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Osmotic Dehydration Combined with Freeze-drying of Apple Cubes and Comparison with Microwave Drying and Hot Air Drying

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Abstract. The effects of the pre-osmotic treatment on the mass transfer kinetics of the freeze-drying (FD) and on the water activity (aw) and the quality – colour, total phenolic content, antioxidant activity – of apple cubes were studied. The fit of the moisture content was carried out using several mathematical models. The comparison among FD, microwave drying (MWD) and hot air drying (HAD) of osmotically treated apple cubes was also performed according to the drying rate and the aw. The apple cubes were osmotically treated with 60ºBrix sucrose or sorbitol solutions at 60ºC, then frozen and freeze-dried. The FD reduced significantly the moisture content from 6.259, 1.086 and 1.031 to 0.138, 0.099 and 0.074 kgwater.kgdry matter-1 for the control and the samples osmotically pre-treated with sucrose and sorbitol, respectively. The modified Page's model presented the highest precision of parameter estimates. The FD of samples osmotically pre-treated with the sucrose solution resulted in a higher drying rate than the others samples. The highest reduction in aw was observed in the fresh samples. After FD, the total phenolic content and the antioxidant activity of the osmotically pre-treated samples decreased around 80%, in comparison with the fresh apple, this reduction being due to the osmotic pre-treatment. The freeze-dried control samples achieved a lower aw in comparison with HAD and MWD. However, FD presented a lower drying rate.

Keywords: Osmotic treatment, mathematical models, water activity, colour, total phenolic content, antioxidant activity

Nomenclature			
a	half of the side of the cube (m)	FD	freeze-drying
aw	water activity	HAD	hot air drying
A, B	Page's and Modified Page's models	k	Newton's parameter
	parameters	m	mass of sample (g)
a, k	Henderson and Pabis' and Two-term	M	moisture content (kg water.kg dry matter-1)
	exponential models parameters	Mm	monolayer moisture content (kg water.kg dry
a, k_1, b, k_2	Two-term model parameters		matter-1)
a, k, c	Logarithimic model parameters	M0	initial moisture content (kg water.kg dry matter-1)
a, b	Wang and Singh's model parameters	M∞	moisture content at equilibrium (kg water.kg dry
a, k, n, b	Midilli et al.'s model parameters		matter-1)
a, k, b, B	Weibull's model parameters	MR	moisture ratio
c, k	GAB's model constants	MWD	microwave drying
De	effective diffusivity (m^2.s-1)	OD	osmotic dehydration
DM	dry matter	SHW	standard half width
Ea	activation energy (W.g-1)	t	time (s)

1 Introduction

Freeze-drying (FD) is considered the best type of drying for the preservation of the product quality, but it is a process that requires expensive equipment and takes a long time [1]. The product is frozen at low temperatures and submitted to a reduced pressure, causing the removal of the water by sublimation [2]. Compared with other types of drying, which normally occur at higher temperatures in order to evaporate water, FD can maintain the original structure and colour of the product. This process also provides a good rehydration ability and a negligible loss of nutritional properties and flavour [2,3].

The osmotic dehydration (OD) is a simple process that results in foods with intermediate moisture and can be used prior to freeze-drying with the aim to accelerate the sublimation kinetics, reducing the consumption of energy during the drying process and also the drying time [4,5]. Ciurzyńska and Lenart [6] studied the effects of the OD prior to freeze-drying of strawberries and found that the pre-treatment, with sucrose and glucose solutions, increased the cell wall thickness. According to Ayala et al. [7], the OD with sucrose solution, followed by freeze-drying was not adequate to dry yellow pitahaya due to the shrinkage and low rehydration capacity of the final product. The OD did not cause significant changes in the water content of freeze-dried pumpkin when compared with no pre-treated samples [8].

Several mathematical models have been proposed to describe the mass transfer kinetics of food drying, thus facilitating the optimization of the processes [9]. The models may be empirical and semi-empirical, mechanistic and phenomenological. The empirical and semi-empirical models have been more used and they are based on polynomial and linear regressions. Newton's, Page's, modified Page's, Henderson and Pabis', Two term's, Midilli et al.'s, Wang and Singh's and logarithmic are examples of these types of models. Rudy et al. [10] studied the freeze-drying of cranberries and found that the best model to describe the drying kinetics of the whole fruit was the logarithmic model, while for the pulped fruits, Page's and Wang and Singh's models were more adequate. Page's model was also able to fit the experimental data of freeze-drying of apple slices [11], strawberries [12], pineapple, guava, and mango pulps [13].

Argyropoulos et al. [1] compared three types of drying (hot air drying, hot air plus microwave vacuum drying and freeze-drying) of mushrooms and found that the freeze-dried samples showed the best colour, the softest structure, and the maximum rehydration capacity. In a sensory evaluation of dried carrots slices, the freeze-dried samples had better appearance than those dried by vacuum microwave drying and air drying [14].

The objectives of this work were: i) to study the effect of the OD on the mass transfer kinetics of the freeze-drying and on the aw and the quality of the processed apples cubes; ii) to test the adequacy of the fitness of several mathematical models to describe the moisture content of the product during the freeze-drying process; iii) to carry out the comparison among freeze-drying, microwave drying and hot air drying of osmotically treated apple cubes.

2 Materials and Methods

2.1 Samples

Apples (Malus spp., variety Royal Gala) with soluble solids content of 16.6 ± 0.8 ºBrix (hand refractometer, Atago, USA) were graciously supplied by Campotec, Portugal, and stored at 4ºC. The samples were cut in cubes (12x12x12 mm) and immersed in a solution with 0.9% sodium chloride for 3 min to prevent enzymatic browning. Then, they were blotted gently with tissue paper in order to remove the excess of sodium chloride solution from the surface.

2.2 Osmotic Dehydration

The apple samples were immersed in a 60ºBrix osmotic solution of sucrose or sorbitol (Fagron, Iberica, Spain) for 8 h at 60ºC and atmospheric pressure. The mass ratio of sample to solution used was 1:4. The OD was carried out at constant temperature (60ºC) and agitation (50 rpm). After 8 h, the samples were rinsed with ultra-pure water to remove the solution adhered to the surface and blotted with tissue paper to remove the excess of water from the surface [15].

2.3 Freeze-drying

After the OD treatment, the samples were frozen at -18ºC. Then the osmotically dehydrated and the control frozen samples were dried in a freeze-dryer (FT33A, Armfield, England), under a vacuum pressure of 1.316 x 10-4 atm (100 militorr); the temperature in the freezing chamber was between -40 and -45 ºC. The FD was carried out during 3, 6, 15, 17 and 24 h.

2.4 Moisture Content and Water Activity Determination

The moisture content was determined in an oven (FP115, Binder, Tuttlingen, Germany) at 105ºC until constant weight [16]. The determinations were performed in triplicate.

The water activity (aw) of the samples was determined during the process. It was determined with a hygrometer (Aqualab Series 3, Decagon Devices Inc., Pullmam, Washington, USA) at 22ºC. Each determination was performed in duplicate.

2.5 Quality Evaluation

In order to evaluate the quality of the final product, the colour, the total phenolic content and the antioxidant activity of the product were determined.

2.6 Colour

The colour of the samples was measured using Minolta CR-300 colorimeter (Konica-Minolta, Osaka, Japan) in the CIE L*a*b* mode CIELAB colour space [17]. The colour was determined by five measures on three replicates for each sample. The total colour difference (ΔE) and the browning index were calculated by the following equations:

$$\Delta E = \sqrt{\left(L_0^* - L^*\right)^2 + \left(a_0^* - a^*\right)^2 + \left(b_0^* - b^*\right)^2} \tag{1}$$

the index “0” indicating the sample before FD.

$$\text{Browning index} = \frac{100.\left(x - 0.31\right)}{0.17} \tag{2}$$

with

$$x = \frac{a^* + 1.75L^*}{5.645L^* + a^* - 3.012b^*} \tag{3}$$

2.7 Total Phenolic Content

The dried apple cubes were ground in liquid nitrogen with a mortar. Subsequently, 1 g of sample was weighted, 10 mL of methanol (Sigma Aldrich) were added and then homogenised using an ultra-turrax (T25, IKA, Germany). The supernatant was used after the centrifugation at 5000 rpm and 4ºC for 15 min (adapted from [18]).

The total phenolic content was determined by the Folin-Ciocalteu method [19]. The reaction was performed by adding 0.5 mL apple extract, 0.5 mL Folin–Ciocalteu reagent, 1 mL sodium carbonate 75 (g.L−1) (Sigma-Aldrich) and 1.4 mL of deionized water. The total phenolic content was determined after 1 h at 750 nm in a UV-visible spectrophotometer (1240, Shimadzu, Japan). Quantification was done with respect to the standard curve of the gallic acid. The determinations were carried out in triplicate.

2.8 Antioxidant Activity

The ABTS method was used to determine the antioxidant activity [20]. After addition of 1 mL of ABTS+ solution (absorbance = 0.700 ± 0.02) to 0.2 mL of extract, the analysis was performed after 6 min at 734 nm and expressed as mg ascorbic acid.g DM-1. The determinations were performed in triplicate.

2.9 Mathematical Models

The moisture ratio (MR) of the samples was used to describe the experimental data during the drying process:

$$MR = \frac{M - M_\infty}{M_0 - M_\infty} \quad (4)$$

M_0 is the initial moisture content, M is the moisture content at time t, and M_∞ is the moisture content at equilibrium, all in dry basis (kgwater.kgdry matter-1). All M∞-values were predicted by the models.

The mathematical models used are described below:

Newton

$$MR = \exp\left(-k.t\right) \quad (5)$$

Page

$$MR = \exp\left(-A.t^B\right) \quad (6)$$

Modified Page

$$MR = \exp\left(-\left(A.t\right)^B\right) \quad (7)$$

Henderson and Pabis

$$MR = a.exp(-k.t) \quad (8)$$

Two-term

$$MR = a.\exp\left(-k_1.t\right) + b.\exp\left(-k_2.t\right) \quad (9)$$

Two-term exponential

$$MR = a.\exp\left(-k.t\right) + \left(1-a\right).\exp\left(-k.a.t\right) \quad (10)$$

Logarithmic

$$MR = a.\exp\left(-k.t\right) + c \quad (11)$$

Wang and Singh

$$MR = 1 + a.t + b.t^2 \quad (12)$$

Midilli et al.

$$MR = a.\exp\left(-k.t^n\right) + b.t \quad (13)$$

Verma et al.'s

$$MR = a.\exp\left(-k.t\right) + \left(1-a\right).\exp\left(-b.t\right) \quad (14)$$

Weibull

$$MR = a - b.\exp\left(-\left(k.t^B\right)\right) \quad (15)$$

Crank

$$MR = \left[\sum_{n=0}^{\infty} \frac{8}{\left(2n+1\right)^2.\pi^2} \exp\left(-\frac{\left(2n+1\right)^2.\pi^2.De.t}{4a^2}\right)\right]^3 \quad (16)$$

The Guggenheim-Anderson-de Boer (GAB)'s model was used to predict the relation between the equilibrium moisture content and the water activity of the dried apple cubes [21]. The GAB's model is expressed as:

$$\frac{M_\infty}{M_m} = \frac{c.k.a_w}{\left(1-k.a_w\right).\left(1-k.a_w + c.k.a_w\right)} \quad (17)$$

c and k are constants and M_m is described as the monolayer moisture content on dry basis (kgwater.kgdry matter-1).

2.10 Statistical Analysis

The statistical analysis was performed using Microsoft Excel 2000 (Microsoft Corporation, Washington, USA) (mean and standard deviation calculations) and IBM SPSS® Statistics 20.0 for Windows® (2012, SPSS Inc., Chicago, USA). The model parameters of the fit of the experimental data were estimated by non-linear regression procedures, and the margin of error of the estimates was calculated at 95% (the margin of error is the half width of the confidence interval at 95%). The regressions were also assessed by ANOVA approaches and the significance level assumed was 5%.

The adequacy of the models fit was evaluated by the determination coefficient (R^2) and by the residual analysis. The residual analysis was performed in order to check the assumptions of independence, randomness and normality. The normality of the residuals was evaluated by Kolmogorov-Smirnov test.

3 Results and Discussion

The freeze-drying experiments were carried out with control samples (without pre-treatment) and with previously osmotically dehydrated samples with sucrose and sorbitol solutions. The moisture content of the apple cubes after the osmotic treatment with sucrose and sorbitol solutions was reduced from 6.259 to 1.086 and 1.031 kgwater.kgdry matter-1, respectively, which represents a decrease of more than 80%. These results are confirmed by previous studies [15]. At the end of the FD process the moisture content was reduced to 0.138 kgwater.kgdry matter-1 for the control and further reduced to 0.099 kgwater.kgdry matter-1 for the samples osmotically pre-treated with sucrose and 0.074 kgwater.kgdry matter-1 for the samples osmotically pre-treated with sorbitol. These values represent a total water removal of around 98%, being slightly higher for the samples osmotically pre-treated with sorbitol.

3.1 Mass Transfer Kinetics An Mathematical Modelling

The experimental data of the freeze-drying of apple cubes were fitted using twelve mathematical models — Crank's, Newton's, Page's, modified Page's, Henderson and Pabis', Two-term, Two-term exponential, logarithmic, Wang and Singh's, Midilli et al.'s, Weibull's and Verma et al.'s. The high values of R^2 and the satisfied assumptions of independence, randomness and normality of residual analysis showed that the Newton's, Page's, modified Page's, Henderson and Pabis', logarithmic and Weibull's models can describe the moisture ratio well during this drying process. The results of the non-linear regression of the experimental data of freeze-drying of apple cubes are presented in Table 1. The other models could not describe the experimental data because they did not follow one or more of those assumptions.

The Newton's model is the most simple model with one parameter, k. The k-values are between 0.331 and 0.426 and no significant differences were observed between the control and the freeze-dried samples osmotically pre-treated with the sucrose solution. OD with the sorbitol solution resulted in the lowest k-value, meaning that the freeze-drying rate of the samples pre-treated with sorbitol was lower. Rahimi et al. [11] also obtained lower k-values in apple slices submitted to different pre-treatments prior to the freeze-drying in comparison with the control (no pre-treatment).

The A parameter of the Page's model presented values of 0.112, 0.460 and 0.201 for the control and the freeze-dried samples osmotically pre-treated with sucrose and sorbitol solutions, respectively. The OD process resulted in an increase of this parameter, meaning that the drying rate increased. These A-values are closer to those obtained by Kırmacı et al. [12] for freeze-died strawberries. For the B parameter, the trend was the opposite, i.e., $B_{control} > B_{OD}$, and the values varied between 0.924 and 1.968. The values of A were higher and the B closer than those obtained by Rudy et al. [10] for freeze-dried cranberries and by Marques and Freire [13] for freeze-dried pulp of tropical fruits, both studies being carried out without pre-treatment.

The modified Page's is very similar to the Page's model and the B-values are equal in both models. As with the Page's model, the drying rate, given by the A-parameter, was higher for samples osmotically pre-treated with the sucrose solution. This parameter was not significantly different between the control and the osmotically dehydrated sorbitol samples.

No significant differences were found in a parameter of Henderson and Pabis' model among all conditions used. The values of a are closer to 1, as it was also observed by Kırmacı et al. [12]. In relation to the pre-treatment, the k parameter was not significantly different between the control and the osmotically pre-treated samples, but this parameter was higher for the freeze-dried samples osmotically pre-treated with the sucrose solution than for those osmotically pre-treated with the sorbitol solution.

The a and c parameters of the logarithmic model presented high values of margin of error, making these parameters not significantly different among the different conditions used (data not shown). The k parameter presented low values of margin of error and varied between 0.333 and 0.416, but the conditions used did not produce significant differences in this parameter. These values are in agreement with Kırmacı et al.'s [12] and Rudy et al.'s [10].

Although the Weibull's model presented high R^2 and random and normally distributed residuals, all four parameters (a, b, k and n) presented high values of margin of error (data not shown). Thus, according to this model, no significant difference was observed between the two OD pre-treatments used.

k (Newton's, Henderson and Pabis', and Logarithmic models) and A (Page's and modified Page's models) parameters can be related with the water diffusion rate, but did not present the same trend using these different models. Considering the precision in the parameter estimation, calculated using the Standard Half Width (SHW = margin of error/parameter value) at 95% of confidence, it is possible to conclude that the modified Page's model presented the highest precision of the parameter estimates, i.e., lowest SHW. Based on this model fit, the highest drying rate was observed for freeze-dried samples pre-treated with the sucrose solution (Figure 1). According to Wang et al. [22], the high uptake of solute can reduce the tissue porosity due to solute infiltration or possible formation of a peripheral layer of solute, hindering the water transfer. This may explain the fact that the samples pre-treated with sorbitol solution presented lower freeze-drying rate since these samples obtained higher solute gain after the osmotic treatment [15].

Table 1. Parameters of the fit of Newton's, Page's, modified Page's and Henderson and Pabis' models of the normalized moisture content of freeze-dried apple cubes

Osmotic agent of OD	Newton		Page			modified Page			Henderson and Pabis		
	k ± margin of error	R^2	A ± margin of error	B ± margin of error	R^2	A ± margin of error	B ± margin of error	R^2	a ± margin of error	k ± margin of error	R^2
-	0.428±0.040	0.995	0.112±0.041	1.968±0.329	0.997	0.328±0.009	1.968±0.329	0.997	1.004±0.024	0.366±0.035	0.990
sucrose	0.420±0.019	0.996	0.460±0.071	0.924±0.125	0.996	0.431±0.029	0.924±0.125	0.996	0.988±0.014	0.416±0.019	0.997
sorbitol	0.331±0.019	0.993	0.201±0.032	1.402±0.127	0.997	0.319±0.009	1.402±0.127	0.997	1.005±0.020	0.333±0.020	0.993

The margin of error of the estimates was calculated at 95%.

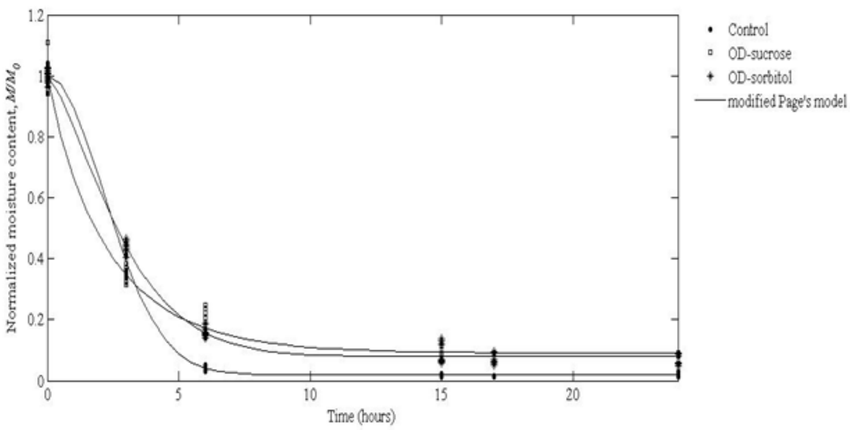

Figure 1. Experimental data and the fit of modified Page's model of the normalized moisture content (M/M0) during the freeze-drying of apple cubes

Based on the results of the fit by modified Page's model of previous works [23, 24], it is possible to make a comparison between different drying processes, because this model could also describe well the mass transfer kinetics of hot air drying (HAD) and microwave drying (MWD) of the osmotically pre-treated apple cubes. Comparing the parameter A, related with the drying rate, of the best condition of each drying — HAD-80ºC, MWD-500W and freeze-drying (FD) — the FD resulted in the lowest A-values. The MWD increased the drying rate 12 to 16-fold when compared with FD, and 3 to 6-fold in comparison with the hot air drying. These results mean that FD is more time consuming than the other two processes, HAD and MWD. Lin et al. [14] also reported the long-time of freeze-drying of carrot slices when compared with vacuum microwave and air drying.

3.2 Water Activity

In spite of the high water content reduction (around 80% in dry basis, referred above), the OD only reduced the initial water activity (aw) from 0.990 to 0.935 (with the sucrose solution) and 0.900 (with the sorbitol solution), which is in agreement with previous studies [15]. During the freeze-drying process, the aw decreased significantly with the decrease of the water content, but the difference in the initial reduction observed with the OD did not quite reflect in the lower final aw. The subsequent aw reduction of samples was 5-fold, 3-fold and 3.5-fold for the control and the samples osmotically pre-treated with sucrose and sorbitol solutions, respectively.

Although GAB's model fitted well the experimental data (high R^2 and random and normally distributed residuals) (Figure 2), the values of its parameters presented high values of margin of error (data not shown), resulting in no significant differences among different conditions. Thus, the monolayer moisture content (Mm) that indicates the theoretical moisture at which a product presents maximum stability, did not present significant difference between the control and the freeze-dried osmotically pre-treated samples. Sette et al. [25] studied the effect of different pre-treatments, including OD, before freeze-drying of raspberries and found that the control samples presented higher Mm values than pre-treated samples.

Comparing the aw of the freeze-dried, the hot air dried and the microwave dried samples, all processes produced samples with final aw values around 0.3. In the control samples, the lowest aw was achieved after the freeze-drying, while in samples osmotically pre-treated with sucrose solution, no significant difference was observed between the final aw of the hot air dried and the freeze-dried samples, both achieved an aw of around 0.3. Samples pre-treated with sorbitol presented the same aw after all drying processes.

3.3 Quality of the Final Product

All the colour parameters were affected by the osmotic pre-treatment (Table 2). The luminosity, given by L*, was significantly affected by the freeze-drying process. After drying, all samples presented higher values of L*. The increase of the luminosity after the FD was also found by Sosa et al. [26] in apple disks with or without pre-treatment. The redness, reflected in the component a*, also increased during the drying process. Rudy et al. [10] also observed these increases in L* and a* in the FD of cranberries. The other parameters did not show a clear pattern in relation to the pre-treatment and/or subsequent FD. A decrease in the browning index of FD control samples was noted and b* (values not shown) was not affected. The total colour difference (ΔE) between the freeze-dried osmotically pre-treated samples did not present significant differences and the highest difference, $\Delta E = 16.67$, was noted for control freeze-dried samples. This high value of ΔE for the control sample is mainly due to a high increase in L* value. The FD did not have an effect on ΔE of the osmotically pre-treated samples.

The TPC of the fresh apple was 6.02±0.07 mg gallic acid.g DM-1. The FD process resulted in a loss of 48% of the total phenolic content (TPC) in the control samples (Table 2). Rahman et. al [27] observed a slight reduction of this compound in relation to the fresh samples of mango. Shofian et al. [28] also found TPC in fresh starfruit, mango, papaya and watermelon higher than in the freeze-dried samples.

There was no reduction of this compound in the pre-treated samples after the FD. As observed in a previous work, using a different drying method, microwave drying [24], the reduction of TPC occurred during the osmotic dehydration and it was around 80%.

The TPC of the dried control samples was higher than the osmotically pre-treated samples. These presented 73 and 62% less TPC than the control samples after the FD, when sucrose and sorbitol were used as osmotic agent, respectively. However, the difference between the samples treated with the different solutes was not significant.

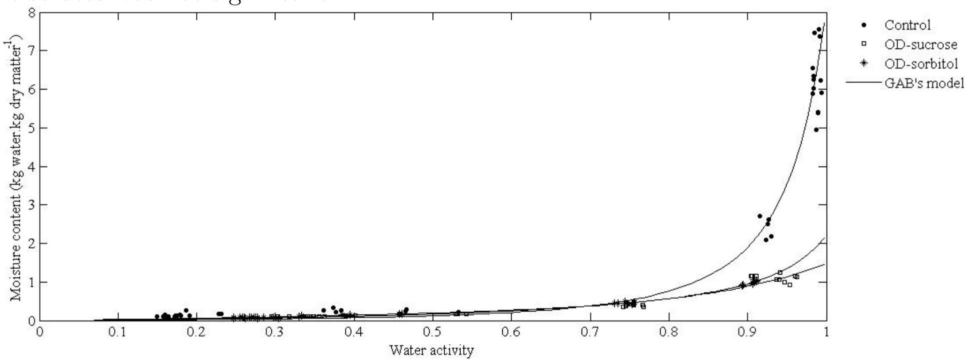

Figure 2. Experimental data and the fit of GAB's model during the freeze-drying of apple cubes

Table 2. Quality parameters of osmotically pre-treated apples cubes dehydrated by freeze-drying

Treatment	L*	a*	ΔE	Browning index	Total phenolic (mg of gallic acid. g DM -1)	Antioxidant activity (mg ascorbic acid. g DM -1)
fresh	69.39±1.79b,c	-4.78±0.54d	0	46.77±1.25c	6.02±0.07a	6.79±0.25a
control (FD)	85.03±3.23a	3.57±0.69c	16.67±3.12a	31.89±5.51d	3.14±0.69b	5.20±0.75b
OD sucrose	61.83±2.96d	-1.90±1.30b	7.61±2.45b	53.18±5.43b	0.96±0.11c	1.02±0.12c
OD sucrose + FD	69.71±2.35b	1.71±0.52a	9.04±2.03b	52.52±5.46b,c	0.84±0.19c	1.10±0.17c
OD sorbitol	62.35±3.75d	-1.50±1.43b	8.23±3.52b	59.09±5.80a	1.10±0.13c	1.24±0.16c
OD sorbitol + FD	65.95±5.92c	2.19±1.39a	8.01±2.39b	59.43±9.43a	1.20±0.15c	1.31±0.13c

Mean separation in columns: different letters mean that the values are significantly different ($P < 0.05$).

The antioxidant activity (AA) of the fresh apple was 6.79±0.25 mg ascorbic acid.g DM-1 and it decreased 23% after FD. The AA was higher in the control samples than in the osmotically pre-treated samples (Table 2). The same trend as for the TPC was observed. The correlation coefficient (R2) between the TPC and the antioxidant activity was 0.990, meaning the phenolic is the main responsible for the antioxidant activity [18].

4 Conclusions

The osmotic dehydration with a sorbitol solution, in alternative to sucrose, and combined with freeze-drying was studied. The osmotic dehydration pre-treatment had an influence on the mass transfer kinetics of the freeze-dried apple cubes, but it did not present a relevant advantage. The pre-treatment with the sucrose solution increased the drying rate, but it resulted in a lower quality, decreasing the total phenolic content and the antioxidant activity. Therefore, with respect to quality sorbitol is more recommended than sucrose as the osmotic agent. The freeze-drying process decreased significantly the water activity of the osmotically dehydrated apple cubes. After FD, the control samples presented lower final aw and lighter colour than the pre-treated samples.

Newton's, Page's, modified Page's, Henderson and Pabis', logarithmic and Weibull's models could describe well the moisture content during the freeze-drying process.

The freeze-drying resulted in a lower water activity when compared with hot air and microwave drying. However, it presented lower drying rate, which is a disadvantage in relation to the energy consumption.

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