Examination of the Effect of Spirulina platensis Microalgae on Drying Kinetics and the Color Change of Kiwifruit Pastille

Esmail Khazaiy Pool
Dept. of food science and technology
Ferdowsi University of Mashhad
Mashhad, Iran
EsmailKhazaiy66@yahoo.com

Fakhri Shahidi
Dept. of food science and technology
Ferdowsi University of Mashhad
Mashhad, Iran
fshahidi@um.ac.ir

Sayed Ali Mortazavi
Dept. of food science and technology
Ferdowsi University of Mashhad
Mashhad, Iran
S.A.Mortazavi@um.ac.ir

Mohebbat Mohebbi
Dept. of food science and technology
Ferdowsi University of Mashhad
Mashhad, Iran
Mohebbatm@gmail.com

Mehran Azizpour
Dept. of food science and technology
Ferdowsi University of Mashhad
Mashhad, Iran
Mehranazizpour@gmail.com

***Abstract*- In this study, the effects of various concentrations of Spirulina platensis microalgae were investigated on drying kinetics and the color of kiwi pastille. Spirulina platensis was applied to the samples at three concentrations of 0, 0.5 and 1% and the samples were dried at 70, 80 and 90°C. Eight models of the entire drying thin layer models were fitted into the moisture ratios obtained during experiments. Coefficient of determination (R^2), Chi-square (X^2) and Root Mean Squared Error (RMSE) were used in order to choose the superlative model. Different concentrations of Spirulina platensis had no effect on drying process. As time increased, a* showed ascending trends whereas L* showed descending trend and these color changes were relatively more intensive at high temperatures. Among the fitted mathematical models, the Midlli was selected as the best one with R^2 of 0.9942.**

Keywords- color parameter, drying kinetics, modeling, kiwi pastille, Spirulina platensis

I. INTRODUCTION

Kiwifruit (Actinidia sp.) has many appealing consumer traits including flavor, color and nutritional content, especially vitamin C [1]. Consumption of kiwifruit offers health benefits including alleviating constipation and improving stool transit time and/or bulking because of constituents such as vitamin C, PPs, carotenoids and fiber polysaccharides Dietary intake of vitamin C is essential for humans because humans cannot synthesize vitamin C [2]. It is characterized by a high content of benefit substances for human health such as vitamins, minerals, polyphenols. Furthermore, it is low fat and contains no cholesterol [3]. Among different substances contained in the kiwifruit a primary role, in the safeguard of the human health, is carried out by some bioactive compounds such as ascorbic, folic, citric and glutamic acids. kiwi seems to be used as one of the major ingredients within the formulation of this category of foods.

Microalgae are nutritional and innovative natural sources that can be used in the development of novel foods. Biological active compounds occur naturally within microalgae cells and are able to resist severe technological conditions in processes [4]. Among the known species of algae, Chlorella Vulgaris and Spirulina platensis are common edible microalgae which have no side effects. The amino acid, carbohydrate and fatty acid profiles of these microalgae are very similar to those of other food materials [5]. Spirulina is a multicellular filamentous blue-green microalgae [6] which was introduced as GRAS after being approved by Food and Drug Administration (FDA) [7]. The value of Spirulina is for its easy digestion caused by the absence of cellulose in the cell wall [8]. Its nucleic acid content is less than 5% that it is less than other microalgae such as chlorella and scenedesmus [9]. Spirulina contains all the essential amino acids and has a high biological value [8, 9 and 10]. Commercial production of microalgae for human nutrition is currently a reality throughout the world. Numerous preparations of microalgae or mixtures with other functional foods could be found in the market in the form of tablets, powders, capsules, pastilles and liquids, as nutritional supplements. They can also be incorporated into common food preparations such as pastas, biscuits, bread, snacks, candies, yoghurts, soft drinks, causing health promotion that are associated with microalgae biomass[11]. The viability of incorporated microalgae biomass in food systems is conditioned by the applied processing type and intensity (e.g. thermal, mechanical), the nature of the food matrix (e.g. emulsion, gel, aerated dough systems) and the interactions with other compounds (e.g. proteins, polysaccharides, lipids, sugars, salts). In addition to coloring and nutritional purposes, introducing microalgae into food formulations can also impart remarkable alterations in the food microstructure and rheological properties [12].

Mathematical modeling of drying is important for optimization of operating parameters and performance improvements of the drying systems. The main advantage of empirical or semi-empirical models in drying simulations is easy to apply [13]. The aim of this research was (1) analysis of the influence of temperature and Spirulina platensis microalgae on the drying kinetic of the Kiwi pastille (2) Examination of the Effect of Spirulina platensis microalgae on Kinetics Color of Kiwi Pastille (3) the study and the modeling of the mass transfer during the hot-air drying process (4) calculating effective diffusivities and activation energy in the drying process.

II. MATERIALS AND METHODS

A. Materials

The materials include kiwi puree, microalgae powder of Spirulina platensis, hydrocolloids (agar and guar), sorbitol, sugar, powdered sugar and citric acid. To create kiwi puree, kiwifruit (Hayward variety) was used. The microalgae powder of Spirulina platensis was purchased from microalgae Sina Company located in Gheshm. Kiwifruit were prepared from orchards in northern Iran. Guar was purchased from Sigma Chemical Company, sorbitol, citric acid and sugar was purchased from Merk Chemical Company, Germany and Agar was purchased from Qulab Chemical Company, Canada.

B. Preparation of Samples

Components of formulation contain 65% w/w kiwi puree, 30% w/w sweeteners (sugar, powdered sugar and sorbitol, 0.25% w/w agar, 0.5% w/w guar, Spirulina platensis at three levels (0, 0.25 and 1% w/w), as well.

To produce fruit pastille based on kiwi puree, the kiwis are fist washed up, skinned and then cut into pieces. Then these pieces are poured into the chopper and were crushed. The prepared puree was mixed into microalgae powder of Spirulina platensis, hydrocolloids and regarded sweeteners (applying 70 °C temperature) with specific ratio. Agar was created as a soluble form in distilled water at 90 °C and then was added to the concerned mixture [14]. After measure pH (pH meter of Hana model made in Portugal) and moderating to PH = 4.3 by adding acid citric in 40 % concentration and controlling the Brix degree (by optical refract meter of Carlze model) to constant Brix of 45, the mixture was prepared. Then the prepared mixture was poured into a network framework of steel origin in the cavities with 1.2×2×1/2 and the molds were hold in the refrigerator for 2 hours with 4 °C to fasten the gel.

Table1. Agar and Guar content in formula.

Formula no	1	2	3
Spirulina platensis	0.25	0.5	1

C. Drying procedure

The obtained gel was taken out of the mold cavities and placed in a glass plate. The samples were then dried at 70, 80 and 90° C in a hot air drier with airflow rate of 1.5 m/s for 6 hours. The samples were evicted every 30 minutes and their weight reduction was measured by a digital balance with accuracy of ± 0.01 g.

D. Mathematical modeling of drying curves

The obtained moisture content was changed into moisture ratio using Eq. (1) and with eight thin layer drying models were fitted by Matlab Software.

$$MR = \frac{M_d - M_e}{M_0 - M_e} \qquad (1)$$

In these models, the moisture ratio (MR) was simplified to M/M_0 instead of the $(M-M_e)/(M_0-M_e)$ as the value of M_e is relatively small compared to M or M_0 [15]. Where M is the moisture content at any time, M_0 is the initial moisture content and M_e is the equilibrium moisture content.

The acceptability of models was determined by the coefficient of determination R^2, sum of squared error (SSE) and root mean square error (RMSE) [16]. The model is said to be good if R^2 value is high, SSE and RMSE values are low.

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}(MR_{pre,i} - MR_{exp,i})^2\right]^{1/2} \qquad (2)$$

$$SSE = \frac{\sum_j^n (MR_{Pre,i} - MR_{Exp,i})^2}{N} \qquad (3)$$

E. Determination of effective moisture diffusivity and activation energy

The experimental drying data for the determination of moisture diffusivity were interpreted by Fick's second law of diffusion. The solution of this equation developed by Crank [17], and the form of Eq. (4) can be applicable for particles with slab geometry by assuming uniform initial moisture distribution:

$$MR = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\frac{(2n+1)^2\pi^2 D_{eff} t}{4L^2}\right] \qquad (4)$$

Where, D_{eff} is the effective diffusivity (m^2/s); L is the half thickness of slab (m). The linear solution of the equation is obtained by using a simple approach that assumes that only the first term in the series equation is significant [18]. Then, Eq. (5) is obtained by taking the natural logarithm of both sides. It shows that the time to reach given moisture content will be directly proportional to the square of the half-thickness and inversely proportional to D_{eff}

$$LnMR = Ln\frac{8}{\pi^2} - \frac{\pi^2 D_{eff} t}{4L^2} \qquad (5)$$

Table 2. Thin-layer drying models

Model number	Model name	model
1	**Newton**	$MR = \exp(-kt)$
2	**Page**	$MR = \exp(-kt^n)$
3	**Henderson & Pabis**	$MR = a\exp(-kt)$
4	**Two-term**	$MR = 1 + at + bt^2$
5	**Logarithmic**	$MR = a\exp(-kt) + c$
6	**Midilli**	$MR = a\exp(-kt^n) + bt$
7	**Verma**	$MR = a\exp(-bt) + c\exp(-dt)$
8	**Wang and Singh**	$MR = a\exp(-kt) + (1-a)\exp(-gt)$

Diffusivities are typically determined by plotting experimental drying data in terms of ln (MR) versus time in Eq. (5), and the plot gives a straight line with a slope of

$$k_0 = \frac{\pi^2 D_{eff}}{4L^2} \quad (6)$$

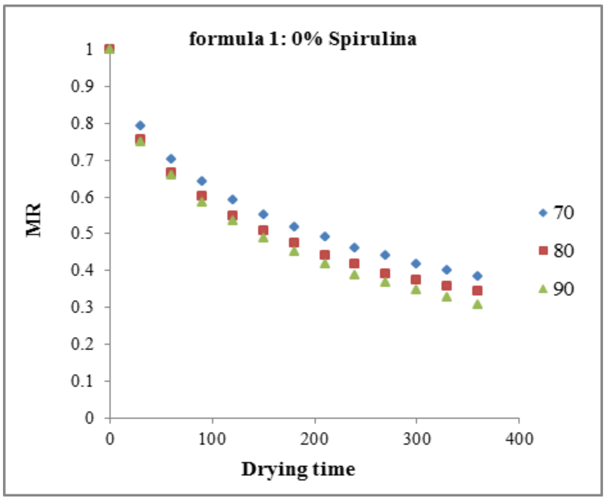
The dependence of the diffusion coefficient (D_{eff}) with the temperature can often be described by an Arrhenius-type equation (Eq. 7); from which the activation energy (Ea kJ/mol) and Arrhenius factor (Do m^2/s) can be determined by preparing a graph of ln D_{eff} against 1/T [19].

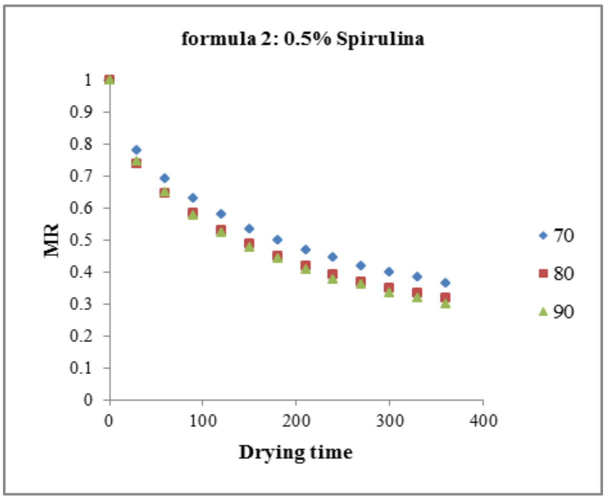
$$D_{eff} = D_0 \exp\left(-\frac{E_A}{RT}\right) \quad (7)$$

III. RESULTS AND DISCUSSION

A. Influence of air temperature

The kiwifruit pastille was dried at 70, 80 and 90°C in the cabinet dryer as thin-layer with thickness of about 10 mm. The moisture ratios versus drying time for samples at the selected temperatures are shown in Fig. 1. The moisture loss rate of kiwifruit pastille was faster at the beginning than that at the end.





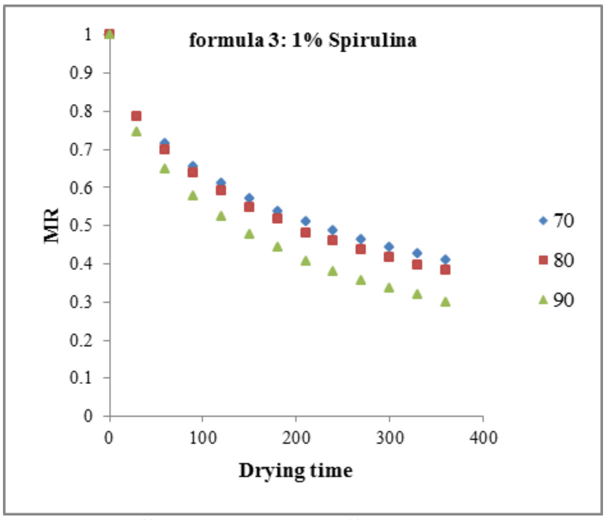


Figure 1. Different air temperature effect on the drying curves.

B. Effects of different concentrations of Spirulina on color parameters

Results obtained from image processing taken from kiwifruit pastille samples showed that color parameters (a*, L* and b*) have descending trend with the increase of Spirulina platensis concentration in the formulation. Rate of color parameters is reduced by increasing Spirulina platensis, in that the results indicate that the effects of Spirulina platensis cause reducing red color and increasing green color in kiwifruit pastille. Gouveia et.al (2008) reviewed the effects of microalgae of Spirulina and Diacronema at the level of 0.75% over jelly products. Their results showed that adding both microalgae is led to the reduction of color parameters a in the product. They have also stated that Spirulina-contained jellies with less than a* and b* values near zero was more attractive and Spirulina pigments showed high resistance in high temperatures [20]. Color parameter b* has a descending trend by adding Spirulina. Yellow and brown Spirulina caused by millard reaction covers completely kiwifruit pastille sample and changes the product's color to blue color. Fradique et.al (2010) showed that the color parameter b* has a descending trend by increasing the percentage of each Spirulina platensis and Chlorella microalgae in spaghetti formulation [21]. The rate of samples' transparency is reduced by increasing Spirulina which is itself a factor in reducing parameter L* in kiwifruit pastille. Results of the study obtained by Gouveia et.al (2007a) showed that adding microalgae Chlorella vulgaris increases biscuit color intensity and the samples' color remained largely stable during storage time. Also, rate of color parameters a*, L* and b* has a descending trend with the increase of microalgae percentage in the samples [22].

D. Changes of color parameter during the drying period

Results of image processing during drying showed that parameter b* had no specific trend by increasing the drying time, but color parameter L* has descending trend and color parameter a* has ascending trend. Reducing color parameter L* is due to the dark color of pastille resulted from millard reaction between the protein section of Spirulina platensis and current sugars in the kiwi pastille formulation. On the other hand, increasing parameter a* shows the reduction of green color in the samples. This ascending trend in parameter is caused by phycocyanin pigment of Spirulina platensis influenced from drying heat. Phycocyanin is a green-blue pigment that has protein phycobili structure. As is indicated in the diagram (Fig 2, 3 and 4), changes intensity of L* and a* in the samples without Spirulina (Formula 1) is higher than the other samples, which this result is probably due to heat sensitivity of kiwifruit pigments, especially chlorophyll. However, changes in parameters L* and a* in Spirulina platensis samples are lower which somewhat indicates thermal stability of most Spirulina pigments than kiwi ones. Fig. 5, regarding the effects of different temperatures of image processing, indicates that L* and a* parameters' changes in the temperature 80 is more than 70 and 90 temperatures. In particular, the intensity of color's change in Formula one is obvious. Results achieved from the studies conducted by Gouveia et.al (2008) showed that the degradation rate of color pigments of jelly products contains Spirulina at 80 temperatures is more than that of 75 and 85 temperatures. They have also indicated that Spirulina pigments in high temperatures showed high resistance and Spirulina-contained gels with a* and b values lower than and near to zero has more attractions than Diacronema- contained gel [23].

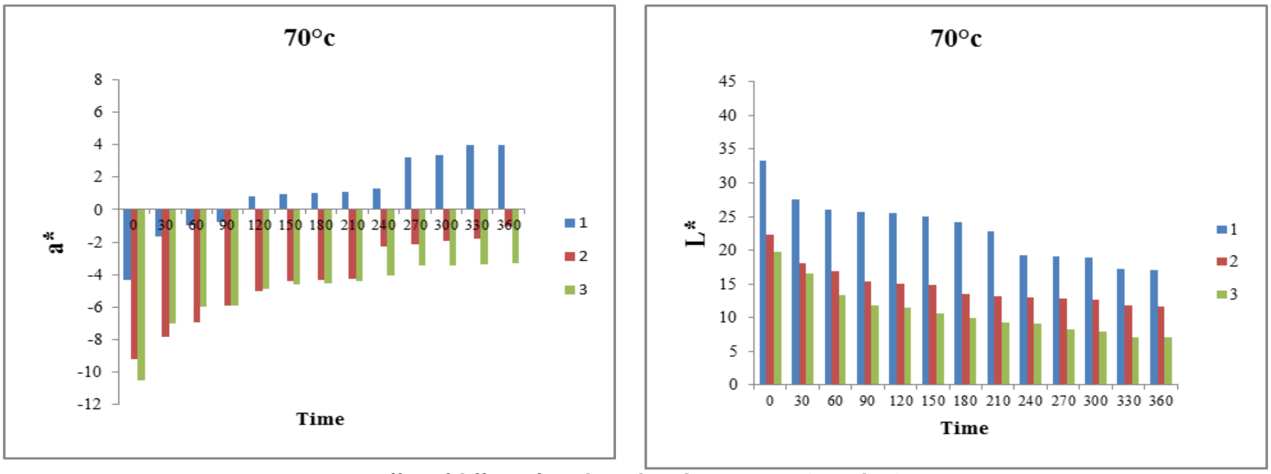


Figure 2. Effect of different formula on the color parameter (a* and L*) at 70°C.

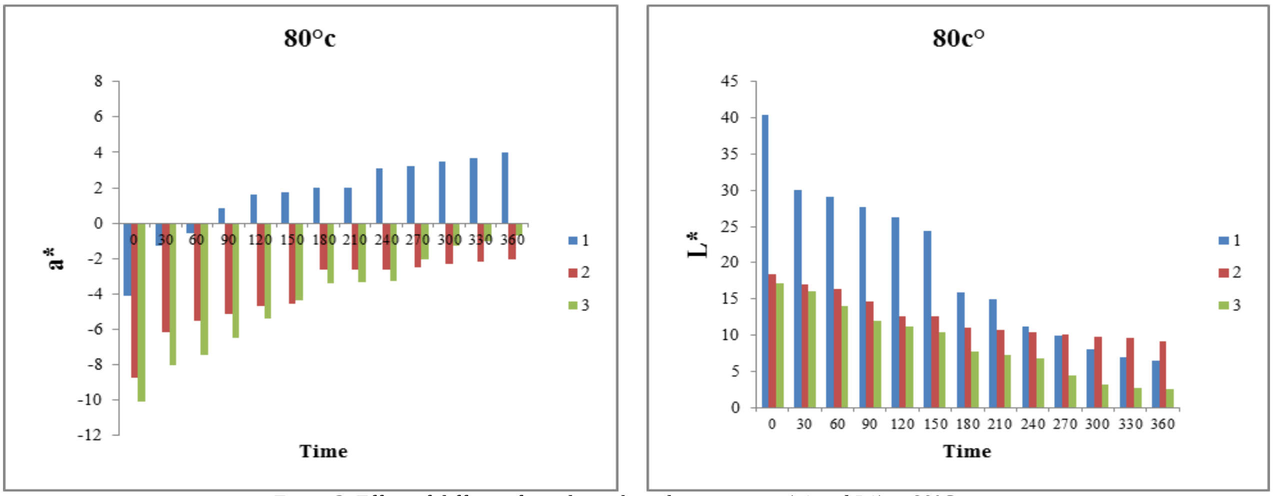


Figure 3. Effect of different formula on the color parameter (a* and L*) at 80°C.

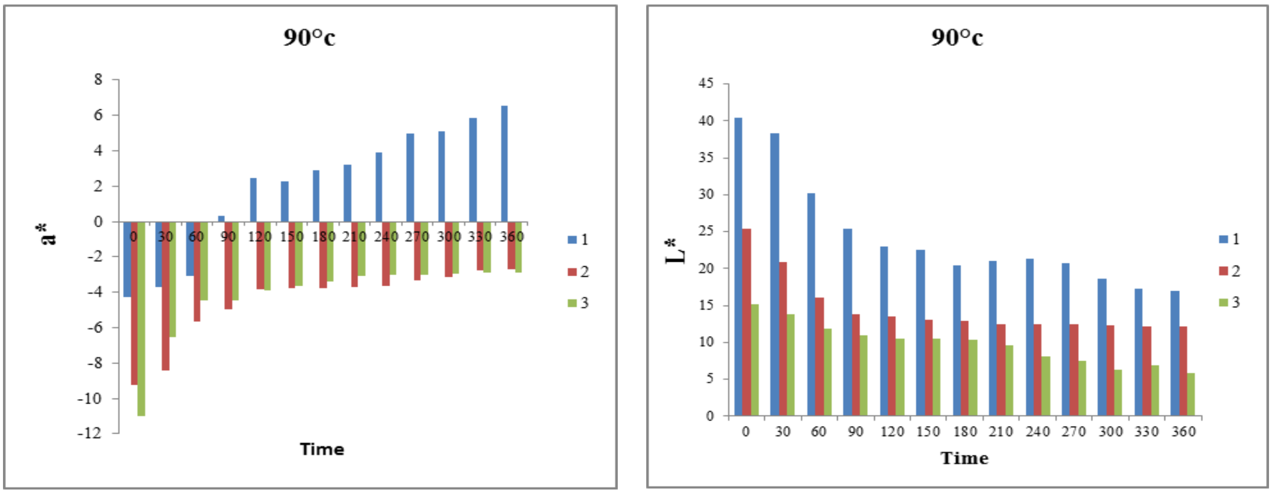


Figure 4. Effect of different formula on the color parameter (a* and L*) at 90°

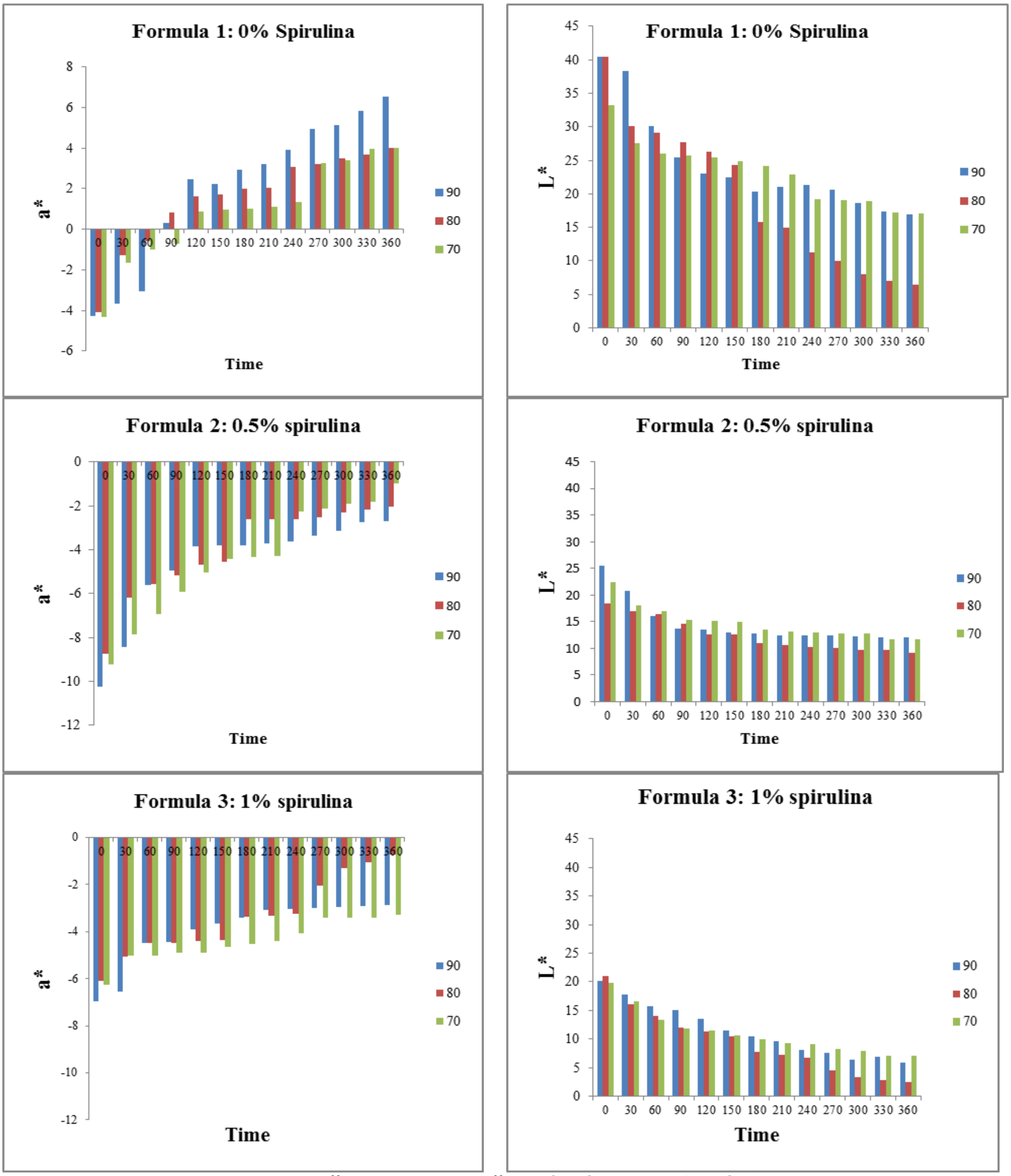


Figure 5. Different air temperature effect on the color parameter (a* and L*).

D. Modeling of drying curves

Tables 3 show the values of R^2, SSE and RMSE. These models were estimated by using the ratio of MR. Table 3 shows that R^2, SSE and RMSE varied in the range of 0.9942-1, 1.547×10^{-5}- 2.856×10^{-3} and 0.001311- 0.002369, respectively. Our results showed that the Midilli model has a good agreement with the experimental data and gave the best results for all drying temperature and formulation. According to R^2 close to one and lower SSE and RMSE, the Midilli model was selected to represent the thin layer drying behavior of Kiwifruit pastille. When the Midilli model analyzed according to the different drying air temperature and formulation, individual constants could be obtained (Table 4).

Table 3. Statistical results of eight models at different drying conditions

Model name	Formula	Drying air temperature								
		70			80			90		
		R^2	SSE	RMSE	R^2	SSE	RMSE	R^2	SSE	RMSE
Newton	1	0.8396	0.06231	0.07142	0.8118	0.06455	0.07334	0.856	0.0684	0.0755
	2	0.8459	0.06231	0.07206	0.9811	0.009236	0.02774	0.8527	0.07128	0.07707
	3	0.8344	0.06329	0.07263	0.8118	0.06455	0.07334	0.8558	0.07029	0.07653
Page	1	0.9999	5.249×10^{-5}	0.002184	0.9998	8.522×10^{-5}	0.002783	0.9999	6.794×10^{-5}	0.002485
	2	0.9998	6.266×10^{-5}	0.002387	0.9812	0.009181	0.02889	0.9999	6.65×10^{-5}	0.002459
	3	0.9999	4.93×10^{-5}	0.002117	0.9998	5.282×10^{-5}	0.002191	0.9298	6.64×10^{-5}	0.002506
Henderson and Pabis	1	0.9263	0.02811	0.05055	0.9148	0.0364	0.05753	0.9284	0.003488	0.05631
	2	0.928	0.0291	0.05144	0.9823	0.008632	0.02801	0.9988	0.0005659	0.007929
	3	0.9243	0.02895	0.0513	0.9174	0.02832	0.05074	0.9904	0.004657	0.02275
Two-terms	1	0.9886	0.004348	0.02198	0.9888	0.00479	0.02307	0.9854	0.006921	0.02631
	2	0.9988	0.0004707	0.007232	0.9831	0.00823	0.03024	0.986	0.006796	0.02607
	3	0.9891	0.004185	0.02156	0.9897	0.003518	0.01977	0.9861	0.00675	0.02598
Logarithmic	1	0.9873	0.004856	0.02204	0.9847	0.006543	0.02558	0.9218	0.03784	0.05865
	2	0.9876	0.005011	0.02238	0.9893	0.00523	0.02287	0.9233	0.03737	0.05829
	3	0.9864	0.005199	0.0228	0.984	0.005501	0.02345	0.9999	4.896e-005	0.002332
vang& sing	1	0.9343	0.02506	0.04773	0.9173	0.03533	0.05668	0.9999	4.667e-005	0.002277
	2	0.9348	0.02637	0.04896	0.9859	0.006874	0.025	0.9914	0.004105	0.02026
	3	0.9313	0.02627	0.04886	0.9256	0.0255	0.04814	0.9904	0.004657	0.02158
*midili	1	1	1.547×10^{-5}	0.001311	0.9999	4.081×10^{-5}	0.002129	0.9999	4.896×10^{-5}	0.002332
	2	1	1.695×10^{-5}	0.001372	0.9942	0.002856	0.01781	0.9999	4.766×10^{-5}	0.002301
	3	0.9999	2.558×10^{-5}	0.001686	0.9999	5.051×10^{-5}	0.002369	0.9999	4.667×10^{-5}	0.002277
verma	1	0.9886	0.004348	0.02085	0.9888	0.00479	0.02189	0.9999	6.794×10^{-5}	0.002485
	2	0.989	0.004446	0.02109	0.9813	0.00914	0.03023	0.9999	6.65×10^{-5}	0.002459
	3	0.9891	0.004185	0.02046	0.9897	0.003518	0.01876	0.9298	0.03335	0.05506

Table 4. Statistical results of Midilli et al. model and its constants and coefficients at different drying conditions

Drying air temperature (°C)	Formula	a	b	k	n	R^2	SSE	RMSE
70	1	1	7.177×10^{-5}	0.03202	0.5893	1	1.547×10^{-5}	0.001311
	2	0.9999	7.688×10^{-5}	0.03233	0.5966	1	1.695×10^{-5}	0.001372
	3	0.9999	5.755×10^{-5}	0.03381	0.5788	0.9999	2.558×10^{-5}	0.001686
80	1	0.9997	7.01×10^{-5}	0.04053	0.5687	0.9999	4.081×10^{-5}	0.002129
	2	1.02	0.0007585	0.001314	1.229	0.9942	0.002856	0.01781
	3	0.9997	1.942×10^{-5}	0.03669	0.5453	0.9999	5.051×10^{-5}	0.002369
90	1	0.9998	8.97×10^{-6}	0.03996	0.5766	0.9999	4.896×10^{-5}	0.002332
	2	0.9998	4.358×10^{-5}	0.03972	0.5863	0.9999	4.766×10^{-5}	0.002301
	3	0.9997	4.30×10^{-5}	0.03924	0.5892	0.9999	4.667×10^{-5}	0.002277

D. Calculation of effective diffusivities and activation energy

The effective diffusivity coefficient was estimated to be between 1.83×10^{-9} and 2.29×10^{-9} m^2/s for the given temperature range. The effect of temperature on the diffusivity was expressed by the Arrhenius equation, where the logarithm of the diffusivity exhibited a lineal behavior against the reciprocal of the absolute temperature (Fig. 5). In addition, 11.503 kJ/mol and D_0 of 9.94×10^{-8} m^2/s were obtained. Similar values of Ea are proposed for other varieties of red bell pepper, such as: 28.4 kJ/mol in the

Kahramanmaras variety of red pepper and 44 kJ/mol in the Jaranda variety of red pepper [24, 25].

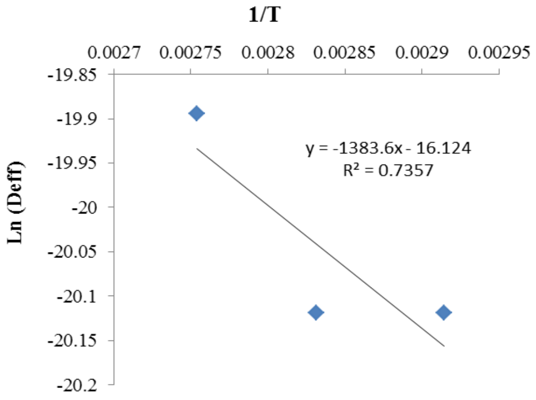


Figure. 5. Arrhenius-type relationship between effective diffusivity and temperature.

IV. CONCLUSIONS

In this study, investigate the effects of three temperatures and different concentrations of Spirulina platensis micro alga on kiwifruit pastille drying kinetic and the color of kiwi pastille. Our result indicated that as temperature increased, the drying time decreased. Different concentrations of Spirulina platensis had no effect on drying process. As time increased, a* showed ascending trends whereas L* showed descending trend and these color changes were relatively more intensive at high temperatures. Of the whole fitted mathematical models, the Midilli was selected as the best one with R2 of 0.9999.

NOMENCLATURE

a, b, c, d, g, k, n	Drying constant
D_{eff}	Effective Diffusivity
D_0	Arrhenius factor
Ea	Activation Energy (kJ/mol)
L	Half thickness of the slab (m)
MR	Moisture Ratio
MRexp,i,	ith experimental moisture ratio
MRpre,i	ith predicted moisture ratio
M	Moisture content in time
M_0	Initial moisture content
M_e	Equilibrium moisture content
N	Number of observations
R	universal gas constant (kJ/mol.K)
R^2	Coefficient of determination
RMSE	Root Mean Square Error
T	Absolute Temperature (°K)
SSE	Sum of squared error
t	drying time (h)

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