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Modeling the Effects of Osmotic Dehydration Pretreatment Parameters and Lyophilization Kinetics on Mass Transfer and Selected Nutritive Parameters of Peaches

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Abstract

The effects of the osmodehydration pretreatment parameters on successive lyophilization mass transfer kinetics of the peaches, dehydrated in the combined dehydration process, were investigated and mathematically modelled. The obtained results showed the statistically significant effect of osmotic dehydration pretreatment and its parameters on the final dry matter content and water activity values of the dehydrated peaches. The maximum dry matter content and minimal water activity values of dehydrated peach samples were 84.60 % and 0.423, respectively, produced in osmodehydration pretreatment in molasses of 80 % concentration, at 50 °C, during a 5-hour process and subsequent 6-hour lyophilization. With the increase of all osmodehydration pretreatment parameters it is possible to reduce the duration of the lyophilization process, reducing the high energy demand of the dehydration method (lyophilization) and substituting it with low energy demanding dehydration method (osmodehydration) without compromising the quality of the final product, regarding the dry matter content and water activity values. Mathematical models describing the effect of the duration of the lyophilization on the dry matter content and water activity values of the fresh and dehydrated peaches were developed. They showed a good correlation between calculated and experimental values, allowing a good prediction of the investigated responses. In the combined method, protein, sugar, K and Fe content of the dehydrated peach samples were enriched and further enhanced in prolonged lyophilization stages.

Keywords

osmodehydration, freeze drying, *Prunus persica*, sugar beet molasses, mathematical modeling

1 Introduction

As an essential source of digestible and indigestible minerals, carbohydrates, and vitamins, fruits are also characterized by high moisture content, in most cases above 75%, hence prone to spoilage by moulds and yeasts. Fruits are produced during peak seasons, but due to the lack of preservation and storage capacities, the market becomes overstocked during such periods [1]. Applying different techniques for lowering water activity values, the shelf-life of fruit products can be increased and stability can be prolonged [2, 3].

New products, based on dehydrated fruits, range from the ready to eat - snacks, to use as ingredients in different foods: dairy, breakfast cereals and confectionery products. Different dehydration technologies, like osmotic dehydration, can be tailored to obtain these products. Over recent years, osmotic dehydration has received much interest from researchers as a minimal processing operation and part of the food production process [4].

The osmotic dehydration process starts with the immersion of the raw material in a selected hypertonic solution, where water diffuses from the food material to the direction of the solution, due to the concentration difference between the osmotic solution and the interstitial fluid. In the opposite direction, the solute, used as osmotic solution agents, flows from the solution to the food, to a minor extent [5, 6]. Sugar beet molasses has proven to be a good choice as an osmotic solution, due to its technological effectiveness in mass transfer phenomena, highly valued nutritive composition and low cost as a by-product of the sugar industry [7, 8].

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As partial dehydration process, osmotic dehydration can reduce the moisture content of foods up to 30 to 50%, where energy is not used for latent heat of evaporation. Applying osmotic dehydration treatment on the upper stream of the dehydration process, hence plays a significant role in enhancing energy efficiency during complex dehydration process [9].

In the lyophilization process, water as ice is removed from a material by sublimation under low pressure. The lyophilization process has many applications for the production of high-quality food materials [10].

The lyophilization process requires high amounts of energy, compared to convective drying. Almost double the amount of energy is needed to remove 1 kg of water from dehydrating material, [11] hence providing the possibility to reduce the high energy consumption of this process is highly desirable.

This investigation aimed to research and develop mathematical models of the osmotic dehydration pretreatment parameters effect on successive lyophilization mass transfer kinetics of peaches, dehydrated in combined dehydration process (osmotic dehydration in molasses as pretreatment and successive lyophilization), and investigate the content of protein, sugar, K and Fe of obtained dehydrated products. Obtained results and models of this research could provide the basis for the reduction of the extent of lyophilization, energy demanding, yet high-quality producing technique, via application of osmotic dehydration in molasses, as a peaches dehydration pre-treatment.

2 Material and methods

2.1 Osmotic dehydration process of peaches

Fresh peaches (*Prunus persica*, var. *nucipersica*), harvested at location Vojvodina, Serbia in August 2021, purchased at the local market, with the initial dry matter content of: 7.40 ± 0.08 %, were prepared by washing with running water, drying with paper towels and peeling and cutting into cubes, of approximately 1 × 1 × 1 cm.

Sugar beet molasses, obtained from sugar factory Crvenka, Serbia, with dry matter content of: 85.04%, was used to prepare osmotic solutions. First, molasses was diluted to the concentrations (C) of 60, 70 and 80% of dry matter by distilled water. The dry matter content of osmotic solutions was determined refractometrically, using Abbe refractometar, Carls Zeiss, Jena, Germany.

The osmotic dehydration process was carried out in laboratory vessels, under atmospheric pressure, at a constant temperature, in a thermostat chamber (Memmert IN160, Büchenbach, Germany). Osmotic dehydration process temperature (t) was maintained constant at: 20, 35 or 50 °C, duration (τ) was varied between 1, 3 and 5 hours, process parameters were chosen on the basis of previous investigations [7, 8].

To reduce excessive solution dilution, peach cubes samples to molasses weight ratio of 1:5 was used. Peach cube samples were submerged in molasses and manually stirred every 15 minutes for better homogenization of molasses and defunded water from the dehydrating peach samples. Then, peach samples were taken out from molasses solutions, after the end of the designated process duration, lightly washed with running water and gently blotted to remove the excess surface water.

2.2 Lyophilization

Fresh and osmotically dehydrated peach samples were frozen and stored at −30 °C until lyophilization. Frozen samples were placed in freeze dryer (Christ ALPHA1-2 LDPLUS, Osterode am Harz, Germany) and lyophilization parameters were set to: a pressure of the 1.6 Pa, condenser temperature of −57 °C. Lyophilization duration was varied between 2, 4 and 6 hours. Dry matter content of the fresh, osmotically dehydrated and lyophilized peach samples was determined by drying at 105 °C for 24 h in a heat chamber (Instrumentaria Sutjeska, Serbia) until reaching constant mass. All analytical measurements were carried out following AOAC [12]. Water activity (a_w) of the dehydrated samples was measured using a water activity measurement device (TESTO 650, Germany) with an accuracy of ± 0.001 at 25 °C.

Preparation of dehydrated peach samples is schematically shown on Fig. 1.

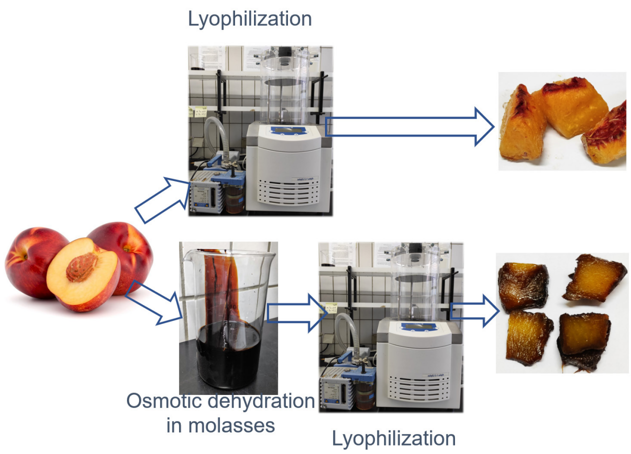

Fig. 1 Schematic description of dehydrated peach samples preparation

2.3 Analysis of chemical and mineral matter content

Selection of chemical and mineral matter content responses was conditioned by the effort to trace the changes that occur during combined dehydration method, especially in the first, osmotic dehydration in molasses stage.

Analysis of chemical content of lyophilized fresh and osmodehydrated peach samples was performed according to the official methods of AACC: proteins [13] and sugar [14].

The K and Fe contents of lyophilized fresh and osmodehydrated peach samples were performed according to ISO 6869:2000 [15].

All measurements were done in triplicates.

2.4 Calculations

In order to describe the mass transfer kinetics of the combined dehydration process, dry matter content (DMC) was calculated, Eq. (1), for different applied parameters of the two dehydration methods:

$$\text{DMC} = \frac{m_f}{m_i} \times 100\%, \qquad (1)$$

where m_i and m_f were the initial and final mass (g) of the samples, respectively [16].

Based on experimental results for DMC and a_w values of peach samples dehydrated in combined process mathematical models of dependence of DMC and a_w values from lyophilization duration, as an independent variable, were formed, Eq. (2):

$$Y_k = f_k \times \left(\text{lyophilization}_{\text{duration}}\right), \qquad (2)$$

where Y_k are tested responses and f_k is function of the model.

Second-order polynomial, Eq. (3), was used for the approximation of experimental data. Fourteen models for 2 responses (DMC and a_w values) in dependence of 1 independent variable (lyophilization duration) were developed, where seven mathematical models were developed for different applied osmotic dehydration process parameters (different τ, molasses' C and t), for each independent variable:

$$Y_k = a_{k0} + a_{k1} \times X + a_{k2} \times X^2, \ k = 1-14, \qquad (3)$$

where: $a_{k0\text{-}2}$ were regression coefficients; Y_k were: DMC (Y_1) and a_w (Y_2), while X was lyophilization duration.

For the responses' analysis, nonlinear, least square regression analysis, with the Levenberg-Marquardt method of estimation was used.

Coefficient of determination (r^2), reduced chi-square (χ^2), mean bias error (MBE), root mean square error (RMSE) and mean percentage error (MPE), were used for the developed model's quality analysis [17].

Analysis of variance (ANOVA) and post-hoc Tukey's HSD test were used to determine the effect and interaction of responses' individual factors' significance.

StatSoft Statistica ver.12.0. a software package was used for ANOVA and second-order polynomial models calculation, while Microsoft Excel ver. 2016 was used for the calculation of the quality of the parameters of the developed models.

3 Results and discussion

Table 1 shows DMC values of lyophilized fresh and osmotically dehydrated peaches samples, at the applied different osmotic dehydration process parameters and lyophilization duration. The effect of osmotic dehydration pretreatment can be analyzed on lyophilization mass transfer kinetics from the presented results. The DMC values of peach samples subjected only to the lyophilization process were statistically significantly lower than any peach samples subjected to the combined dehydration method of osmotic dehydration pretreatment and lyophilization (from 3.86 up to 4.88 times lower, at lyophilization duration point of 6 h), indicating statistically significant, $p<0.05$, effect of osmotic dehydration pretreatment on the DMC values of the final, dehydrated peaches. The profound effect of osmotic dehydration pretreatment can be best seen by comparing results of dehydrated peach samples subjected to only lyophilization in the duration of 6 h, and peach samples subjected to the shortest osmotic dehydration pretreatment (τ=1 h, C=80% and t=50 °C), without lyophilization (0 h), where it can be seen statistically significantly, $p<0.05$, higher DMC value of only osmodehydrated sample (higher for 23.53% of relative value). This result indicates that the maximal DMC level of the peaches, which can be achieved in 6-hour lyophilization process, is statistically significantly, $p<0.05$, lower than the DMC level obtained in the shortest osmodehydration pretreatment. These results can be explained by the fact that lyophilization is a process that requires a long operation period for high dehydration effects [18], while osmotic dehydration is the process that provides the highest dehydration rates at the beginning of the process [19].

The effect of individual osmotic dehydration pretreatment parameters on lyophilization kinetics can be analyzed from the results also shown in Table 1. With the increase of all three osmotic dehydration parameters, with two other parameters constant, it can be observed

Table 1 Average values and standard deviations of lyophilized fresh and osmodehydrated peaches' DMC

			Lyophilization duration (X), h			
			0	2	4	6
Lyophilized fresh sample			DMC, %			
			7.40 ± 0.11^{a}	9.30 ± 0.07^{b}	13.41 ± 0.09^{c}	17.34 ± 0.20^{d}
Lyophilized osmodehydrated samples						
Osmotic dehydration parameters	τ = 5 h, C = 80%	t = 20 °C	35.11 ± 0.25^{e}	50.63 ± 0.43^{g}	66.74 ± 0.58^{i}	72.29 ± 0.04^{j}
		t = 35 °C	39.49 ± 0.40^{f}	58.11 ± 0.59^{h}	71.51 ± 0.35^{j}	76.35 ± 1.00^{k}
		*t = 50 °C	50.81 ± 0.54^{g}	66.41 ± 0.77^{i}	78.43 ± 0.45^{l}	84.60 ± 1.02^{m}
	τ = 5 h, t = 50 °C	C = 60%	41.90 ± 0.53^{e}	56.95 ± 0.14^{h}	65.58 ± 0.27^{j}	72.19 ± 0.69^{k}
		C = 70%	48.11 ± 1.04^{f}	61.83 ± 0.66^{i}	72.74 ± 1.53^{k}	80.84 ± 1.28^{m}
		*C = 80%	50.81 ± 0.54^{g}	66.41 ± 0.77^{j}	78.43 ± 0.45^{l}	84.60 ± 1.02^{n}
	C = 80%, t = 50 °C	τ = 1 h	21.42 ± 0.16^{e}	41.15 ± 0.85^{f}	59.51 ± 1.18^{h}	66.91 ± 0.53^{i}
		τ = 3 h	42.66 ± 0.92^{f}	59.94 ± 0.62^{h}	72.61 ± 1.23^{j}	79.83 ± 0.67^{k}
		*τ = 5 h	50.81 ± 0.54^{g}	66.41 ± 0.77^{i}	78.43 ± 0.45^{k}	84.60 ± 1.02^{l}

[a–n] Different letters in superscript of the sets of data regarding fresh sample and two constant osmotic dehydration parameters indicate on statistically significant difference between values, at level of significance of $p<0.05$ (based on post-hoc Tukey HSD test).
* Results in marked table rows are repeated for easier comparison between varied osmotic dehydration parameters.

that achieved the DMC level of the dehydrated peaches, were statistically significantly, $p<0.05$, higher at the same lyophilization duration point. The obtained results are in accordance with previous work investigating osmotic dehydration kinetics of different raw materials [7, 16, 20], and point at the statistically significant, $p<0.05$, effect of each osmotic dehydration pretreatment parameter (t, C and τ) on the final DMC values of the dehydrated peaches.

With the increase of t from 20 to 35 °C, the same level of statistical significance was obtained in final, DMC level of the dehydrated peaches, lyophilized after 4 hours and after 6 hours, respectively. With the increase of t from 20 to 50 °C, and decrease of lyophilization processes from 6 to 4 hours, the final DMC values of the dehydrated peaches statistically significantly increased by 6.14% ($p<0.05$), indicating that with the increase of osmotic dehydration pretreatment, it is possible to reduce lyophilization process duration, for the same final product quality.

The increase of C from 60 to 70% and the successive lyophilization process duration reduction from 6 to 4 hours, provided final dehydrated peaches' DMC results of the same statistical significance, even for 0.76% higher. However, the increase of C from 60 to 80%, and reduction of successive lyophilization process duration from 6 to 4 hours, respectively, provided statistically significantly, $p<0.05$, higher final dehydrated peaches' DMC results, with an increase of 8.64%.

As in the case of the previous osmotic dehydration pretreatment parameter, the increase of molasses concentration, can provide the possibility to reduce lyophilization process duration, for the same final product quality.

The increase of τ had more significant effects on final dehydrated peaches' DMC values than two previous osmotic dehydration pretreatments parameters (increase from minimal to maximal values of t, C and τ had produced increase of DMC values for 15.70%, 8.91% and 29.39%, respectively). With an increase of τ from 1 to 3 hours, and successive lyophilization process duration reduction from 6 to 4 hours, respectively, final DMC values of the dehydrated peaches were statistically significantly, $p<0.05$, higher, for 8.52%. In case of τ increase from 1 to 5 hours, the same statistically significant, $p<0.05$ level of final DMC values was obtained, while reducing lyophilization process duration from 6 to only 2 hours. These data indicate that with the increase of osmotic dehydration pretreatment time, it is possible to significantly reduce lyophilization process duration, for the same final product quality.

Data presented in Table 1 showed that lyophilization duration had a statistically significant, $p<0.05$, effect on final DMC values of all tested samples, regardless of dehydration method (with or without osmotic dehydration stage), pointing at higher dehydration levels with increased lyophilization duration, as in case of other research [18, 21].

Maximal obtained DMC value of peach samples subjected to osmotic dehydration pretreatment in molasses of 80% concentration, at 50 °C, during 5 hour process and subsequent 6 hour lyophilization was: 84.60%. The DMC result is in accordance to the previulsly reported results of combined osmodehydration and lyophilization of 70.10% and 83.63% with simillar applied process parameters [22, 23].

Table 2 shows a_w values of lyophilized fresh and osmotically dehydrated peaches samples, at applied different osmotic dehydration process parameters and lyophilization duration.

From presented results, the effect of osmotic dehydration pretreatment can be analyzed, via dehydrated peaches a_w values, on lyophilization dewatering process kinetics. The a_w values of fresh peach samples subjected only to the lyophilization process were statistically significantly, $p < 0.05$, higher than those subjected to the combined dehydration method of osmotic dehydration pretreatment and lyophilization.

Dehydrated peach samples in combined method (osmotic dehydration and lyophilization) had from 1.55 up to 2.10 times lower a_w values, than fresh lyophilized peach sampels, at the same lyophilization duration point of 6 h. These results indicate statistically significant, $p < 0.05$, effect of osmotic dehydration pretreatment on final, a_w values of the dehydrated peaches, same as in the case of DMC response. Analysis of the effect of osmotic dehydration pretreatment on a_w values can be carried out by comparing obtained results for fresh peach samples subjected to only lyophilization for 6 h and peach samples values subjected only to the osmotic dehydration of different process parameters. The same a_w values of peach samples subjected to these two different dehydration methods were obtained for osmotic dehydration parameters of: $\tau = 5$ h, $C = 80\%$ and lowest $t = 20$ °C, while lower a_w values were obtained in processes of: $\tau = 5$ h, $C = 70\%$, $t = 50$ °C and: $\tau = 3$ h, $C = 80\%$, $t = 50$ °C (all of these osmotic dehydration parameters were not in the highest range of tested parameters). These results indicate good starting point, regarding obtaining low a_w values of molasses osmodehydrated material, for further technological processing [24–26], such as lyophilization.

The results shown in Table 2 can also be used to affect individual osmotic dehydration pretreatment on kinetics analysis of the lyophilization dewatering process. The increase of all three osmotic dehydration parameters (t, C, τ), with two other parameters constant, monitored at the same lyophilization duration points, has led to the statistically significant, $p < 0.05$, decrease of final dehydrated peaches a_w values. The obtained results follow the previously investigated effects of osmotic dehydration in the parameters of the molasses on the change of a_w values of different raw materials [20, 27, 28].

The increase of t from 20 to 35 °C has provided the same final dehydrated peaches a_w values in processes of lyophilization of 6 and 4 hours, respectively, while the further increase of t to 50 °C further decreased final dehydrated peaches a_w values for 9.92%, also in lyophilization process duration of 4 hours. These results indicate, the same as in the case of DMC response, that with the increase of osmotic dehydration pretreatment temperature, it is

Table 2 Water activity of lyophilized fresh and osmodehydrated peaches-average values and standard deviations

			Lyophilization duration (X), h			
Lyophilized fresh sample			0	2	4	6
			a_w			
			0.940 ± 0.009^{a}	$0.920 \pm 0.011^{a,b}$	$0.910 \pm 0.010^{b,c}$	$0.890 \pm 0.017^{c,d}$
Lyophilized osmodehydrated samples						
Osmotic dehydration parameters	$\tau = 5$ h, $C = 80\%$	$t = 20$ °C	$0.890 \pm 0.013^{c–e}$	0.830 ± 0.002^{f}	0.590 ± 0.003^{h}	0.554 ± 0.005^{i}
		$t = 35$ °C	$0.870 \pm 0.008^{d,e}$	0.720 ± 0.006^{g}	0.553 ± 0.005^{i}	0.530 ± 0.005^{i}
		*t=50 °C	0.860 ± 0.011^{e}	0.590 ± 0.005^{h}	0.504 ± 0.004^{j}	0.423 ± 0.005^{k}
	$\tau = 5$ h, $t = 50$ °C	$C = 60\%$	$0.882 \pm 0.012^{d,e}$	0.741 ± 0.007^{f}	0.598 ± 0.005^{h}	0.560 ± 0.004^{i}
		$C = 70\%$	$0.869 \pm 0.016^{d,e}$	0.665 ± 0.009^{g}	0.550 ± 0.005^{i}	0.489 ± 0.008^{j}
		*$C = 80\%$	0.864 ± 0.006^{e}	0.588 ± 0.008^{h}	0.504 ± 0.007^{j}	0.423 ± 0.006^{k}
	C=8 0%, $t = 50$ °C	$\tau = 1$ h	$0.901 \pm 0.010^{b,c}$	0.860 ± 0.010^{e}	0.673 ± 0.005^{f}	$0.575 \pm 0.008^{g,h}$
		$\tau = 3$ h	$0.875 \pm 0.004^{d,e}$	0.672 ± 0.004^{f}	0.552 ± 0.011^{h}	0.498 ± 0.003^{i}
		*$\tau = 5$ h	0.864 ± 0.010^{e}	0.588 ± 0.004^{g}	0.504 ± 0.009^{i}	0.423 ± 0.004^{j}

$^{a–k}$ Different letters in superscript of the sets of data regarding fresh sample and two constant osmotic dehydration parameters indicate on statistically significant difference between values, at level of significance of $p < 0.05$ (based on post-hoc Tukey HSD test).

* Results in marked table rows are repeated for easier comparison between varied osmotic dehydration parameters.

possible to reduce lyophilization process duration, without compromising achieved final product a_w values.

The increase of C from 60 to 70% and lyophilization process duration reduction from 6 to 4 hours, has provided the 1.82% decrease of final dehydrated peaches a_w values, while the increase of C to 80% with the same lyophilization process duration reduction, has provided statistically significant, $p < 0.05$, final dehydrated peaches a_w values decrease, of 11.11%.

As in the case of the previous osmotic dehydration pretreatment parameter and as in the case of DMC response, the increase of molasses concentration, can provide the possibility to reduce lyophilization process duration, for achieving the same or even lower final product a_w values.

As in the case of DMC response, the increase of τ had more significant effects on final a_w values, than two previous osmotic dehydration pretreatments parameters. Increasing τ from 1 to 3 hours, and successive lyophilization process duration reducing from 6 to 4 hours, has led to the final a_w values decrease of 4.17%. The same as in the case of DMC, with the τ increase from 1 to 5 hours, the same statistically significant, $p < 0.05$, level of final a_w values were obtained, while reducing lyophilization process duration from 6 to only 2 hours. These results indicate that by increasing osmotic dehydration pretreatment time, lyophilization process duration can be significantly reduced without affecting achieved final product a_w values.

Lyophilization duration had a statistically significant, $p < 0.05$, effect on final a_w values, regardless of dehydration method (with or without osmotic dehydration stage), indicating on obtaining higher dehydration levels with increased lyophilization duration, as in case DMC response.

Minimal achieved a_w value of peach samples subjected to the same, osmotic dehydration pretreatment in molasses of 80% concentration, at 50 °C, during 5 hour process and subsequent 6 hour lyophilization, as in case of DMC response, was: 0.423.

Tables 3 and 4 show regression coefficients of developed mathematical models for the dependence of the DMC and a_w values of the fresh and dehydrated peach samples from lyophilization duration in the form of second-order polynomial Eq. (3). Based on second-order polynomial Eq. (3) regression coefficients (a_0–a_2), shown in Tables 3 and 4, mathematical models can be formed to describe the dependence of the DMC and a_w values of the fresh and dehydrated peaches from the lyophilization duration.

Table 3 also shows the statistical significance of regression coefficients for developed mathematical models for DMC response. It can be seen that linear coefficients were statistically significant, $p < 0.05$, in the cases of peach samples subjected to osmotic dehydration of following parameters: τ = 5 h, C = 80%, t = 35 and 50 °C; τ = 5 h, C = 70%, t = 50 °C; τ = 3 h, C = 80%, t = 50 °C; while quadratic coefficients were statistically significant, $p < 0.05$, in following cases: τ = 5 h, C = 70%, t = 50 °C and τ = 3 h, C = 80%, t = 50 °C.

Table 4 shows the statistical significance of regression coefficients for developed mathematical models for a_w values response. It can be seen that linear coefficients were statistically significant, $p < 0.05$, in the cases of peach samples subjected to osmotic dehydration of following parameters: τ = 5 h, C = 70%, t = 50 °C and τ = 3 h, C = 80%, t = 50 °C; while quadratic coefficient was statistically significant, $p < 0.05$, in one case: τ = 3 h, C = 80%, t = 50 °C.

Comparing the coefficients of the mathematical models, statistical significance for DMC and a_w values show more profound effects of lyophilization duration on DMC values

Table 3 Regression coefficients of DMC dependence from lyophilization duration in observed peach samples

Regression coefficients				
Lyophilized fresh sample		a_0	a_1	a_2
		7.280500*	0.935250	0.126875
Lyophilized osmodehydrated sample				
Osmotic dehydration parameters				
τ = 5 h, C = 80%	t = 20 °C	34.55558*	10.11955	−0.62292
	t = 35 °C	39.32332*	11.36632*	−0.86123
	t = 50 °C	50.69524*	9.20644*	−0.58946
τ = 5 h, t = 50 °C	C = 60 %	42.12316*	8.13732	−0.52716
	C = 70 %	48.11299*	7.55924*	−0.35076*
C = 80%, t = 50 °C	τ = 1 h	20.93999	12.36492	−0.77056
	τ = 3 h	42.61873*	9.98109*	−0.62870*

* Statistically significant at the significance level of $p < 0.05$

Table 4 Regression coefficients of a_w value dependence from lyophilization duration in observed peach samples

Regression coefficients				
Lyophilized fresh sample		a_0	a_1	a_2
		0.939600*	−0.007700	0.000000
Lyophilized osmodehydrated sample				
Osmotic dehydration parameters				
τ = 5 h, C = 80%	t = 20 °C	0.904000	−0.069750	0.001375
	t = 35 °C	0.880400*	−0.107050	0.007875
	t = 50 °C	0.854550*	−0.143475	0.012188
τ = 5h t = 50 °C	C = 60 %	0.887350*	−0.094075	0.006438
	C = 70 %	0.867250*	−0.116375*	0.008937
C = 80% t = 50 °C	τ = 1 h	0.912750*	−0.036875	−0.003563
	τ = 3 h	0.874150*	−0.118425*	0.009313*

* Statistically significant at the significance level of $p < 0.05$

than on a_w values of peaches subjected to the combined dehydration method.

Tables 5 and 6 show parameters of quality fit for the developed mathematical models, where it can be seen that all developed models were characterized by very high r^2 values and low χ^2, MBE, RMSE and MPE values.

These data indicate the good correspondence of calculated values with experimental data [17].

To emphasize the kinetics of changes during the lyophilization stage and provide more practical insight in chemical characterization of obtained, lowered moisture content, peach product, that can be utilized in the formulation of final products, the content of protein, sugar, K and Fe are investigated.

In Table 7 the results of fresh and dehydrated peaches' protein, sugar, K and Fe content after osmotic dehydration pretreatment (duration of 5 hours in at 50 °C and in molasses of 80% concentration) and subsequent lyophilization of different durations, are shown.

The change of chemical and mineral composition of dehydrated peach samples during the lyophilization stage can be monitored from the presented results.

Table 5 Validation of the developed models for DMC values dependence from lyophilization duration

		Model fit quality parameters				
		$\chi 2$	RMSE	MBE	MPE	r^2
Lyophilized fresh sample		9.5 E-02	2.7 E-01	2.4 E-10	2.2 E+00	0.995
Lyophilized osmodehydrated sample						
Osmotic dehydration parameters						
τ = 5 h, C = 80%	t = 20 °C	2.1 E+00	1.2 E+00	1.2 E-08	2.0 E+00	0.993
	t = 35 °C	1.9 E-01	3.7 E-01	3.5 E-09	5.5 E-01	0.999
	t = 50 °C	8.6 E-02	2.5 E-01	1.2 E-12	3.3 E-01	1.000
τ = 5 h, t = 50 °C	C = 60%	3.2 E-01	4.9 E-01	5.3 E-12	7.5 E-01	0.998
	C = 70%	1.9 E-06	1.2 E-03	−1.6 E-12	1.6 E-03	1.000
C = 80%, t = 50 °C	τ = 1 h	1.5 E+00	1.1 E+00	4.4 E-13	2.2 E+00	0.996
	τ = 3 h	1.2 E-02	9.4 E-02	2.4 E-10	1.3 E-01	1.000

* Statistically significant at the significance level of $p < 0.05$

Table 6 Validation of the developed models for a_w values dependence from lyophilization duration

		Model fit quality parameters				
Lyophilized fresh sample		$\chi 2$	RMSE	MBE	MPE	r^2
		1.1 E-06	8.9 E-04	8.4 E-11	8.7 E-02	0.997
Lyophilized osmodehydrated sample						
Osmotic dehydration parameters						
τ = 5 h, C=80 %	t = 20 °C	2.4 E-03	4.2 E-02	1.6 E-10	5.5 E+00	0.913
	t = 35 °C	4.7 E-04	1.9 E-02	8.6 E-16	2.6 E+00	0.982
	t = 50 °C	6.0 E-04	2.1 E-02	1.7 E-16	3.4 E+00	0.984
τ = 5 h, t = 50 °C	C = 60%	1.9 E-04	1.2 E-02	4.5 E-11	1.6 E+00	0.991
	C = 70%	2.0 E-05	3.9 E-03	1.1 E-11	5.8 E-01	0.999
C = 80%, t = 50 °C	τ = 1 h	9.2 E-04	2.6 E-02	3.3 E-15	3.2 E+00	0.961
	τ = 3 h	4.8 E-06	1.9 E-03	−5.6 E-15	2.8 E-01	1.000

* Statistically significant at the significance level of $p < 0.05$

Table 7 The protein, sugar, K and Fe contents of fresh and osmodehydrated peaches' after different lyophilization process

		Lyophilization duration, h			
		0	2	4	6
Protein content, g/100 $g_{of\ sample}$	L.F.S.[1]	0.62 ± 0.01^a	0.77 ± 0.01^b	1.12 ± 0.02^c	1.44 ± 0.01^d
	L.O.S.[2]	4.21 ± 0.03^e	5.49 ± 0.02^f	6.49 ± 0.07^g	6.96 ± 0.07^h
Sugar content, g/100 $g_{of\ sample}$	L.F.S.	5.61 ± 0.06^a	7.01 ± 0.05^b	10.31 ± 0.13^c	13.29 ± 0.15^d
	L.O.S.	37.44 ± 0.09^e	48.91 ± 0.53^f	57.89 ± 0.84^g	62.51 ± 0.65^h
K, mg/100 $g_{of\ sample}$	L.F.S.	13.42 ± 0.16^a	17.19 ± 0.27^a	24.43 ± 0.14^a	31.53 ± 0.38^a
	L.O.S.	803.17 ± 8.31^b	1051.45 ± 19.58^c	1248.22 ± 11.76^d	1345.63 ± 0.60^e
Fe, mg/100 $g_{of\ sample}$	L.F.S.	3.53 E-03 ± 2.82 E-05[a]	4.29 E-03 ± 5.23E-05[a]	6.34 E-03 ± 9.36E-05[a]	7.70 E-03 ± 5.77E-05[a]
	L.O.S.	2.42 ± 0.02^b	3.01 ± 0.03^c	3.61 ± 0.01^d	3.91 ± 0.03^e

[a–h] Different letters in superscript of the sets of data regarding the same chemical and mineral matter content response indicate on statistically significant difference between values, at level of significance of $p < 0.05$ (based on post-hoc Tukey HSD test)
[1] Lyophilized fresh sample
[2] Lyophilized osmodehydrated sample

The results in Table 7 are expressed on 100 g of sample basis, for the reason of monitoring the kinetics of changes during lyophilization stage and chemical characterization of obtained dehydrated peach product.

Trends in the protein content of the peach samples show that lyophilization duration and the osmodehydration pretreatment, statistically significantly, $p < 0.05$, affected the increase of protein content of the samples. In addition, similar trends of lyophilization duration and osmodehydration pretreatment statistical significance are noticed in peach samples' sugar content and both mineral matter contents (K and Fe).

These effects can be explained by secondary mass transfer, which is characteristic of the osmodehydration process, incorporating osmotic solution – molasses, into dehydrating material, increasing and enriching the solid matter of peach samples with molasses constituets [27].

Since molasses is rich in the mineral matter [29], the increase of K and Fe content in peach samples dehydrated in combined method, in comparison to samples subjected to only lyophilization, is much more profound, than the increase of the protein and sugar content of samples also dehydrated in combined method, in comparison to only lyophilization.

Maximal obtained values of protein, sugar, K and Fe content of peach samples subjected to 5-hour osmotic dehydration, at 50 °C in 80% molasses concentration and subsequent 6 hour lyophilization were: 6.96 g/100 $g_{of\ sample}$, 62.51 g/100 $g_{of\ sample}$, 1345.63 mg/100 $g_{of\ sample}$ and 3.91 mg/100 $g_{of\ sample}$, respectively, indicating on obtained high nutritive value product, the same as in previous research [23].

4 Conclusion

From the presented results, the followings can be concluded:

- Osmotic dehydration pretreatment and each osmotic dehydration pretreatment parameter produced a statistically significant effect on DMC and a_w values of the dehydrated peach samples;
- With the increase of osmotic dehydration pretreatment temperature, time, and concentration of the molasses it is possible to reduce lyophilization process duration, reducing application extent of high energy demanding dehydration method (lyophilization) and substituting it with low energy demanding dehydration method (osmotic dehydration), without compromising final product quality, regarding obtained DMC and a_w values;
- Maximal and minimal obtained DMC and a_w values of dehydrated peach samples were 84.60 % and 0.423, respectively, produced in osmotic dehydration pretreatment in molasses of 80 % concentration, at 50 °C, during 5 hour process and subsequent 6-hour lyophilization;
- All developed mathematical models describing the DMC and a_w dependence from lyophilization duration showed a good correlation between calculated and experimental values, allowing good prediction of investigated responses within the limits of the applied technological parameters range of osmotic dehydtaion time, temperature, molasses concentration and lyophilization duration;
- The chemical and mineral matter content of peach samples dehydrated with the combined method was

enriched, due to molasses, as an osmotic solution, application, where prolonged lyophilization stages only emphasized these favorable nutritive changes. The new type of product from enriched, dehydrated peach was proposed, ready for application in different final food products.

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