DEHYDRATION AND REHYDRATION CHARACTERISTICS OF PRETREATED PUMPKIN SLICES

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ABSTRACT

The influence of an alternative chemical pretreatment on dehydration and rehydration of an Italian ecotype pumpkin was investigated. The pretreatment consisted of soaking the slices in a diluted solution of trehalose, sucrose and NaCl. Hot air-drying was performed in a convective dryer at temperatures of 55, 60, 65 and 70°C. Samples treated prior to drying showed a shorter (about 1/4) drying time, less volume shrinkage and colour changes, but showed higher rehydration capacity compared to untreated ones, especially in the range 55-65°C. Moreover, the pretreatment was effective in retention of total phenolic content and antioxidant activity. The Midilli model was the most appropriate for describing drying behaviour, while the Weibull model for rehydration.

1. INTRODUCTION

Pumpkin (*Cucurbita maxima*) belongs to *Cucurbitacae* family. Botanically it is a squash fruit, most commonly orange in colour when ripe, that has been used traditionally both as human and as animal feed (GUINÉ *et al.*, 2011). Its nutritive value is encouraging an increase in the consumption and its use for nutritional and technological applications. Pumpkin is rich in antioxidants and vitamins, which have an important health-protecting effect. It is also poor in total solids (AREVALO-PINEDO and MURR, 2006) and in calories, which means that it is adequate for low calories regimes and it is often recommended in diets (SHELKE *et al.*, 2015).

Fresh pumpkin should be stored at temperature between 10 and 13°C and relative air humidity between 50% and 70%. When stored at low temperature, unfavourable physiological processes occur. The above-mentioned processes cause chill damages. Therefore, it is desirable to use optimum methods of pumpkin preservation, appropriate for the specific final use of the fruit (SOJAK and GLOVACKI, 2010). Pumpkin is generally processed to obtain the juice, pomace, pickles, dried products in many countries worldwide.

Drying is an excellent method to preserve the pumpkin flesh that can add variety to meals and provide delicious and nutritious ready-to-eat crispy snacks. Dried pumpkin may be a finished product or a half-finished product, subject to further processing (SEREMET *et al.*, 2016). Dried and rehydrated pumpkins are key ingredients in dairy products, breakfast cereals, traditional foods (such as puddings, desserts, cakes, biscuits) and dietetic foods formulated for people suffering from physiological disorders or for healthy people with additional needs. Rehydration product behaviour must be known when a total or partial reconstitution is required (Contreras *et al.*, 2012).

Pumpkin slices are generally dried using the convective method (SOJAK and GLOVACKI, 2010), because of its simplicity and low cost. Using this technique, mass and heat transfer occur simultaneously (ADILETTA *et al.*, 2014). Hot air drying produces stable dehydrated products, but unfortunately their final quality (i.e. colour, texture) is drastically reduced when compared to the fresh product due to the high temperatures and longer times involved in the process (BRASIELLO *et al.*, 2017; BRASIELLO *et al.*, 2013; RUSSO *et al.*, 2013).

Drying combined with a pretreatment appears to be a cost-effective method of preservation. Several methods of pretreatment have been widely utilised: such as immersion in chemical solutions (ADILETTA *et al.*, 2016a), hot-water blanching (XIN *et al.*, 2015) and physical pretreatments (DI MATTEO *et al.*, 2000; SENADEERA *et al.*, 2014; ADILETTA *et al.*, 2016b). Pretreatments prior to drying have been reported to help reducing some of undesired changes such as antioxidant activity reduction, colour and textural changes. Also, they reduce drying time by relaxing tissue structure and yield good quality dried products (ADILETTA *et al.*, 2016a; SENADEERA *et al.*, 2014; ATKAS *et al.*, 2007; BRASIELLO *et al.*, 2011). In this way, when pretreatments are used, final products differ from those without pretreatment. The differences are evident in many properties, including also the rehydration capacity (PEREZ and SCHMALKO, 2009).

In the literature, several works have been reported on the effect of pretreatment on drying kinetics and quality of pumpkin. They include blanching, salt coating, osmotic dehydration, SO₂ or citric acid treatments. Many researchers have focused on novel anti-browning agents to replace sulphites (ADILETTA *et al.*, 2016a; FALADE and SHOGAOLU, 2010; MAYOR*ET al.*, 2011).

WORKNEH *et al.* (2014) studied the effect of two pretreatments on the quality of dried pumpkin slices: blanching (60°C for 1 min) and 10 % of salt solution (room temperature for 10 min). Salted pumpkins that were subjected to oven-drying at 60°C required shorter

drying time than those blanched to attain 10 % moisture content. Moreover, salted pumpkin slices showed higher total soluble sugars, ascorbic acid, sugar to acid ratio, pH value, lower total acidity and shorter time of drying (18 h) with respect to the untreated pumpkin slices (28.3 h).

FALADE and SHOGAOLU (2010) investigated the effect of three pretreatments on air-drying pattern and colour of pumpkin slices. Untreated, sulfited (1,000 ppm), blanched (100°C for 3 min) and osmotically pretreated pumpkins (40, 50 and 60°Brix) were air dried at 50-80°C. At 60°C fresh (untreated) pumpkin slices showed the higher initial drying rate compared to the pretreated ones. Moreover, sulfited and blanched pumpkin slices showed higher drying rate than the osmotically pretreated ones due to water removal during osmotic pretreatment of pumpkin. Similar trends were observed by air-drying at 50, 70 and 80°C. The difference in the drying rates of osmotically and un-osmotically treated pumpkin could be related to the increase in internal resistance to water movement caused mainly by shrinkage and solid uptake during the osmotic step.

Mayor *et al.* (2011) studied the changes in volume, density, porosity and shape factors of pumpkin tissue during osmotic dehydration carried out with solutions of sucrose, sodium chloride and mixtures of both solutes at different temperatures and air drying conducted at 70°C. The osmotic dehydration experiments were conducted with sodium chloride solutions (5, 10 and 20 kg/100 kg at 25, 38 and 12°C, respectively) and with binary solutions 3.75% NaCl-58% sucrose and 7.5% NaCl-45% sucrose (25°C). The authors observed a linear decrease of volume with water loss during osmotic dehydration: this decrease is more accentuated in the case of NaCl solutions, followed by sucrose solutions and NaCl/sucrose solutions.

In the studies reported above, blanching at high temperature and osmotic solutions of sugar and salt exceeding 10% for long contact time were used. The blanching pretreatment is used to: inactivate the enzymes, maintain the freshness, colour, stabilize the texture and nutritional quality, expel the air between the cells and destroy the microorganisms to some extent. However, blanching treatment causes undesirable changes in the quality properties of food such as the loss of soluble nutrients (i.e. sugars, minerals and vitamins) (XIN *et al.,* 2015). Moreover, it causes loss of aroma and negatively impacts the sensory properties associated with texture (LESPINARD *et al.,* 2009).

Dipping of plant tissue in solutions containing 15–30% sugars or salts for a long time results in shortening of the drying process and, hence, in lower energy requirements. Osmotic dehydration offers high retention of initial food characteristics, such as colour and flavour (SHELKE *et al.,* 2015). On the other hand, osmotic dewatering adversely affects reconstitution properties of dry material and causes softening of the tissue (LEWICKI, 2006).

In this framework, the aim of this work was to investigate the influence of an alternative pretreatment, by dipping pumpkin slices in a diluted solution of trehalose, NaCl and sucrose, on drying behaviour, rehydration capacity and some physico-chemical properties (i.e. colour, total phenolics, antioxidant activity, shrinkage) of pumpkin. The drying kinetics at four temperatures 55, 60, 65 and 70°C were fitted with different kinetic models found in literature. The effective moisture diffusivities were then estimated by using Fick's second law of diffusion for the present operating conditions. Also, the rehydration kinetics were fitted with empirical models.

2. MATERIALS AND METHODS

2.1. Sample preparation

The pumpkin used in this study is a *C. maxima* ecotype known as "di Teggiano" which is cultivated in Campania region, Italy. Fresh whole pumpkin was washed, peeled, sliced. Cylindrical slices with a diameter of 30 mm and thickness of 6 mm were prepared using a suitable steel mould. The zone near the peel (<10 mm) was removed because of its different texture. The initial moisture content was 0.93 g H_2O /g of sample (or on dry basis (db) 15.23±0.05 g H_2O /g db) (AOAC, 1990).

Two types of samples were used: (1) without pretreatment (UTR), with pretreatment (TR). The pretreatment was carried out by soaking the samples in an aqueous solution of 0.8% (w/v) trehalose, 0.1% (w/v) NaCl and 0.2% (w/v) sucrose for 5 min at 25°C. Following submersion, the samples were removed from the bath and blotted with tissue paper.

2.2. Drying kinetics: experiments

The drying experiments were conducted at constant temperatures of 55, 60, 65 and 70°C using a convective dryer (Zanussi FCV/E6L3) with a constant air flow rate of 2.3 m/s, until they reached a moisture content under 5% (wet basis) as suggested by GUINÉ *et al.* (2011). During drying at fixed times, pumpkin samples were withdrawn from the dryer and their weight was measured by a digital balance (mod. Gibertini E42, Italia). Drying tests were replicated three times at each temperature.

The results were reported in terms of moisture ratio:

$$M_R = (M_t - M_e)/(M_0 - M_e) \qquad (1)$$

where M_t is the actual moisture content (g H_2O/g db), M_0 is the initial moisture content (g H_2O/g db), M_e is the final moisture content at the end of process (g H_2O/g db) until no measurable weight change was observed, which is assumed equivalent to the equilibrium moisture content. All samples obtained at different drying temperatures were then characterized.

2.3. Drying kinetics: modelling procedure

Empirical models that are commonly applied for vegetables were here adopted (Table1) (HENDERSON and PABIS, 1961; PARK *et al.*, 2002; DOYMAZ, 2007; KASHANINEJAD and TABIL, 2004; MIDILLI *et al.*, 2002; HENDERSON, 1974).

Table 1. Mathematical models applied to drying curves.

Model name	Eqution	Reference
Henderson and Pabis	$M_R = aexp^{(-kt)}$	Henderson and Pabis (1961); Park *et al.* (2002)
Page	$M_R = exp^{(-kt)}$	Doymaz (2007); Kashaninejad and Tabil (2004)
Midilli	$M_R = aexp^{(-kt)} + bt$	Midilli *et al.* (2002)
Two term	$M_R = a_1exp^{(-k_1t)} + a_2exp^{(-k_2t)}$	Henderson (1974)

The empirical constants for the drying models were determined from normalized drying curves (M_R vs time) at each drying temperature. Non-linear least square regression

analysis was used to evaluate the parameters of the selected model with the Levenberg-Marquardt procedure.

The goodness of fit for each model was evaluated based on the statistical parameters: R^2, RMSE, χ^2. These parameters were calculated from the following equations:

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

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(M_{R,pre,i} - M_{R,exp,i}\right)^2}{N-z} \qquad (3)$$

where $M_{R,exp,i}$ and $M_{R,pre,i}$ are experimental and predicted dimensionless moisture ratios, respectively, N is the number of observations, and z is the number of constants. R^2 was used as the primary comparison criteria for selecting the best model to fit the experimental data. Its value should be higher and close to one. Also, a model is considered better than another if it has a lower value of RMSE and χ^2.

The continuous decrease in moisture ratio with increase in drying time shows that the results can be interpreted by using Fick's second law of diffusion. Considering pumpkin cylindrical slice to be infinite cylinder, the solution of Fick's diffusion equation was as follows (CRANK, 1975; SENADEERA *et al.*, 2003):

$$M_R = \frac{(M_t - M_e)}{(M_0 - M_e)} = \sum_{n=1}^{\infty}\frac{4}{\beta_n^2}exp\left[-\frac{\beta_n^2 D_{eff}t}{r_c^2}\right] \qquad (4)$$

where, M_R is the dimensionless moisture ratio, M_t is the moisture content on dry basis at time t (g H_2O/g db), M_0 is the initial moisture content (g H_2O/g db), M_e is the equilibrium moisture content (g H_2O/g db), β is the roots of the Bessel function, D_{eff} is the effective diffusion coefficient (m^2/s), r_c is the cylinder radius and n is the positive integer.

The aforementioned equation is based on the following assumptions: i) isothermal drying conditions, ii) constant effective diffusivity, iii) negligible shrinkage, iv) uniform initial moisture content, v) negligible external resistance. For long drying times (M_R< 0.6), when r_c is small and t is large, limiting form of equation is obtained for cylindrical geometry by considering only the first term in the series expansion.

Then Eq. (4) can be written as Eq. (5):

$$M_R = \frac{(M_t - M_e)}{(M_0 - M_e)} = \frac{4}{\beta_1^2}exp\left[-\frac{\beta_1^2 D_{eff}t}{r_c^2}\right] \qquad (5)$$

A general form of Eq (5) can be written in logarithmic form (Eq. 6):

$$\ln M_R = A - Bt \qquad (6)$$

where, the constant B is $\frac{\beta_1^2 D_{eff}}{r_c^2}$. The slope B is calculated by plotting $\ln M_R$ versus time according to Eq. (6). The effective diffusivity is the derived from the slope B.

The dependence of the effective moisture diffusivity on temperature is generally described by the Arrhenius equation as given in Eq. (7).

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

Where D_o (m²/s) is the temperature-independent constant, E_a (J/mol) the activation energy, R (8.314 J/mol K) the universal gas constant and T (K) the absolute temperature. Activation energy was calculated by plotting the natural logarithm of D_{eff} against the reciprocal of the absolute temperature.

2.4. Chemical and physical characterization

2.4.1 Colour parameters

Pumpkin slices colour was determined by two readings on the two different symmetrical faces of the slices in each replicate, using a Minolta Chroma Meter II Reflectance CR-300 colorimeter (Minolta, Osaka, Japan), calibrated with a white standard tile. It was recorded using CIE L*a*b* uniform colour space (CIE-Lab). The colour coordinate L* measures the whiteness value of a colour and ranges from black at 0 to white at 100. The chromaticity coordinate a* measures red when positive and green when negative, and the chromaticity coordinate b* measures yellow when positive and blue when negative (BERNS, 2000). Also, the overall colour difference (ΔE) (Eq.8), was calculated from L*, a* and b* values and used to describe the colour change during drying.

$$\Delta E = \sqrt{(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2} \tag{8}$$

2.4.2 Total phenolic content and antioxidant activity (EC50)

Total phenolic content (TPC) was extracted from fresh and dried samples with solution MeOH:H_2O=80:20 for three times following the method described by DINI *et al.* (2013). All extractions were performed in triplicate. The concentration of TPC was measured using the Folin Ciocalteu reagent (ADILETTA *et al.*, 2017). The absorbance was evaluated after 90 min at room temperature at $\lambda = 760$ nm using a spectrophotometer (Lambda Bio 40; Perkin Elmer, Waltham, MA, USA). Quantification was based on a standard curve generated with gallic acid.
Total phenolic content of extracts were then expressed as mg gallic acid equivalents per gram of dried basis (mg GAE/g db) that was derived from a calibration curve.
The free radical scavenging capability of the extract was determined using the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay (Dini *et al.*, 2013). Aliquots (200 mL) of extract solutions were added to 3 mL of DPPH solution ($6·10^{-5}$ mol/L). Then, the absorbance of DPPH without antioxidant (control sample) was used for baseline measurements. The scavenging activity was expressed as the 50% effective concentration (EC_{50}), which was defined as the sample concentration (mg) necessary to inhibit the DPPH radical activity by 50% during a 60-min incubation.

2.5. Shrinkage

The initial pumpkins volume (V_0) was calculated by measuring for each sample (about 10 slices) diameter and thickness by means of a digital Vernier caliper (0.01 mm accuracy). At given times during drying experiments for the same slices, the diameter and the height (or thickness) of the sample were measured and the volume (V) was calculated. In order to reduce the measurement error during drying, both dimensions were measured at different positions of the sample and their average value was considered. For the evaluation of shrinkage during drying, the mean volume shrinkage (V/V_0) was reported as a function of the relative moisture ratio M_R (ADILETTA *et al.*, 2014).

2.6. Rehydration tests

Rehydration curves were obtained by soaking the dried samples at room temperature in distilled water. Approximately 1 g of dried samples was added to 100 mL distilled water. The samples were removed, dried off with tissue paper and weighed at regular intervals. Weights of dried and rehydrated samples were measured by using an electronic digital balance (mod. Gibertini E42, Italia). The measurements were repeated three times.

The curves were reported in terms of moisture ratio (M_t/M_d) versus time, where M_t is the actual and M_d is the initial moisture content on dry basis of the dried sample.

The degree of structural disruption after the process was evaluated by means of the coefficient of rehydration defined as follows:

$$COR = \frac{m_{rh}(100 - X_0)}{m_{dh}(100 - X_{dh})} \qquad (9)$$

where m_{rh} is the mass of the rehydrated sample (kg), m_{dh} is the mass of dried sample prior to the rehydration test (kg), X_0 is the moisture percentage of the sample before drying (% wet basis), and X_{dh} is the moisture percentage of the dried sample prior to the rehydration test (% wet basis) (MCMINN and MAGEE, 1997). Each test was performed in triplicate and the reported data were average of these three tests.

2.7. Rehydration kinetics: modelling

The rehydration kinetics were described by the models reported in Table 2 (PELEG, 1988; GOULA and ADAMOPOULOS, 2009). The Peleg equation is a two-parameter, non-exponential, empirical model for the description of moisture sorption curves. This model has been widely used due to its simplicity and has been reported to adequately describe the hydration of various foodstuffs (PELEG, 1988; GARCÍA-PASCUAL*et al.*, 2006; MOREIRA *et al.*, 2008).

In the Peleg equation t is the time (min), A_1 is a kinetic parameter (Peleg rate constant), A_2 is a parameter related to the equilibrium moisture content (Peleg capacity constant), M_t is the moisture content at time t, and M_d is the moisture content of dried sample used for rehydration test.

Furthermore, for the rehydration process, a power law equation based on the probabilistic Weibull model was used. In the Weibull equation A, β and α are kinetic constants of the model. The Weibull distribution has found wide application in food processing, and has been suggested for food rehydration process by several authors (GOULA and ADAMOPOULOS, 2009; MARABI *et al.*, 2003; VEGA-GÁLVEZ *et al.*, 2009).

Table 2. Mathematical models applied to rehydration curves.

Model name	Equation	Reference
Peleg	$M_t/M_d = 1 + (t/A_1 + A_2 t)$	Peleg (1988)
Veibull	$M_t/M_d = A + (1 - A)exp\left[-\left(\frac{t}{\beta}\right)^{\alpha}\right]$	Goula and Adamopoulos, (2009)

Non-linear least square regression analysis was used to evaluate the parameters of the selected model with the Levenberg-Marquardt procedure. Fit quality of the models used on the experimental data was evaluated by means of statistical tests: linear regression

coefficient (R^2), root mean square error (RMSE) (Eq. 2), chi-square (χ^2) (Eq. 3) and the mean relative error, MRE (Eq. 10), which indicates the relative error of the predictions, and values below 10% are indicative of a reasonably good fit for most practical purposes (GOULA and ADAMOPOULOS, 2009). Therefore, the lowest values of MRE, RMSE and χ^2, together with the highest values of R^2, were selected as optimum criteria to evaluate fit quality of the models used.

$$MRE = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{M_{R,pre,i} - M_{R,exp,i}}{M_{R,exp,i}} \right| \qquad (10)$$

2.8. Statistical analysis

The means and standard deviations of experimental results were calculated from three replicates. One-way ANOVA (analysis of variance) at the level of significance $p < 0.05$ using Tukey's HSD test was performed for comparison of means in the case of colour, total phenolic content and antioxidant activity.

3. RESULTS AND DISCUSSION

3.1. Drying kinetics and empirical models

The average moisture content of fresh samples was 15.23±0.05 g water/g db (93.84% wb). Pumpkin slices were dried up to the final moisture of 0.60±0.10 g water/g db (about 4% wb) using different air temperatures (55, 60, 65 and 70°C) at 2.3 m/s.
The effect of air temperature and pretreatment on the drying kinetics (M_R versus drying time) of pumpkin slices is shown in Fig. 1a-d. It can be observed that after an initial constant rate drying period, the drying process for treated/untreated pumpkins occurred in the range of the falling-rate period. In this latter stage the diffusion is the dominant mechanism governing moisture transport inside the sample. This result is in agreement with the drying behaviour of various vegetables and also for pumpkin (GUINÉ et al., 2011; DOYMAZ, 2007; AGRAWAL and METHEKAR, 2017; ONWUDE et al., 2016).
By analysing the Fig. 1, the plateau value of M_R (<0.05) for the UTR samples was obtained at the following times: 260, 220, 180 and 140 min at the air-drying temperatures of 55, 60, 65 and 70°C, respectively.
Pretreatment affects significantly drying time. Samples dipped prior to drying in sodium chloride, sucrose and trehalose solution (at low concentration) had a shorter drying time compared to control samples: at each temperature, the treated samples reached the plateau of M_R in a shorter time. It was equal to 200, 160, 140 and 120 min at 55, 60, 65 and 70°C, respectively. These results show that pretreatment solution contributed to reduce the internal mass transfer resistance that moisture encounters during drying.
Such behaviour is probably due to sugars, which effect on cell components results mainly from protecting functionality of proteins and stabilising the three-dimensional structure of protein (LEWICKI, 1998).
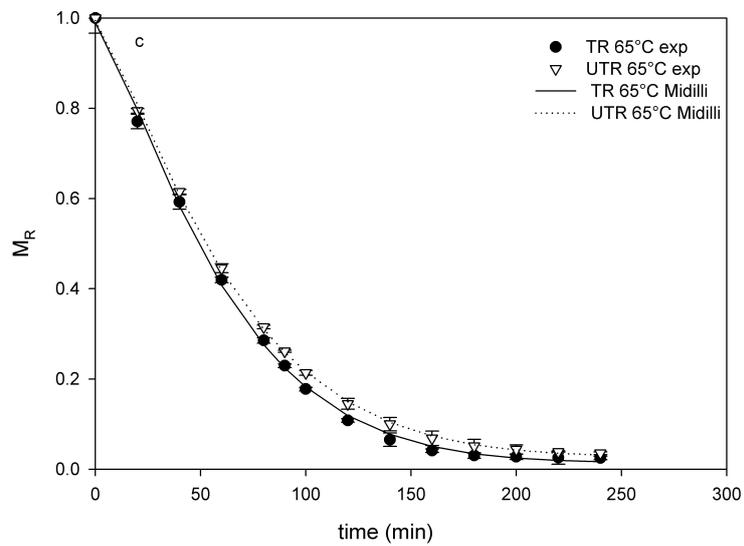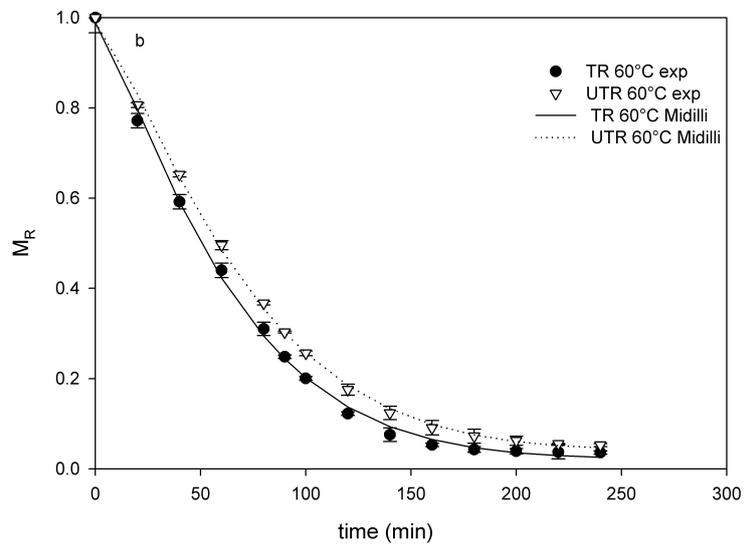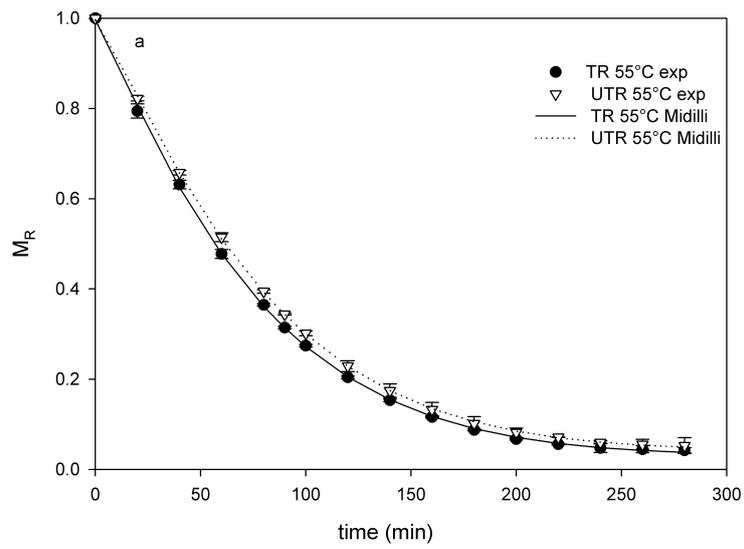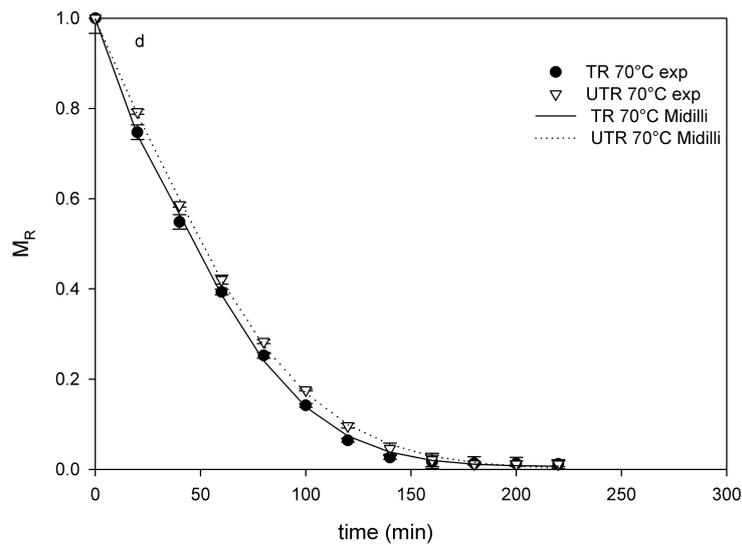
Figure 1. Experimental (symbols) and predicted (lines) drying curves of untreated (UTR) and pretreated (TR) samples at (a) 55°C, (b) 60°C, (c) 65°C and (d) 70°C.

Disaccharides such as trehalose or sucrose maintain general protein structure in the dry state, hence, the membrane is protected and upon rehydration its functionality is restored. With regard to the effect of NaCl, CURRY *et al.* (1976) suggested that NaCl penetrates tissue as ions and reassociates upon drying to form crystals. During rehydration the crystals of NaCl dissociate and form concentrated spots of Na and Cl ions. Solvation of the ions results in faster and better rehydration, as described in paragraph 3.6.

The moisture ratio data of pumpkin slices dried at different temperatures with and without pretreatment were fitted with the four models listed in Table 1. The values of R^2, χ^2, RMSE are summarized in Table 3.

Nonlinear regression was used to obtain each parameter value of every model. The best model describing the thin-layer drying characteristics of pumpkin slices was chosen as the one with the highest R^2 values and the lowest χ^2 and RMSE values. The values of parameters for each model were reported in Table 4.

The results in Table 3 show that all R^2 values are greater than 0.988, indicating a good fitting. The Midilli model gave the highest R^2 value, which varied from 0.9999 to 0.9982 for both UTR and TR samples in the experimental conditions considered in this study. The values of correlation coefficients RMSE and χ^2 for the Midilli model were the lowest for all the models considered. From the Tables 3-4, it is obvious that the Midilli model represents the drying characteristics of pretreated and untreated pumpkins better than the other models (Henderson and Pabis, Page or Two Term) considered in this study. These results confirm previous findings where Midilli model was found to be suitable in describing the drying kinetics of fruits and vegetables such as apple slices (ZAREIN *et al.*, 2013), chili (MIHINDUKULASURIYA *et al.*, 2013), mango slices (CORZO *et al.*, 2011) and pumpkin slices (AKPINAR, 2006).

Comparison between experimental data and best-fitting model results were reported in Fig 1 (a-d).

Table 3. Correlation coefficients (R^2, RMSE, χ^2) of the drying models.

Model name	Temperature (^{o}C)	Treated			Untreated		
		R^2	RMSE	χ^2	R^2	RMSE	χ^2
Henderson and Pabis	55	0.9983	0.0116	0.0002	0.9975	0.0144	0.0002
	60	0.9931	0.0255	0.0008	0.9931	0.0251	0.0007
	65	0.9920	0.0284	0.0009	0.9942	0.0234	0.0006
	70	0.9896	0.0359	0.0015	0.9883	0.0391	0.0018
Page	55	0.9992	0.0084	0.0001	0.9988	0.0106	0.0001
	60	0.9978	0.0142	0.0002	0.9979	0.0139	0.0002
	65	0.9985	0.0117	0.0002	0.9991	0.0097	0.0001
	70	0.9972	0.0174	0.0004	0.9989	0.0113	0.0001
Midilli	55	0.9998	0.0039	0.0000	0.9999	0.0027	0.0000
	60	0.9982	0.0125	0.0002	0.9999	0.0095	0.0001
	65	0.9988	0.0106	0.0002	0.9996	0.0057	0.0001
	70	0.9993	0.0083	0.0001	0.9995	0.0069	0.0001
Two Term	55	0.9983	0.0116	0.0002	0.9975	0.0144	0.0003
	60	0.9931	0.0255	0.0009	0.9931	0.0251	0.0009
	65	0.9920	0.0284	0.0011	0.9942	0.0234	0.0008
	70	0.9896	0.0359	0.0019	0.9883	0.0391	0.0023

Table 4. Parameters of the Midilli model for drying kinetics.

Model name	Temperature (^{o}C)	Parameter	Sample	
			Treated	Untreated
Midilli	55	a	0.9965	0.9971
		k	0.0073	0.0056
		n	1.1298	1.1729
		b	0.0001	0.0001
	60	a	0.9892	0.9896
		k	0.0052	0.0038
		n	1.2473	1.2813
		b	0.0001	0.0001
	65	a	0.9899	0.9944
		k	0.0047	0.0049
		n	1.2792	1.2539
		b	0.0000	0.0001
	70	a	0.8375	0.9115
		k	0.0008	0.0016
		n	1.6710	1.5163
		b	0.0000	0.0000

3.2. Calculation of effective diffusivity and activation energy

Effective diffusivity values for UTR and TR samples at different drying temperatures are reported in Table 5. Effective diffusivity was calculated using equations (Eq. 4-6) described in the Materials and Methods section.

Table 5. Effective moisture diffusivity for drying of untreated and treated pumpkins.

Temperature (^{o}C)	D_{eff} (m^2/s)	
	Untreated	Treated
55	6.75×10^{-9}	7.07×10^{-9}
60	6.87×10^{-9}	7.43×10^{-9}
65	7.68×10^{-9}	8.59×10^{-9}
70	8.51×10^{-9}	9.39×10^{-9}

The D_{eff} values of pretreated samples were higher than those of the untreated samples as shown in Table 5. These values are within the range of $6.75 \cdot 10^{-9}$- $8.51 \cdot 10^{-9}$ m^2/s and $7.073 \cdot 10^{-9}$- $9.39 \cdot 10^{-9}$ m^2/s for UTR and TR samples, respectively. This means that the pretreatment considered in this study facilitates water transport from inside to the pumpkin surface because of the preservation of pumpkin structure.

The D_{eff} values obtained for pretreated pumpkin in this study were higher than those of $0.13-4.27 \cdot 10^{-9}$ m^2/s for pumpkins oven dried at 40-80°C reported by TUNDE-AKINTUNDE and OGUNLAKIN (2011), and $3.88-9.38 \cdot 10^{-10}$ m^2/s obtained for pumpkin slices oven dried at 50-60°C. A plot of ln D_{eff} versus $1/T$ was reported in Fig. 2 and the activation energy (E$_a$) of UTR and TR samples dried in the range 55-70°C was obtained from Eq. (7).

The values of activation energy were found to be 28.28 and 18.63 kJ/mol for UTR and TR slices, respectively. This is an indication that less energy is required for the drying of TR samples, hence, the pretreatment aids moisture diffusion and evaporation and thus reduces energy involved in the drying process.
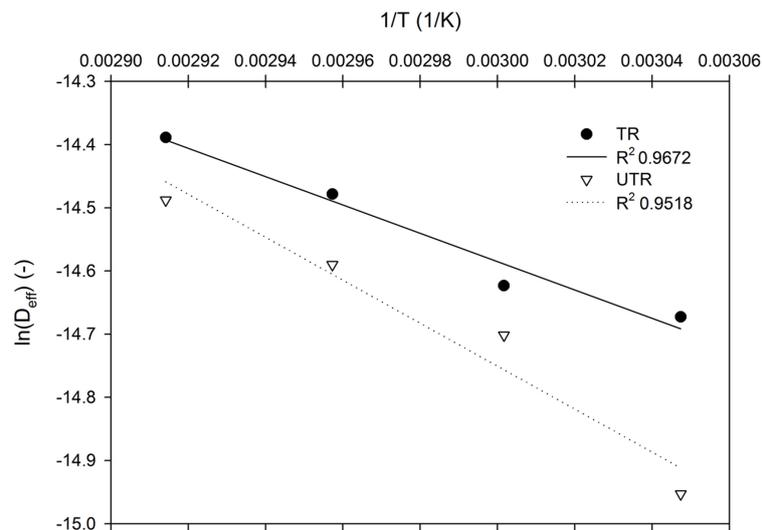
Figure 2. Relationship between diffusivity and absolute temperature for untreated (UTR) and treated (TR) samples.

3.3. Colour evaluation

The colour of dried products is an important quality factor because it reflects the sensory appeal and the quality of the foods. The average values of the colour parameters, L^* (lightness), a^* (redness), b^* (yellowness) and (ΔE) (total colour change), for fresh and dried pumpkins are presented in Fig. 3. The drying process determined a decrease of $L^*a^*b^*$ values for UTR samples with respect to fresh one. On the contrary, when the pumpkin was treated before drying, the colour values do not change significantly (p<0.05) after drying process, except for the a* value that decreases significantly at 70°C. Significant differences between UTR and TR samples dried at different temperatures were observed in Fig. 3.
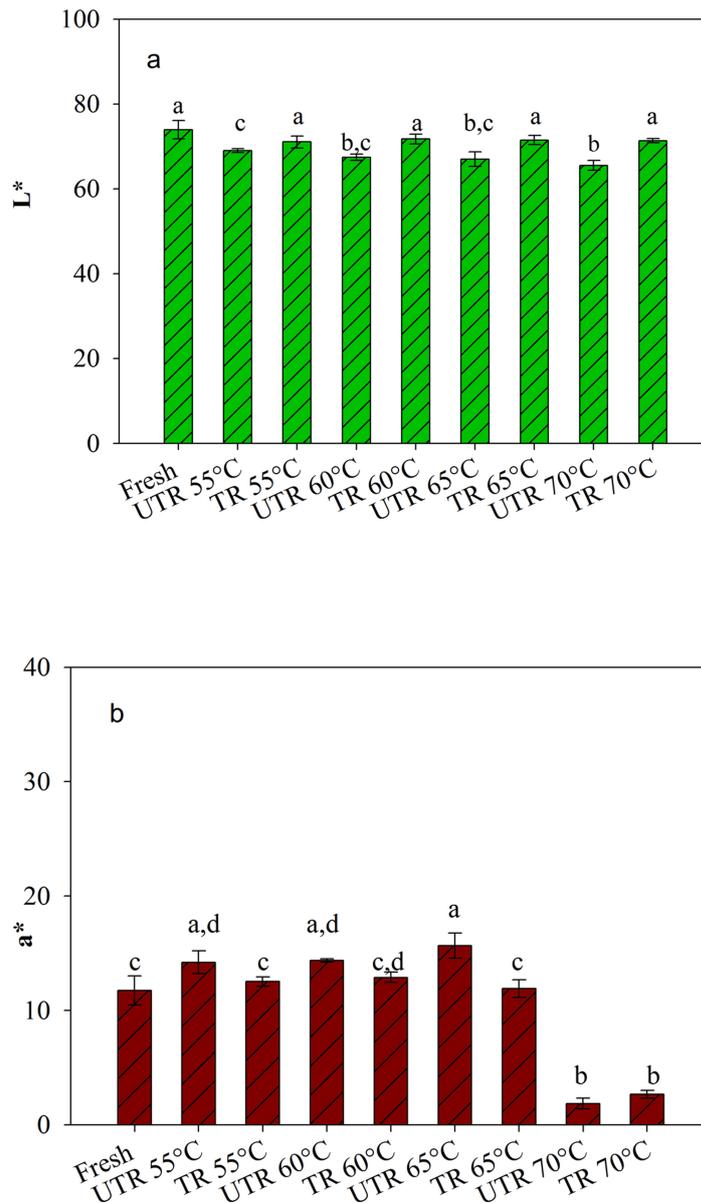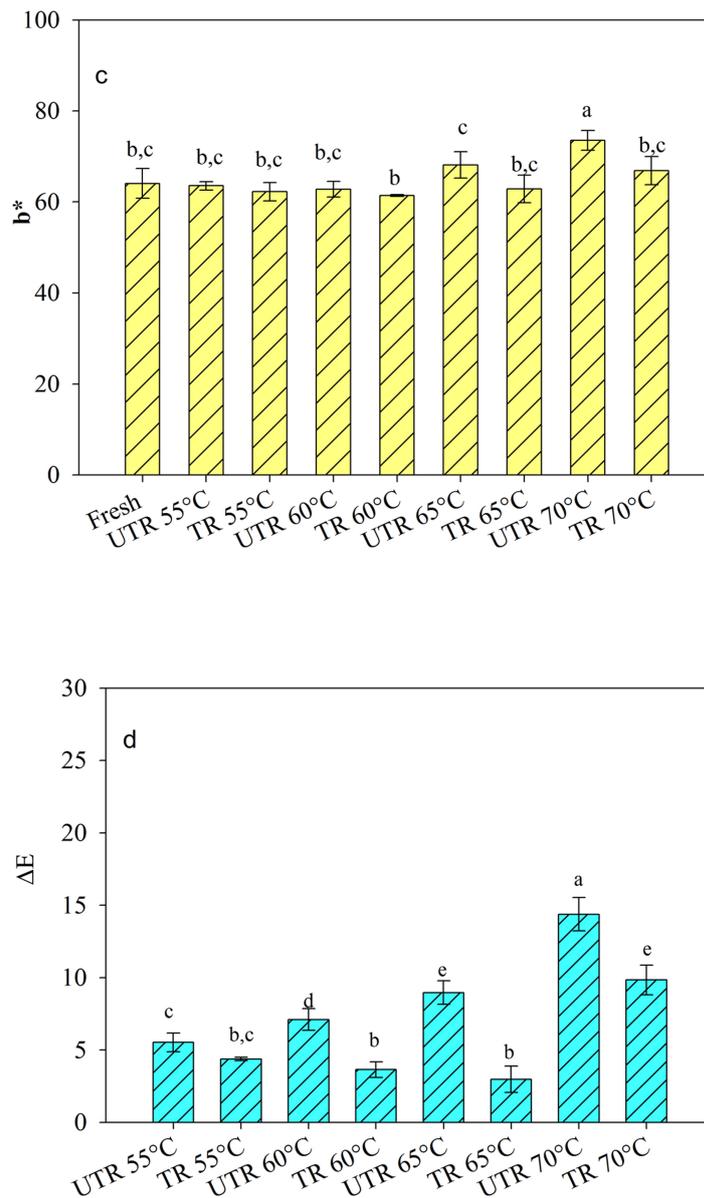
Figure 3. Colour parameters L* (a), a* (b), b* (c) and ΔE (d) for fresh, untreated (UTR) and pretreated (TR) dried samples at 55, 60, 65 and 70°C.

In particular, the lightness (L*), a property that varies from 0 (black) to 100 (white), of TR pumpkins was similar to fresh sample ($p < 0.05$) and higher than that of UTR ones. Among all samples analysed, the lowest lightness was found in the UTR samples dried at 70°C. The loss of lightness may be explained by the degradation of thermo-labile pigments resulting in the formation of dark compounds that reduce luminosity, and non-enzymatic browning reaction due to heat effect, as reported by DUTTA *et al.* (2006) and GONCALVES *et al.* (2007). However, the effect of temperature on L* coordinate was smaller than that on a* and b* parameters, which turned the samples as the temperature rises.

For the greenness-redness parameter (a*), no significant differences were found between fresh and TR samples dried at 55, 60 and 65°C, while the TR one dried at 70°C presented a redness value almost ten times lower. With regard to the UTR samples, the redness values were higher than those of fresh and dried TR samples up to 65°C. At 70°C both samples became darker, and redness and vivid characteristics were lost. These colour alterations may be explained by heat carotenoid degradation; non-enzymatic browning (Maillard reaction) could also cause the degradation of colour.

A significant increase of ΔE was observed between fresh and UTR samples ($p < 0.05$) at increasing temperatures: at 70°C the maximum ΔE was obtained. Herein, both non-enzymatic browning and heat-sensitive component loss probably contributed to the changes of UTR surface colour. A significant discoloration also for TR samples was observed at 70°C. While at 55-65°C, the total colour variation (ΔE) for TR pumpkins showed the lowest values, indicating that the minimum difference in colour from the fresh sample was obtained in this temperature range.

In conclusion, the colour data showed that the pretreatment reduced the browning and preserved the L*a*b* values of pumpkin samples up to a temperature of 65°C.

3.4. Total phenolic content and antioxidant activity (EC50)

During the drying process pumpkins slices were exposed to high temperature for a long time (about 300 min), which contributed to a loss of antioxidants (ADILETTA *et al.*, 2016b). Hence, the search of the optimal conditions (pretreatment and drying temperature) necessary to preserve the original antioxidant activity is a key factor in drying process. Results on total phenolic content and antioxidant activity were summarized in Table 6.

Table 6. Total phenolic content and antioxidant activity of fresh and dried samples.

Sample	EC50 (mg/mL)	TCP (mg(GAE)/100g db)
Fresh	12.10[h]±0.05	662.41[a]±30.36
UTR dried at 55° C	43.22[d]±1.08	258.01[e]±10.21
TR dried at 55° C	19.41[g]±0.11	486.25[b]±11.04
UTR dried at 60°C	49.56[c]±1.18	215.83[f]±12.54
TR dried at 60° C	22.28[f]±0.08	414.0[c]±10.12
UTR dried at 65°c	64.54[b]±2.41	170.11[g]±8.27
TR dried at 65°C	33.84[e]±1.04	363.26[d]±14.55
UTR dried at 70°C	71.81[a]±2.87	59.14[h]±6.57
TR dried at 70°C	51.49[c]±1.94	182.07[g]±9.54

Fresh pumpkin had the highest total phenolics (662.41 mg GAE/100g db). The drying of pumpkins, as the temperature increased, induced a decrease in the total phenolic content for UTR samples (reduction range of 61-91% in the temperature range 55-70°C).

The pretreatment was effective in retention of total phenolic content because it reduces the drying times: in the temperature range analysed a reduction of 28, 37, 45% and 71% was obtained at 55, 60, 65 and 70°C, respectively.

The higher levels of phenolics might be responsible of the higher antioxidant activity of the different pumpkin samples as shown in Table 6. Fresh sample had the highest antioxidant activity equal to EC$_{50}$ value of 12.10±0.05 mg/mL. The samples subjected to

pretreatment exhibited higher antioxidant activities than those of the samples without pretreatment (Table 6). Therefore, the antioxidant activity of samples dried in the range 55-65°C can be successfully preserved when the pretreatment was applied before drying.

3.5. Shrinkage effect

The removal of water during drying of biological products leads to cellular structural modifications due to reduced tension inside the cells. This phenomenon causes alterations in the shape and dimension of products including volume shrinkage (BRASIELLO *et al.*, 2017; ADILETTA *et al.*, 2015).

The Fig. 4 shows the variation of V/V_0 as a function of moisture ratio M_R during drying at the four temperatures. For both TR and UTR samples, the volume ratio V/V_0 showed a linear decrease with the moisture ratio
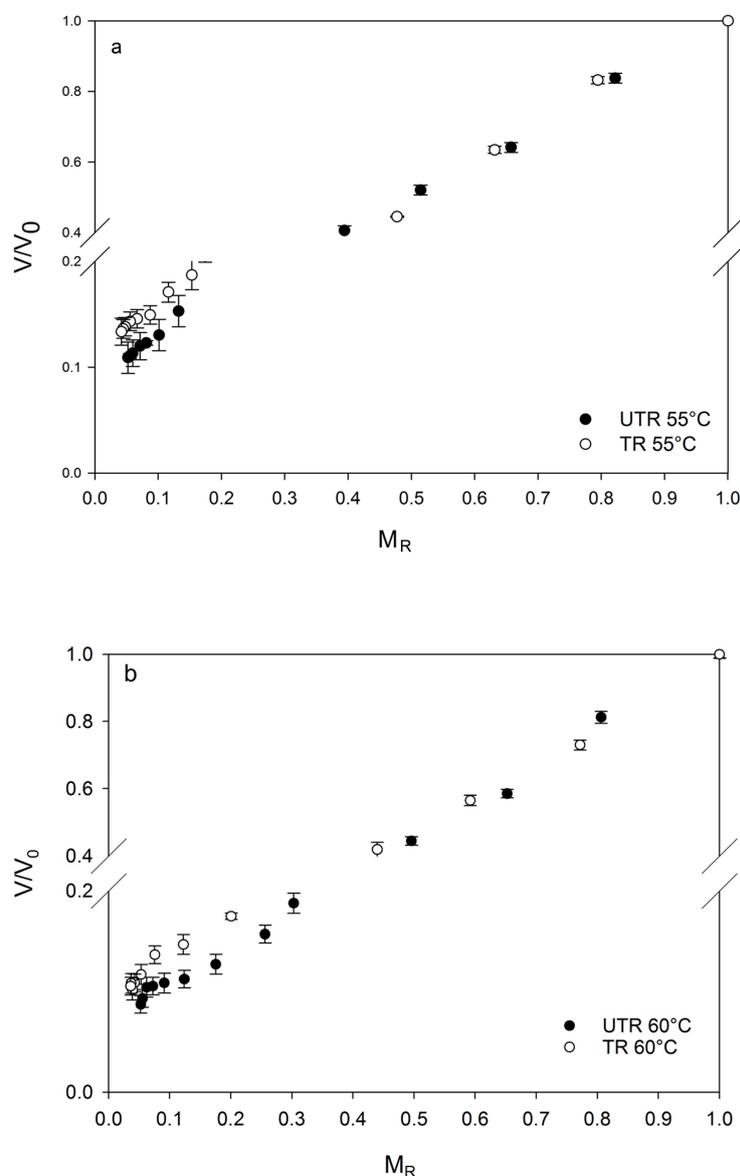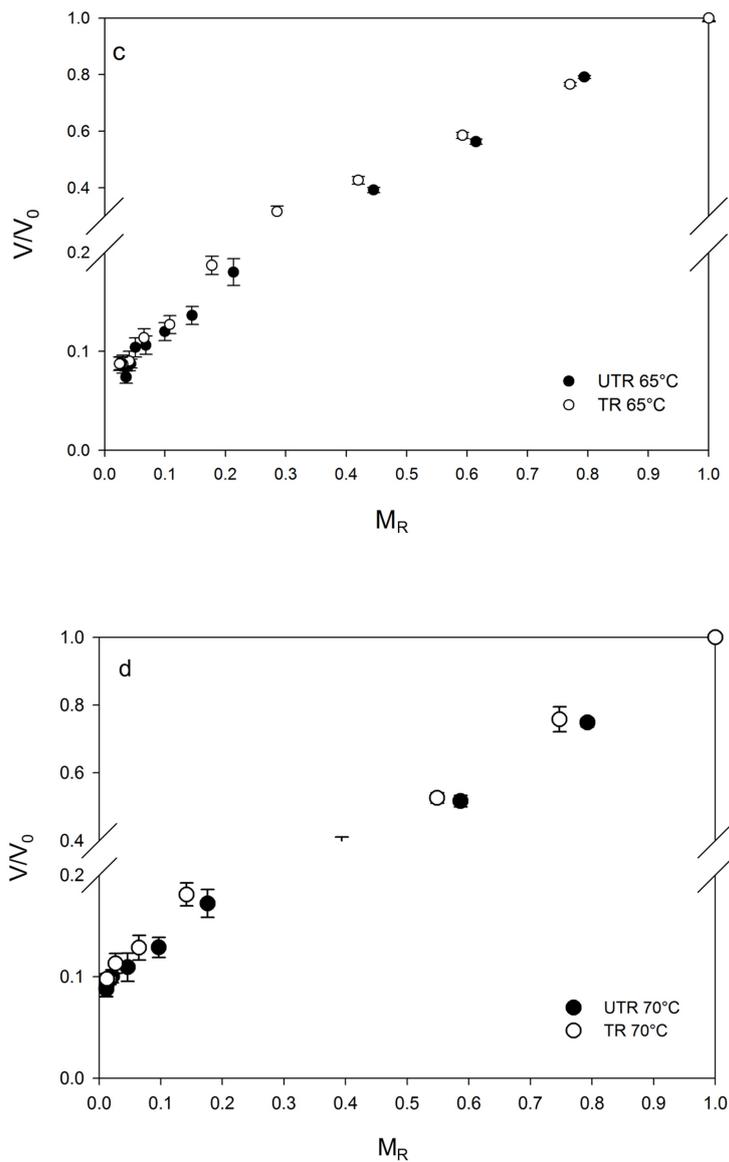
Figure 4. Volume ratio (V/V$_0$) vs moisture ratio (M_R) during pumpkins drying at: 55°C (a), 60°C (b), 65°C (c) and 70°C (d).

In order to quantify the effect of shrinkage, the V/V$_0$ ratio was fitted by using a linear relationship with the moisture ratio as (Mayor *et al.*, 2011):

$$\frac{V}{V_0} = \beta_1 + \beta_2 \frac{M_t}{M_0} \qquad (11)$$

The values of the fitting parameters and of the correlation coefficient (R^2) of Eq (11) were reported in Table 7. It was found that in the case of TR samples the β_1 value, which represents the V/V$_0$ ratio when pumpkin is completely dried, was higher than that of the UTR samples for each temperature investigated. The higher β_1 value was found for

pumpkin treated before drying at 70°C, where probably a porous outer rigid crust that fixes the slices volume at early stages of drying process was formed.

It can be concluded that the pretreatment reduces volume shrinkage and structure modifications, assuring, as confirmed by drying kinetics and D_{eff} values, a faster transport of water from inside to the surface of the product and then evaporation.

Table 7. Fitting parameters and correlation coefficient (R^2) of the shrinkage correlation.

Temperature (°C)	Treated			Untreated		
	β₁	β₂	R²	β₁	β₂	R²
55	0.0686	0.9060	0.9887	0.0390	0.9431	0.9955
60	0.0515	0.8984	0.9992	0.0158	0.9497	0.9889
65	0.0459	0.9318	0.9960	0.0216	0.9356	0.9881
70	0.0689	0.8980	0.9920	0.0541	0.8782	0.9847

3.6. Rehydration capacity

Rehydration capacity is an important physical property of dried pumpkin, because it reflects the intrinsic property and molecular structure of the dried product. Rehydration is a diffusion process, during which water moves from the outside of the cells into the interior, and the rehydration capacities of samples depend on the pretreatment and the drying process that were used (ADILETTA *et al.*, 2016a). The rehydration capacity of dried pumpkin slices was quantified using the coefficient of rehydration (COR): the degree of structural disruption after the process.

The coefficient of rehydration of UTR and TR pumpkins dried at 55°C, 60°C, 65°C and 70°C are presented in Fig. 5.

The shrinkage that takes place during dehydration prevents rehydration and produces products with lower rehydration capacity. As seen in Fig. 5, the COR of all TR samples resulted in higher rehydration in comparison with UTR samples. The highest values of coefficient of rehydration were observed in the case of TR samples dried at 60 and 65°C (70 and 68%, respectively), followed by TR samples dried at 55 and 70°C (62 and 57% respectively), while it was minimum in the untreated samples.

The higher COR values might be the result of the preservation of the porous structure developed during drying, which promotes improved rehydration of the samples (BADWAIK *et al.*, 2014) as we already observed for eggplants in a recent study (ADILETTA *et al.*, 2016a).

3.7. Rehydration kinetics

Experimental rehydration curves of pumpkin slices dried at different temperatures are shown in Fig. 6. It can be observed that the drying temperature and the pretreatment influenced water absorption of pumpkins. All curves showed typical rehydration behaviour with a higher water absorption rate at the beginning of the process, then the rate decreases.

It was observed that the moisture ratio (M_t/M_d) ratio of the TR samples was higher than that of the untreated ones. These latter samples showed lesser rehydration after longer drying periods, indicating the possible presence of shrunken and closed structures that obstacle the absorption of water in agreement with shrinkage results (Fig. 4).

To examine the controlling mechanism of the rehydration processes, Peleg and Weibull models were used to test experimental data. The best rehydration kinetic curves obtained by the rehydration experiments are reported in Fig. 6 with experimental data.
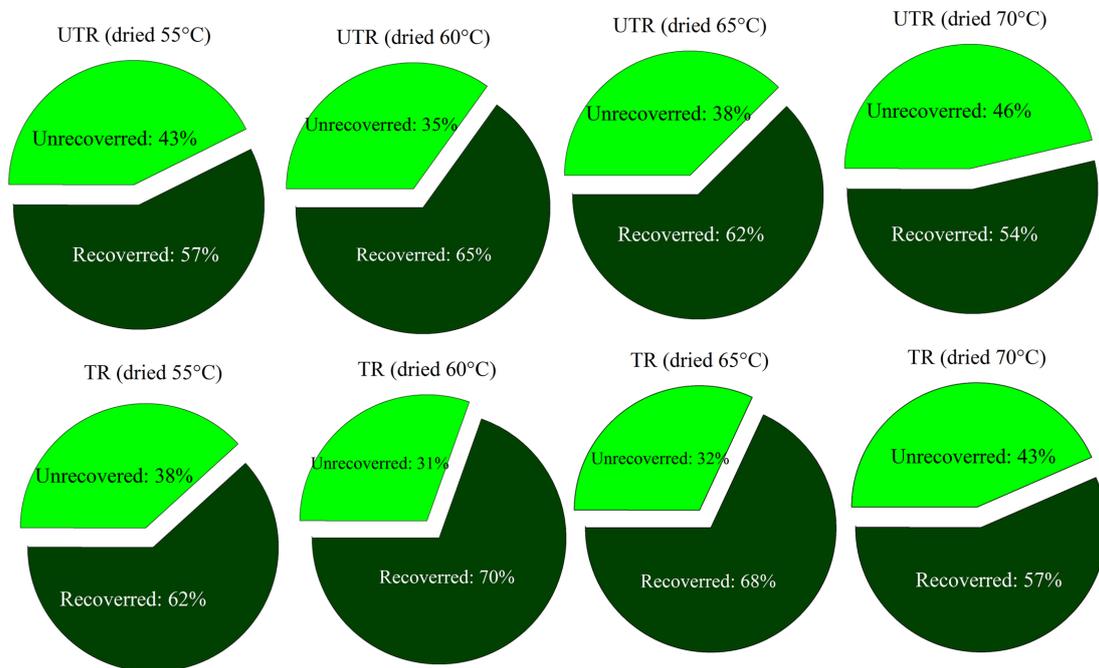
Figure 5. Coefficients of rehydration (COR) for pumpkin samples dried under different temperatures.
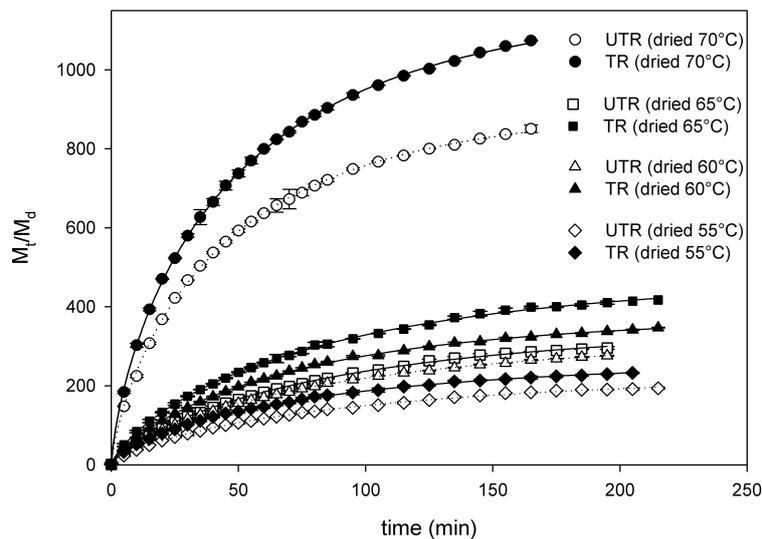
Figure 6. Experimental (symbols) and predicted (lines) rehydration curves of untreated (UTR) and pretreated (TR) samples dried at (a) 55°C, (b) 60°C, (c) 65°C and (d) 70°C.

The values of R^2, MRE, χ^2, RMSE were summarized in Table 8. Nonlinear regression was used to obtain each parameter value of every model. The best model describing the

rehydration characteristics of pumpkins slices was chosen as the one with the highest R^2, MRE below 10% (an indicator of a reasonably good fit) and the lowest χ^2 and RMSE. The values of parameters for each model were reported in Table 9.
The results in Table 8 show that all R^2 values were higher than 0.997, indicating a good fitting.
From the analysis of the results given in Table 8, the Weibull model was the best model for describing the water uptake in pumpkins during rehydration with the lowest values of MRE (<0.8813), RMSE (<6.0241) and χ^2 (<2.6533).

Table 8. Correlation coefficients (R^2, MRE, RMSE, $\chi2$) of the rehydration models.

Model name	T (^oC)	Treated				Untreated			
		R^2	MRE	RMSE	χ^2	R^2	MRE	RMSE	χ^2
Peleg	55	0.9978	2.4374	2.9222	9.1495	0.9976	2.7975	2.6084	7.2730
	60	0.9992	1.7421	2.7332	7.9858	0.9989	1.8624	2.5450	6.9567
	65	0.9982	2.4407	5.9473	25.0370	0.9985	2.4173	3.1755	10.8309
	70	0.9986	0.7982	7.9582	39.3140	0.9994	1.0954	5.5797	33.7280
Weibull	55	**0.9996**	0.8813	1.3121	1.9128	**0.9993**	0.6881	1.4037	2.1816
	60	**0.9996**	0.6365	2.4117	1.4759	**0.9998**	0.6294	1.0850	1.3132
	65	**0.9994**	0.5806	4.8396	2.3177	**0.9996**	0.2151	3.3250	1.7266
	70	**0.9999**	0.3957	6.0241	2.6533	**0.9997**	0.3007	4.2487	1.9387

Table 9 shows the Weibull parameters: A increased with drying temperature, a ranged between 0.7679 and 0.8447 and b varies between 46.6227 and 94.3970.

Table 9. Parameters of the Weibull model for rehydration kinetics.

Model name	Temperature (^oC)	Parameter	Samples	
			Treated	Untreated
Weibull	55	A	265.4958	231.4673
		β	77.6382	94.3970
		α	0.7679	0.7733
	60	A	376.1352	322.1087
		β	71.3801	84.6131
		α	0.8263	0.7992
	65	A	478.9671	349.3444
		β	83.0645	85.8291
		α	0.7909	0.8142
	70	A	1172.4673	906.4519
		β	50.4266	46.6227
		α	0.8447	0.7763

4. CONCLUSIONS

The effect of an alternative chemical pretreatment on drying of Italian ecotype pumpkin slices at four temperatures was investigated in this study. The increase in drying air temperature from 55 to 70° C decreased significantly the drying time of samples, especially when the samples were pretreated before drying. The drying kinetics were well described by the Midilli model for both untreated and treated pumpkin slices. The water effective diffusion coefficients resulted to be higher in the treated samples with respect to the non-treated ones indicating the faster water transfer during drying: D_{eff} was in the range $6.75 \cdot 10^{-9}$ - $8.51 \cdot 10^{-9}$ m^2/s for UTR samples and of $7.073 \cdot 10^{-9}$ - $9.39 \cdot 10^{-9}$ m^2/s for TR ones. While the activation energy for moisture diffusion was found equal to 28.28 and 18.63 kJ/mol for UTR and TR slices, respectively, indicating that less energy is required for the drying of TR samples.

Moreover, the pretreatment effectively protected the quality of dried pumpkin slices. Compared with fresh samples, TR pumpkin slices dried in the temperature range 55-65°C, had lower changes of colour, shrinkage, phenolic content, antioxidant activity and rehydration capacity then UTR ones.

The higher rehydration capacity and the lower shrinkage, was probably due to the preservation of the porous structure developed during drying assuring, according to the D_{eff} values, a faster transport of water from inside to the surface of the product and then evaporation. In fact, the use of disaccharides, such as trehalose or sucrose, in the pretreatment solution has the main effect of maintaining general protein structure in the dry state. In this way, the cell membrane is protected and upon rehydration its functionality is restored.

At temperature of 70°C structure changes and loss of colour and of phenolic compounds are more evident.

Regarding to the rehydration kinetics, it was found that the Weibull model was the best model for describing the water uptake in pumpkins during rehydration.

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