model name	Model equation	References
1.	Lewis	$MR = \exp(-k \cdot t)$	[8]
2.	Henderson and Pabis	$MR = a \cdot \exp(-k \cdot t)$	[9]
3.	Logarithmic	$MR = a \cdot \exp(-k \cdot t) + c$	[10, 11]
4.	Two-term exponential	$MR = a \cdot \exp(-k_0 \cdot t) + b \cdot \exp(-k_1 \cdot t)$	[12, 13]
5.	Page	$MR = \exp(-k \cdot t^n)$	[14]
6.	Modified Page	$MR = a \cdot \exp(-k \cdot t^n)$	[15]
7.	Wang and Singh	$MR = 1 + a \cdot t + b \cdot t^2$	[16]
8.	Midilli *et al.*	$MR = a \cdot \exp(-k \cdot t^n) + b \cdot t$	[17, 18]
9.	Diffusion approach	$MR = a \cdot \exp(-k \cdot t) + (1-a) \cdot \exp(-k \cdot b \cdot t)$	[19]
10.	Modified Henderson and Pabis	$MR = a \cdot \exp(-k \cdot t) + b \cdot \exp(-g \cdot t) + c \cdot \exp(-h \cdot t)$	[20]
11.	Verma *et al.*	$MR = a \cdot \exp(-k \cdot t) + (1-a) \cdot \exp(-g \cdot t)$	[21]

$$SSE = \sum_{i=1}^{N} \left(MR - MR_{\mathrm{mod}} \right)^2, \quad (3)$$

where MR_{mod} is the predicted moisture ratio.

$$SST = \sum_{i=1}^{N} \left(MR - \overline{MR} \right)^2, \quad (4)$$

where $\overline{MR}$ is the average value of the experimental moisture ratio.

$$R^2 = 1 - \frac{SSE}{SST}, \quad (5)$$

$$R_{adj}^2 = 1 - \frac{N-1}{N-p} \cdot \frac{SSE}{SST}, \quad (6)$$

where N is the number of observations and p is the number of regression coefficients.

$$\chi^2 = \frac{SSE}{N-p} = \frac{\sum_{i=1}^{N} \left(MR - MR_{\mathrm{mod}} \right)^2}{N-p}, \quad (7)$$

$$MSE = \frac{\sum_{i=1}^{N} \left(MR - MR_{\mathrm{mod}} \right)^2}{N}, \quad (8)$$

$$RMSE = \sqrt{MSE} = \sqrt{\frac{\sum_{i=1}^{N} \left(MR - MR_{\mathrm{mod}} \right)^2}{N}}, \quad (9)$$

$$MBE = \frac{\sum_{i=1}^{N} \left(MR_{\mathrm{mod}} - MR \right)}{N} \quad (10)$$

Moisture diffusivity

Fick's diffusion equation for the particles spherical in shape was used for the calculation of effective moisture diffusivity [23]. Since the Canola seeds have spherical geometry, the equation is expressed as:

$$MR = \frac{8}{\pi^2} \cdot \exp\left(\frac{-\pi^2 \cdot Deff \cdot t}{L^2} \right), \quad (11)$$

where $Deff$ is the effective diffusivity in $m^2 s^{-1}$, t is the time of drying in seconds, and L is the slab thickness in metres. Eq. (11) can be further simplified to only the first term of the series and expressed in a logarithmic form for long drying periods:

$$\ln(MR) = \ln\left(\frac{8}{\pi^2} \right) - \left(\frac{\pi^2 \cdot Deff}{L^2} \right) \cdot t \quad (12)$$

The effective moisture diffusivity was calculated from the slope (K) of a straight line, plotting experimental drying data in terms of ln(MR) versus time according to Eq. (12) [24].

$$K = \frac{\pi^2 \cdot Deff}{L^2} \quad (13)$$

Then,

$$Deff = \frac{K \cdot L^2}{\pi^2} \quad (14)$$

The relationship between effective moisture diffusivity and air temperature is assumed to be an Arrhenius-type equation [20, 24]:

$$Deff = D_0 \cdot \exp\left(\frac{E_a}{R \cdot (T + 273.15)} \right) \quad (15)$$

Here D_0 is the pre-exponential factor ($m^2 s^{-1}$), E_a is the activation energy ($kJ\ mol^{-1}$), R is the universal gas constant (8.314×10^{-3} $kJ\ mol^{-1} K^{-1}$), and T is temperature (°C). The equation can be linearized by taking natural logarithm on both sides:

$$\ln\left(Deff \right) = \ln\left(D_0 \right) \cdot \left(-\frac{E_a}{R} \right) \cdot \left(\frac{1}{T + 273.15} \right) \quad (16)$$

RESULTS AND DISCUSSION

The time taken for drying of mushroom slices at different temperatures is given in Table 2. The final moisture content of mushroom slices ranged from 1 to 2 % (w.b.). It is evident that drying air temperature has an important effect on drying. When the temperature was increased, the drying time reduced. The results are similar with the earlier observations on drying of garlic slices, onion slices, egg plants, peach slices [25] and plum slices [22].

Table 2. Drying time of *Morchella esculenta* mushroom.

Drying temperature (°C)	Drying time (min)
35	170
45	150
55	120

The changes in the moisture content of mushroom slices with drying time for 35°C, 45°C and 55°C air temperatures are given in Fig. 2 and Fig. 3. As seen from the figures, the moisture content decreases continuously with the drying time. Drying of mushroom slices takes about 2 - 3 h in the dryer. As seen from Fig. 2 and Fig. 3, one of the main factors influencing the drying kinetics of the mushroom slices is the air temperature. An increase in air temperature results in a decrease in drying time.

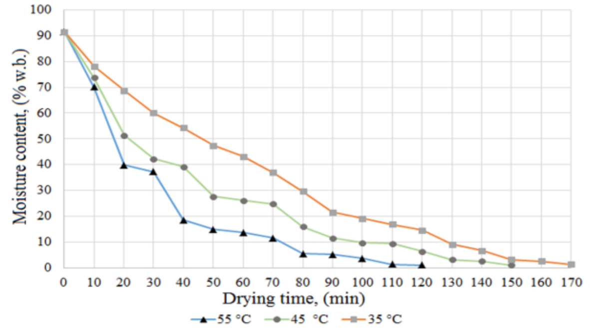

Fig. 2. Variation of moisture content with drying time during for *Morchella esculenta* mushroom.

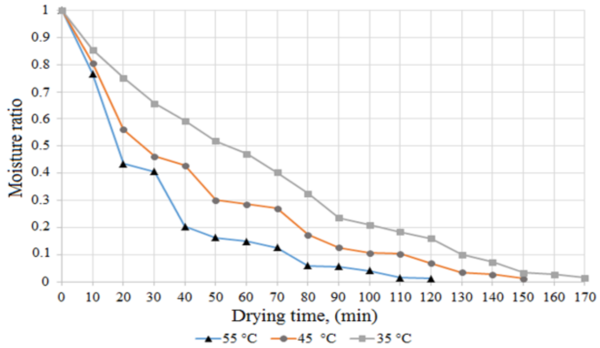

Fig. 3. Moisture ratio with drying time for *Morchella esculenta* mushroom.

The average moisture ratio of *Morchella esculenta* mushroom dried at different temperatures was test verified with eleven different drying models to find out their suitability to describe the drying process. The correlation coefficient and results of statistical analyses obtained from nonlinear regression analysis using MATLAB are summarized in Table 3. The best model to describe the drying behaviour of *Morchella esculenta* mushroom was selected on the basis of high R^2 and low reduced χ^2. *MBE* and *RMSE* values must be low too. It is observed from Table 3 that for 35°C the best model is Logarithmic model (Model 3, Table 1), for 45°C the best model is Midilli et al. model (Model 8, Table 1) and for 55°C the best models with the same R^2 are Midilli et al. and Verma et al. models (Model 8 and Model 11, Table 1). They gave comparatively the higher R^2 values of in all the drying temperatures, where as the χ^2, *MBE* and *RMSE* values were also found to be the lowest.

Since the models are different number of coefficients is correct to look for models with maximum adjusted R^2 and minimal reduced χ^2. For 35°C the best model - Logarithmic model is confirmed, for 45°C is also confirmed Midilli et al. model, and for 55°C most appropriate is Lewis model. In case we want to use one model for the three temperatures, then a good option would be Midilli *et al*. Model. The effective moisture diffusivity, *Deff* was calculated using the method of slopes (Eq. (12)). Figures 4, 5 and 6 depict the relationship between ln(*MR*) and drying time for *Morchella esculenta* mushroom dried at different temperatures.

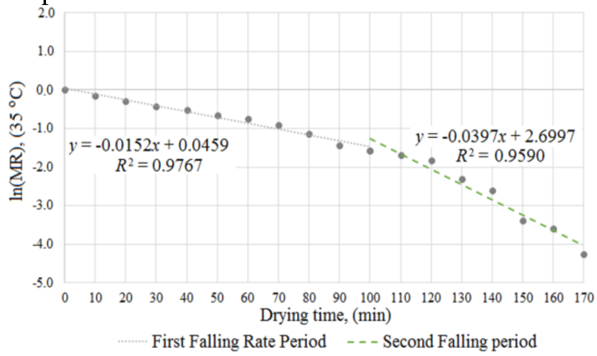

Fig. 4. Relationship between ln(*MR*) and drying time for *Morchella esculenta* mushroom dried at 35°C

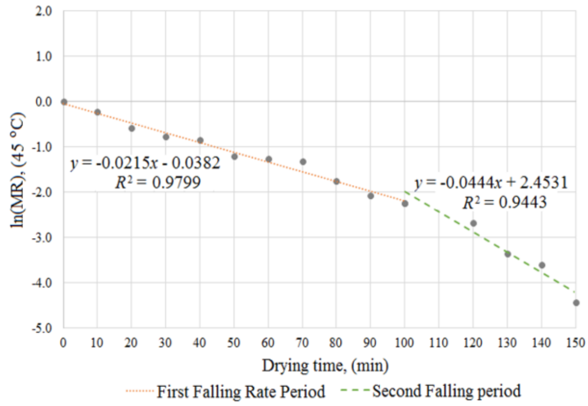

Fig. 5. Relationship between ln(*MR*) and drying time for *Morchella esculenta* mushroom dried at 45°C.

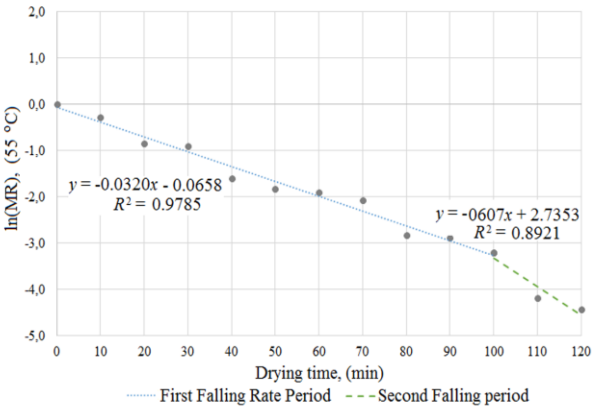

Fig. 6. Relationship between ln(*MR*) and drying time for *Morchella esculenta* mushroom dried at 55°C

From these figures, using the slope of the best fit linear equations, the moisture diffusivity values were calculated using Eq. (11) and Eq. (12).

The best-fit regression equations for different temperatures during initial and later stages of drying with coefficient of correlation and effective moisture diffusivity *Deff* are given in Table 4.

Table 3. Statistical results of 11 mathematical models for the ID hot-air drying model.

№	Temperature	Constants				*SSE*	R^2	R^2 *adj.*	χ^2	*RMSE*	*MBE*
	35 °C	k = 0.01495				0.0305	0.9807	0.9807	0.0018	0.0412	0.0056
1.	45 °C	k = 0.02270				0.0151	0.9880	0.9880	0.0010	0.0307	0.0016
	55 °C	k = 0.03434				0.0152	0.9868	**0.9868**	0.0013	0.0341	-0.0024
	35 °C	k = 0.0154	a = 1.0298			0.0286	0.9820	0.9808	0.0018	0.0399	0.0085
2.	45 °C	k = 0.0222	a = 0.9788			0.0144	0.9886	0.9878	0.0010	0.0300	0.0004
	55 °C	k = 0.0347	a = 1.0107			0.0150	0.9870	0.9858	0.0014	0.0340	-0.0017
	35 °C	k = 0.0099	a = 1.2083	c = -0.2256		0.0048	**0.9970**	**0.9966**	0.0003	0.0163	0.0000
3.	45 °C	k = 0.0220	a = 0.9808	c = -0.0035		0.0143	0.9886	0.9869	0.0011	0.0299	0.0000
	55 °C	k = 0.0306	a = 1.0319	c = -0.0393		0.0202	0.9824	0.9789	0.0020	0.0394	-0.0078
	35 °C	k_0 = 0.0158	k_1 = 4.1527	a = 1.0553	b = -0.0553	0.0269	0.9830	0.9794	0.0019	0.0387	0.0077
4.	45 °C	k_0 = 0.0215	k_1 = 4.1527	a = 0.9480	b = 0.0520	0.0133	0.9895	0.9869	0.0011	0.0288	0.0017
	55 °C	k_0 = 0.0352	k_1 = 4.1527	a = 0.8435	b = 0.1629	0.0495	0.9569	0.9426	0.0055	0.0617	-0.0352
	35 °C	k = 0.0066			n = 1.1881	0.0165	0.9896	0.9889	0.0010	0.0303	0.0076
5.	45 °C	k = 0.0301			n = 0.9295	0.0130	0.9897	0.9890	0.0009	0.0285	0.0025
	55 °C	k = 0.0333			n = 1.0082	0.0151	0.9868	0.9856	0.0014	0.0341	-0.0026

№	Temperature	Constants						*SSE*	R^2	R^2 *adj.*	χ^2	*RMSE*	*MBE*
	35 °C	*k* = 0.0041	*a* = 0.9532		*n* = 1.2869			0.0138	0.9913	0.9902	0.0009	0.0277	0.0037
6.	45 °C	*k* = 0.0301	*a* = 1.0001		*n* = 0.9293			0.0130	0.9897	0.9882	0.0010	0.0285	0.0025
	55 °C	*k* = 0.0351	*a* = 1.0113		*n* = 0.9970			0.0150	0.9870	0.9843	0.0015	0.0340	-0.0016
	35 °C		*a* = -0.0110	*b* = 0.00003				0.0087	0.9945	0.9942	0.0005	0.0219	0.0049
7.	45 °C		*a* = -0.0160	*b* = 0.0001				0.0619	0.9510	0.9475	0.0044	0.0622	0.0140
	55 °C		*a* = -0.024	*b* = 0.0001				0.0669	0.9419	0.9366	0.0061	0.0717	0.0131
	35 °C	*k* = 0.0128	*a* = 0.9895	*b* = -0.0009	*n* = 0.9744			0.0049	**0.9969**	**0.9963**	0.0003	0.0165	0.0000
8.	45 °C	*k* = 0.0422	*a* = 1.0085	*b* = -0.0004	*n* = 0.8229			0.0101	**0.9920**	**0.9900**	0.0008	0.0251	-0.0001
	55 °C	*k* = 0.0323	*a* = 1.0099	*b* = 0.0001	*n* = 1.0247			0.0148	**0.9871**	**0.9828**	0.0016	0.0337	-0.0004
	35 °C	*k* = 0.0273	*a* = -2.1783	*b* = 0.8058				0.0152	0.9904	0.9891	0.0010	0.0291	0.0065
9.	45 °C	*k* = 0.1885	*a* = 0.0681	*b* = 0.1117				0.0127	0.9900	0.9884	0.0010	0.0281	0.0032
	55 °C	*k* = 0.0694	*a* = 0.0133	*b* = 0.4909				0.0152	0.9868	0.9842	0.0015	0.0341	-0.0021
	35 °C	*k* = -2.0268	*a* = 0.0497	*b* = 0.0496	*g* = -2.0268			0.1338	0.9156	0.8804	0.0111	0.0862	0.0143
10.	45 °C	*k* = -2.0894	*a* = 0.0453	*g* = -2.0894	*b* = 0.0453	*h* = -2.0894	*c* = 0.0453	0.1161	0.9080	0.8620	0.0116	0.0852	0.0142
	55 °C	*k* = -2.2169	*a* = 0.0393	*g* = -2.2169	*b* = 0.0393	*h* = -2.2169	*c* = 0.0393	0.0952	0.9172	0.8581	0.0136	0.0856	0.0159
	35 °C	*k* = 0.0158	*a* = 1.0553	*g* = 1.5367				0.0269	0.9830	0.9807	0.0018	0.0387	0.0077
11.	45 °C	*k* = 0.0215	*a* = 0.9480	*g* = 1.5367				0.0133	0.9895	0.9879	0.0010	0.0288	0.0017
	55 °C	*k* = 0.0346	*a* = 1.0161	*g* = 1.5367				0.0148	**0.9871**	0.9845	0.0015	0.0338	-0.0010

Table 4. Moisture diffusivity equations, coefficient of correlation and effective moisture diffusivity *Deff* (m^2s^{-1}) at different temperatures for drying of *Morchella esculenta* mushroom

Drying temperature, (°C)	First falling rate of drying			Second falling rate of drying		
	Equation	R^2	*Deff* (m^2s^{-1}), $\times 10^{-9}$	Equation	R^2	Deff (m^2s^{-1}), $\times 10^{-9}$
35	$y = -0.0152x + 0.0459$	0.9767	6.17	$y = -0.0397x + 2.6997$	0.9590	16.11
45	$y = -0.0215x - 0.0382$	0.9799	8.72	$y = -0.0444x + 2.4531$	0.9443	18.01
55	$y = -0.0320x - 0.0658$	0.9785	12.98	$y = -0.0607x + 2.7353$	0.8921	24.63

Effective moisture diffusivity of *Morchella esculenta* mushroom ranged from 6.17 to 12.98 × 10^{-9} m^2s^{-1} and 16.11 to 24.63 × 10^{-9} m^2s^{-1} during the first falling rate period and second falling rate period, respectively (Table 4). These values are within the general range of 10^{-9} – 10^{-11} m^2s^{-1} for drying of food materials [26]. The drying temperature greatly affected the *Deff* values of *Morchella esculenta* mushroom. It is observed from the Table 4 and Fig. 7 that the moisture diffusivity increased as drying air temperature was increased.

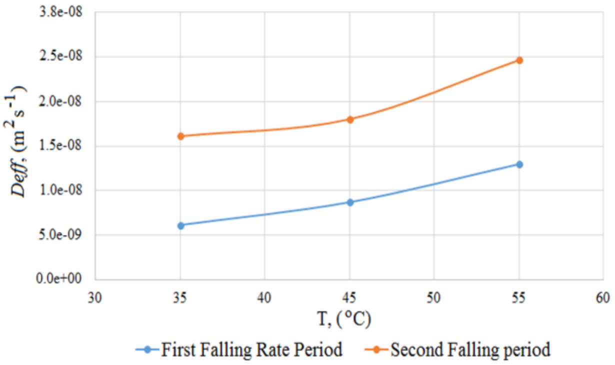

Fig. 7. Relationship between effective moisture diffusivity *Deff* (m^2s^{-1}) at different temperatures (°C) for drying of *Morchella esculenta* mushroom.

A similar result of the influence of drying temperature on moisture diffusivity during air drying has been found in apricots [21], peach [25] and plums [22].

The activation energy used to detach and remove water molecules during drying was calculated for *Morchella esculenta* mushroom using the Arrhenius expression between effective moisture diffusivity and absolute temperature.

A plot of ln(*Deff*) as a function of $1/(T + 273.15)$ is produced a straight line with a slope equal to ($-E_a/R$), so E_a can be easily estimated (Fig. 8) [20, 24].

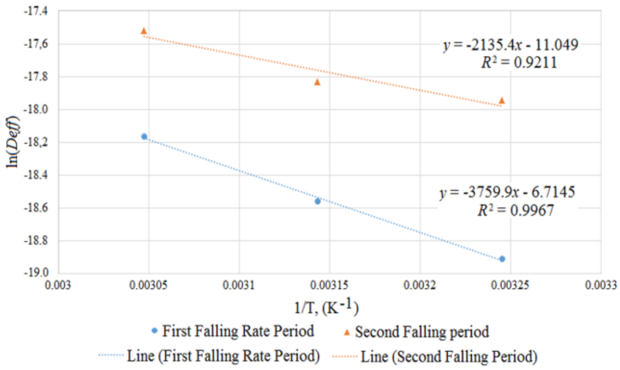

Fig. 8. Relationship between ln(*Deff*) and reciprocal temperatures (1/*T*) in *K* for drying of *Morchella esculenta* mushroom.

Activation energy for the moisture diffusivity was 31.26 kJ mol^{-1} during the first period, respectively 17.75 kJ mol^{-1} during the second one, to detach and remove the water during the drying process. The values of activation energy lie within the general range of 12.7 - 110 kJ mol^{-1} for food materials [27].

CONCLUSIONS

1. Increase in drying air temperature decreased the drying time.
2. The best model for 35°C is the logarithmic model; for 45°C the best model is Midilli *et al.* model; for 55°C the best model is Lewis drying model which showed a better fit with the highest adjusted correlation coefficient and low reduced χ^2 values during the drying behaviour of *Morchella esculenta* mushroom.
3. The effective moisture diffusivity ranged from 6.17 to 24.63 × 10^{-9} m^2s^{-1}, with higher values for high temperature-dried samples.
4. The values of the activation energy lie within the general range of 12.7 - 110 kJ mol^{-1}.

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