Assessment of the impact of drying processes on orange peel quality characteristics

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Abstract

Orange peel was dried applying three different processes: convective drying, microwave drying, and freeze-drying. Some physicochemical properties (moisture content, water activity, and color parameters) and phytochemical characteristics (total phenolic compounds and total antioxidant activity) were assessed in fresh and dried samples. Four kinetic models were tested aiming for convenient modeling of the convective drying curves. The Page and Approximation of diffusion models were adequate in data fitting, which was assessed by the magnitude of the adjusted coefficient of determination (R^2_{adj}) and reduced χ^2.

The moisture content and water activity of peel dried with the three processes were within acceptable levels for safe storage of products. All processes affected peel color. However, the browning index of freeze-dried samples was equivalent to fresh ones, being higher when convective and microwave drying were applied. Higher chroma parameters were obtained in dried samples indicating a more intense color than fresh peel.

Freeze-drying enhanced total phenolic compounds and total antioxidant activity of orange peel when compared to convective and microwave drying. Therefore, from a quality point of view this process seems to be the most appropriate to produce dried orange peel.

Keywords: orange peel by-product; drying modeling; total phenolic compounds; total antioxidant activity; convective, microwave and freeze-drying.

Practical Applications

Dried orange peel transformed in flour, or slices, cubes or different geometrical features, may be suitable for incorporation as an ingredient in many types of foods such as cakes, biscuits, or bread, enriching their content in phenolic compounds and total antioxidant activity, therefore creating a value-added product. Within the drying conditions used in this study, it was found that the freeze-drying process is preferable when a lighter and more yellow dried orange peel is desired, with improved phytochemical characteristics. On the other hand, when a darker product with colour similar to the fresh peel needs to be attained, the micro-wave drying process should be chosen.

1. Introduction

The concentration of antioxidants and bio-active compounds present in waste parts of many fruits is considerably higher than in their respective edible tissues (Fundo et al., 2018). Orange peel is one example of an excellent natural source of phytochemicals (Okpala & Akpu, 2014; Obafaye & Omoba, 2018). The dietary intake of phytochemicals may promote health benefits like protection against chronic degenerative disorders, cardiovascular and neurodegenerative diseases (Okpala & Akpu, 2014). Furthermore, the orange peel essences have analgesic, antiseptic and anti-inflammatory properties (Egbuonu & Osuji, 2016).

It is challenging the development of strategies to transform orange peel into forms that can be consumed. Drying is one process that can be applied for such purposes. It reduces water activity, and consequently, microorganisms survival and deteriorative enzymes activity is affected (Bejar et al., 2011). Drying processes increase the products shelf life, facilitate storage and decrease the cost of packaging and transportation. However, chemical modifications, including Maillard reactions, lipids oxidation, color changes, vitamins degradation, and flavor losses may occur when a drying process is applied (Oliveira et al., 2015a). The quality of the final product is usually negatively affected by high temperatures and long drying periods (Bejar et al., 2011).

Convective dehydration is the most common and effective drying process, being considerably less expensive when compared to other methods (Mundada et al., 2010). It has been mostly used for drying fruits and vegetables. However, certain disadvantages are associated to this technology, namely low process rates, significant quality decay of final products, and high energetic consumption due to the use of high temperatures (Sagar & Kumar, 2010; İncedayi et al., 2016; Oliveira et al., 2015a; İzli, 2017). In air-drying methods, the temperature level has a great impact in nutritional and visual characteristics.

Microwave technology has been used in the food industry to dry vegetables, fruits, snack foods and dairy products (Sagar & Kumar, 2010; Bejar et al., 2011; Kamiloglu et al., 2016; Oliveira et al., 2015a). This process increases the probability of reducing drying time as it is energy efficient. Therefore, it may improve the quality of the ended product. The main disadvantage of this technology is associated with the non-uniformity of heating, which creates hot spots in some parts of the food. Moreover, excessively high temperatures in the edges and corners of products might lead to overheating and irreversible drying out compromising the overall quality (Nijhuis et al., 1998). Yang et al. (2010) found that microwave drying could provide more phenolic compounds and stronger antioxidant activity in sweet potato when compared to hot-air drying and vacuum-freeze drying, despite the loss of ascorbic acid and carotene.

In the freeze-drying process, food materials are dried under vacuum at very low temperatures, preventing deterioration and microbiological reactions and therefore resulting in products with higher quality (Kamiloglu et al., 2016). Moreover, the freeze-drying technique is more effective in preserving antioxidants but has some disadvantages, such as long drying times and high operational costs (Mundada et al., 2010; Pragati and Preeti, 2014). Due to being expensive, at the industrial scale, this process is usually applied to high-value products, like exotic fruits and vegetables, mushrooms, coffee, and berries (Pragati and Preeti, 2014). When comparing the effects of air-drying and freeze drying on the content of phenolic compounds in kale, its value decreased 60 % and 49 %, respectively, and for blanched leaves, 49 % and 28 %, respectively (Korus, 2011). On the contrary, the content of phenolic compounds was 4.6 times higher in hot air-dried than in freeze-dried pumpkin flour (Que et al., 2008). According to the study of Rahman et al. (2018), the total phenolic compounds of pomelo pulp waste augmented by 27 % after freeze drying, and 55 % after oven drying at 50 °C. Among the five different drying methods that were tested by Nindo et al. (2003), the higher total antioxidant activity retention in asparagus was obtained by freeze-drying (Oliveira et al., 2015a).

Previous studies on orange peel drying are scarce, and only three research papers approaching drying kinetics were found. Slama and Combarnous (2011) presented the drying kinetics in the form of an exponential model and they studied the efficiency of a solar dryer. Erdem et al. (2014) tested several models to fit drying data of different microwave powers and concluded that the Midilli-Kucuk model presented the best fit. Bechlin et al. (2020) adjusted the Page model and the first term of Fick’s second law to drying data of orange peels. They reported that the application ozone prior to drying, increased moisture diffusion.

A study that developed a dielectric isotherm methodology to determine water activity in orange peel by readjusting the GAB model was carried out by Talens et al. (2016). They determined as well, how the isosteric heat of the model was affected by microwave power coupled with hot air drying.

Regarding research on physicochemical or phytochemical properties of dried orange peel, it was only found the work of Bechlin et al. (2020). These authors reported that the application of ozone increased the antioxidant capacity of peels and the yield of extracted essential oil. Therefore, in order to fill in some gaps in the scientific knowledge of orange peel drying, the main objectives of this study were: i) to compare convective, microwave and freeze-dried orange peel regarding some physicochemical properties (color, moisture content, water activity) and phytochemical features (total phenolic compounds and total antioxidant activity); and ii) to model the convective drying data and analyze the characteristic drying curves.

2. Materials and Methods

2.1. Sample preparation

Fresh oranges (*Citrus sinensis* L. cv 'Bollo') without visual defects were purchased in a local supermarket and stored at refrigerated conditions for posterior analysis. Oranges were randomly sampled and peeled. Orange peel was cut into pieces of around 4 cm x 0.35 cm. Part of the samples was dried by convective (CD), microwave (MD) and freeze-drying (FD), and the other part did not suffer any process, being considered fresh peel (F).
Three replicates of each drying process were carried out. Dried orange peel samples were packaged tightly in polyethylene plastic bags (20 x 19 cm), by removing air as much as possible. Samples were then stored in the dark at room temperature for 24 h prior to further analysis.

2.2. Drying processes

2.2.1. Convective drying

Approximately 140 g of chopped orange peel were placed on the upper second tray of the convective dryer (Armfield UOP8, Ringwood, England – Figure 1) until constant weight, which lasted approximately 4.5 hours. The dryer comprised a shielded propeller fan to distribute the hot air, an air oven provided with a heater, and a drying chamber with various trays directly exposed to the continuous hot air. The weight measure system was directly attached to the drying trays, and the samples' weight was recorded by linking the scale to a computer with a data acquisition program (Ramos et al., 2014).
During the drying processes, the air relative humidity averaged 51.12 ± 1.67 %, the temperature 50.14 ± 0.99 °C and air velocity 1.01 ± 0.03 m/s.

Figure 1 here, please.

2.2.2. Microwave drying

Approximately 60 g of orange peel were placed in a glass container positioned in the middle of the microwave (Beko 20 liter, P.C.R, dimensions: 454 mm (W) × 330 mm (D) × 262 mm (H)), for 1 h at 340 W of power. The equipment has an air vent that allows water to be removed from its interior.

2.2.3. Freeze drying

Approximately 60 g of orange peel samples were frozen at -80 °C for 20 h (Eurofrio Soft Lino, Italy), kept in plastic containers covered with parafilm with small holes. Thereafter, the samples were transferred to the freeze dryer equipment (SB4, Armfield, UK) at -50 °C, with vacuum ranging from 150 to 200 Pa, for 5 days.

2.3. Determination of physicochemical properties

2.3.1. Moisture content

Approximately 3 g of orange peel samples were weighted in an analytical balance (Mettler Toledo AE 200, Marshall Scientific, UK) with a precision of 0.0001 g. The samples were dehydrated in an air oven (Memmert, Labmetro, Germany) at 103 °C to allow for the release of moisture until constant weight, following the method 984.25 from AOAC International (2002). After removed from the oven, they were cooled down in a desiccator and were weighted again. Moisture content on a wet basis was calculated by the difference in wet and dry weight divided by wet weight (%), determined in triplicate.

2.3.2. Water activity

Water activity (a_w) was measured by using a Hygrolab meter (AquaLab 3TE, Decagon Devices Inc., Washington, USA) at 22 °C, calibrated with deionized water (a_w of 1.000). This equipment uses the chilled mirror dew point technology. Each sample was measured in triplicate.

2.3.3. Color parameters

Fresh peel was cut into small pieces, and dried samples were ground to a fine powder, with particles' size ranging between 500 µm to 1 mm. Color was determined in triplicate using a

Minolta CR-400 colorimeter (Konica-Minolta, Osaka, Japan), based on CIE $L^*a^*b^*$ coordinates. L^* is a measure of lightness ranging from 0 (black) to 100 (white), a^* ranges from -100 (greenness) to +100 (redness), and b^* from -100 (blueness) to +100 (yellowness). The colorimeter was calibrated with a standard white plate.

Total color difference (TCD), chroma, hue angle, and browning index (BI) were calculated according to the following equations (Alibas, 2009; Ihns et al., 2011):

$$\text{TCD} = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2} \quad (1)$$

where L_0^*, a_0^*, and b_0^* refer to fresh sample. Higher TCD values indicate more noticeable colour alterations in relation to fresh orange peel.

Chroma is related to color saturation; higher values correspond to brighter samples and lower values to duller ones.

$$\text{Chroma} = \sqrt{a^{*2} + b^{*2}} \quad (2)$$

Color maybe also defined by Hue angle: red at 0 °, yellow at 90 °, green at 180 °, and blue at 270 ° (Hammond, 2007).

$$\text{Hue angle } (^\circ) = \tan^{-1}(b^*/a^*) \quad (3)$$

The browning index represents the purity of brown color and is reported as an important parameter in processes where enzymatic or non-enzymatic browning occurs (Buera et al., 1986; Guerrero et al., 1996):

$$\text{BI} = 100\,(x - 0.31) / 0.17 \quad (4)$$

being

$$x = (a^* + 1.750\,L^*) / (5.645\,L^* + a^* - 3.012\,b^*) \quad (5)$$

2.4. Determination of phytochemical properties

Total phenolic compounds (TPC) were determined by using the Folin-Ciocalteu reagent method, and total antioxidant activity (TAA) was determined by using ABTS radical method. These methods are briefly described below and in Oliveira et al. (2015b) and Fundo et al.

(2018), and the same equipment and reagents were used. The sample extraction and the determination of TPC and TAA were prepared and analyzed in triplicate for each sample.

2.4.1. Samples extraction

The extraction from orange peels was done using the method of Oliveira et al. (2015b) and Fundo et al. (2018), with slight modifications for total antioxidant activity and total phenolic compounds. Three grams of fresh samples or 0.45 g of dried samples were weighted by using an analytical balance (Mettler Toledo AE 200, Marshall Scientific, UK) having a precision of 0.0001 g, extracted with 20 mL of pure methanol (HPLC Gradient grade, Fisher Scientific UK) and homogenized with an ultra-turrax homogenizer (Ika digital T25, IKA®-Werke GmbH & Co, Staufen, Germany). Then, they were centrifuged at 5000 rpm and 4 °C for 10 minutes, with a centrifuge machine (Multifuge X3 FR centrifuge, Barcarena, Portugal) and filtered using filter papers. Further analysis was carried out on the same day.

2.4.2. Total phenolic compounds

In a brief explanation, the chromophore development reaction occurred by oxidation of polyphenols with the Folin-Ciocalteu reagent. The calibration curve for total phenolic compounds determination was made with different concentrations of Gallic acid in pure methanol: 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35 and 0.40 mg/mL. The reaction was attained by adding the standard solution or the orange peel extract to the Folin-Ciocalteu's phenol reagent, Na_2C0_3 75 g/L and distilled water. After incubating the mixture for 1 h in the dark at room temperature, the absorbance at 750 nm was measured in triplicate, using an UV/VIS spectrophotometer (Model 5625, ATI Unicam, UK).

The results of total phenolic compounds were calculated by interpolating the corresponding absorbance values in the calibration curve, and were expressed as mg of Gallic Acid Equivalent (GAE) per 100 g of the sample on dry basis (db).

2.4.3. Total antioxidant activity

In a concise explanation, the calibration curve for total antioxidant activity was done with different ascorbic acid standards in pure methanol, with concentrations of 0, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20 and 0.25 mg/mL. The reaction was developed by adding the ascorbic acid standards or the orange peel extract to the ABTS solution. The mixture incubated 6 min in the dark at room temperature, and then the absorbance values at 734 nm were read in triplicate.

The results of total antioxidant activity were calculated by interpolating the absorbance values in the calibration curve, and expressed as mg of Ascorbic Acid Equivalent (AAE) per 100 g of the sample on dry basis (db).

2.5. Data analysis

Data were analyzed by one-way analysis of variance (ANOVA) and Tukey's test for post-hoc analyses, to assess significant differences between the drying processes applied.
Levene and Shapiro-Wilk test were used to evaluate the homogeneity and normality of data, respectively. Whenever these assumptions were not verified, alternative non-parametric tests were used. Kruskal-Wallis test was used instead of ANOVA and Mann-Whitney test for multiple comparisons of data. The significance level assumed was 5 % in all analyses. The results were expressed as average plus or minus the margin of confidence interval at 95 %.
SPSS statistics (version 20) for Windows was used in all analyses performed.

2.6. Modeling of convective drying data

Four kinetic models were used in convective drying data fitting (Table 1): Approximation of diffusion, Henderson and Pabis, Newton and Page. These models have been used by several authors and extensive lists may be found in Kucuk et al. (2014) and Onwude et al. (2016).

Table 1 here, please.

In all models X represents the water content on dry basis, at time t, X_0 the initial water content on dry basis, X_e the equilibrium water content on dry basis, and k the drying rate. The remaining letters (a, b and n) are different model parameters and were an output predicted by each model, as well as X_e and k.
Randomness, normality and homoscedasticity of residuals were primary criteria for model selection. In the models in which these assumptions were verified, the following additional criteria were the adjusted coefficient of determination (R^2_{adj}) and reduced χ^2, defined as follows (Yaldiz et al., 2001):

$$R^2_{adj} = 1 - \sum_{i=1}^{n}\left(X_{exp,i} - X_{model,i}\right)^2 (n-1) / \sum_{i=1}^{n}\left(X_{exp,i} - \bar{X}_{exp}\right)^2 (n-p) \quad (10)$$

$$\chi^2 = \sum_{i=1}^{n}\left(X_{exp,i} - X_{model,i}\right)^2 / (n - p) \quad (11)$$

where n is the total number of data points, p the number of model parameters, and the indexes *exp* and *model* refer to experimental observations and values predicted by the model, respectively; $\bar{X}_{exp}$ is the average value of experimental data.

The above presented coefficients can be used to evaluate model adequacy and goodness of fit. R^2_{adj} represents the proportion of the variance for a dependent variable that is explained by the model assumed; the closer to 1 the more adequate is the model. Reduced χ^2 expresses a mean deviation between experimental observations and model predictions; the lower the values of the reduced χ^2, the better the goodness of the fit (Yaldiz et al., 2001).

The software SPSS statistics (version 20) for Windows was used to fit the models to the drying curves.

3. Results and Discussion

3.1. Physicochemical properties of dried orange peel

3.1.1. Moisture content and water activity

Moisture content in wet basis and water activity of fresh and orange peel dried by the three different methods (convective, microwave, and freeze drying) are presented in Table 2. The fresh orange peel contains 75.66 ± 0.33 to 78.23 ± 0.35 % of water in wet basis, which is similar to the value obtained by Slama and Combarnous (2011) – 76 %, but lower than moisture content in frozen orange peel (79.80 ± 0.015 %) reported by Hiri et al. (2015). The dried orange peels presented values from 11.10 ± 0.35 to 11.46 ± 0.22 of water content (wet basis) for the microwave dried ones; from 10.85 ± 0.37 to 13.03 ± 0.56 for the convective dried; and 5.49 ± 0.09 to 5.79 ± 0.26 for the freeze-dried peels. According to FAO (2010), the desired final moisture content of dried fruits is 15 % for conventionally dried fruits and 20-25 % for osmotically dried fruits (wet basis).

Table 2 here, please.

In the present study, the water activity of fresh orange peel was around 0.990 ± 0.00. For microwave, convective and freeze dried samples a_w values were respectively 0.399 ± 0.00 to

0.425 ± 0.00, 0.332 ± 0.00 to 0.381 ± 0.00, and 0.085 ± 0.00 to 0.090 ± 0.00. The highest acceptable a_w value for safe storage of food products is 0.60 (Hiri et al., 2015; Oliveira et al., 2015a). In the study of Maltini et al. (2003), the maximum water activity required for dried fruit and bonbons ranged from 0.60 to 0.65.

Therefore, the dried orange peels produced in this research attained the acceptance levels of water activity and moisture content, that allow their safe storage.

3.1.2. Color

Browning index (eq. 4) and chroma values (eq. 2) of fresh and dried orange peel samples are presented in Figure 2. The highest browning index was obtained for CD orange peel (112 ± 4.5), followed by MD samples (103 ± 2.5). Both values were significantly higher than the ones observed for fresh and freeze-dried samples, which means that CD and MD processes induced browning. No significant differences were observed for FD and fresh samples ($p>0.05$), being the lowest values observed.

The Chroma value of CD sample (54.9 ± 1.8) was significantly higher than the remaining ones, corresponding to the brightest orange peel with the highest color saturation. No significant differences were obtained for Chroma of FD (51.0 ± 0.6) and MD (50.9 ± 0.9) samples. The lowest Chroma value was for fresh orange peel (45.3 ± 2.9), which means that this was the dullest sample.

Figure 2 here, please.

In relation to Hue angle (Figure 3), similar values were obtained for fresh, CD, and MD orange peels (79.9 ± 2.6, 79.1 ± 1.5, and 79.1 ± 1.2 º, respectively). The highest significant value was for FD orange peel, 86.0 ± 1.4 º, which reveals yellowness.

Figure 3 here, please.

L^*, a^*, and b^* values that allow TCD assessment are in Table 3. Samples dried with all processes are lighter than fresh orange peel, with FD with the highest values of L^*. The FD samples also showed the lowest a^* parameter, considerably lower than the one of fresh peel (*i.e.*, less red). The b^* parameter was also higher in FD samples than in fresh ones, revealing a more yellow color.

Table 3 here, please.

Results of TCD are also presented in Figure 3. The average TCD of orange peels for FD, CD and MD processes is, respectively 14.4 ± 3.4, 11.5 ± 2.4, and 7.0 ± 1.5. Statistically, there is no significant difference between FD and CD processes, yet MD allowed the lowest differences when compared to fresh orange peel. This means that FD and CD processes have more effect on color changes of orange peels than MD process. This could be perceived by visual inspection of the samples, whose pictures are included in Figure 4.

Figure 4 here, please.

Regarding color characteristics and within the conditions used in this study, the overall conclusion is that the FD process is better when a lighter and more yellow dried peel is desirable, and the MD process when a darker product, with color similar to the fresh peel, needs to be attained.

3.2. Phytochemical properties of dried orange peel

3.2.1. Total phenolic compounds

Data of TPC in samples dried with the different drying methods were normalized in relation to the ones of fresh orange peel, on a dry basis (db). Results are presented in Figure 5. Statistically, there are significant differences among MD, CD, and FD samples ($p<0.05$). The TPC of orange peel microwave dried at 340 W was reduced by 13.7 % when compared to fresh peel. However, CD and FD processes increased the TPC values of the orange peel by 6.4 % and 19.5 %, respectively.

Figure 5 here, please.

These results are in accordance with the ones obtained by Bejar et al. (2011). Those authors concluded that microwave drying at 180 W decreased TPC in orange peels up to 6.1 %. However, at 450 W the content increased till 75.5 %. The microwave power affected TPC of orange peels and, at certain levels, TPC increased. At those levels, the structure of the fiber matrix may become larger and looser and successively facilitate the extraction with solvent.

Contrary, at certain microwave powers, TPC decreased due to the longer drying times that could destroy some of them.

The FD process had a stronger effect on the variation of TPC in dried orange peels than CD. According to the study of Rahman et al. (2018), TPC of pulp waste of Pomelo augmented by 27.0 % after freeze drying, and 55.0 % after oven drying at 50 °C. The reason for the high TPC content might be caused by the occurrence of non-enzymatic reactions, such as Maillard reactions and caramelisation, when high temperatures are involved. The contents of phenolic compounds vary also among different types of fruits, the structure of tissues, cultivar, cultivation conditions, and geographical location.

3.2.2. Total antioxidant activity

Data of TAA in samples dried with the different methods were normalized in relation to the ones of fresh orange peel, on a dry basis (db). Results are presented in Figure 6. Statistically, there is a significant difference between MD and FD samples ($p<0.05$). However, TAA in CD peel is equal to MD and to FD ones. The highest increase of TAA was observed in FD samples; the value increased 44.1 % when compared to the one detected in fresh peel. CD allowed an increase of 25.0 % while MD 18.1 %.

Figure 6 here, please.

As stated by Kamiloglu et al. (2016), the FD process is more effective in preserving antioxidants and originates higher quality on final products. When TPC increases, antioxidant activity may also increase due to phenolics compounds enhance (Bejar et al., 2011; Rahman et al., 2018).

3.3. Characteristic drying curves

The characteristic drying curves of orange peel are shown in Figure 7. One may observe that there is the settling down period and the falling rate period (FRP), and there is almost no constant rate period (CRP) in these curves. The first stage of these convective drying curves demonstrates that the samples are starting to be heated until the solid surface conditions reach equilibrium with the drying air temperature. Then, the drying rate is constant (CRP) during a small period of time when samples reach around 2.5 and 2 $g_{H2O}.g_{db}^{-1}$. Subsequently, the drying rate falls down in the FRP at the critical moisture content, around 2 $g_{H2O}.g_{db}^{-1}.min^{-1}$.

Figure 7 here, please.

The absence of a constant-rate drying period or a short one, is observed when drying most foods (Mazza & Le Maguer, 1980) and it is associated with small water quantities at the food surface. A long falling-rate period like in this case, indicates that drying is controlled by internal water transfer (Foust et al., 1980) and external resistance is negligeable.

3.4. Modeling drying curves

Table 4 presents the results of the regression analyses performed with convective drying data, including parameter estimates, the margin of 95% confidence and goodness of fit indicators (R^2_{adj} and χ^2). The residuals from Henderson and Pabis model and the Newton model were not normally distributed, and consequently, these models were not adequate for data fitting.

Table 4. here, please

The Approximation of diffusion and Page models revealed random residuals with normal distribution and homoscedasticity. Also, both models had the highest R^2_{adj}values (which are equal to 1.000) and low χ^2 values; however, the Page model presented the smallest values. Data fits of Page and Approximation of diffusion models can be seen in Figures 8 and 9, respectively. The two models are adequate for convective drying prediction at the conditions of this study. Conclusions may be different if other drying processes are being studied. Erdem et al. (2014) reported that the Page and Approximation of diffusion models were not the most adequate models to describe microwave drying of orange peel (at 180, 360, 540, 720 and 900 W), and the Midilli-Kucuk model was the selected one.

Figure 8 here, please.

Figure 9 here, please.

Drying rates of convective dried orange peels estimated with the Page model were obtained for the 3 replicates: $0.144\text{x}10^{-2}$, $0.230\text{x}10^{-2}$, and $0.296\text{x}10^{-2}$ min^{-n} (Table 4) with ‘n’ values varying between 1.347 and 1.536. Bechlin et al. (2020) determined an average drying rate of 0.0067 with a ‘n’ value of 1.06 for the Page model, which are in the same order of magnitude of the ones obtained in this study. This was for orange peel samples pretreated with ozone at 4 g.L^{-1}. Toĝrul and Pehlivan (2004) reported for open-air sun drying of apricots, grapes, peaches, figs, and plums, drying rates of respectively 0.401x10^{-2}, 0.0460x10^{-2}, 0.250x10^{-2}, 0.099x10^{-2}, and 0.032x10^{-2} min^{-n}, and 'n' values between 0.63534 and 0.956815.

For amaranth seeds from open sun drying and solar tent drying, Ronoh et al. (2009) also concluded that the Page model showed the best performance among the six tested drying models.

Drying rates of convective dried orange peel estimated with the Approximation of diffusion model were 2.6x10^{-2}, 2.6x10^{-2} and 2.2x10^{-2} min^{-1} (Table 4), with 'a' values ranging from 2.8 to 3.3 and 'b' values of 1.4 and 1.5. Toĝrul and Pehlivan (2004) estimated drying rates with this model, for apricots, grapes, peaches, figs, and plums, which were respectively 0.454x10^{-2}, 0.100x10^{-2}, 0.549x10^{-2}, 0.47x10^{-2}, and 1.081x10^{-2} min^{-1}, with 'a' values varying from 0.032756 to 0.501645 and 'b' values from 0.004417 and 0.149185.

All these different drying rate values may be related to the use of diverse fruit species, with different characteristic dimensions, as well as the use of different equipments and air condition drying patterns.

4. Conclusions

Moisture content and water activity of dried orange peels obtained from the three drying methods attained acceptance levels for safe storage of products.

According to what was expected, the freeze-dried orange peels presented better quality parameters, when compared to the other drying techniques. Freeze-dried orange peel was brighter, more yellow, and less red than the fresh product. Moreover, the FD process enhanced considerably the amount of total phenolic compounds and total antioxidant activity when compared to the remaining applied drying processes. However, the microwave drying originated products with a color close to the one observed for the fresh one.

The characteristic drying curves of convective drying revealed a settling down and a falling rate periods, with a very short constant rate interval. Water removal from orange peel in the convective drying process occurred mainly in the falling rate period, starting from initial to final moisture contents within the range 0.034–0.227 $g_{H2O}.g_{db}^{-1}$. This reveals that convective drying of orange peels is manly driven by internal water transfer.

The kinetic study showed that the models that best fitted the convective drying data were the Page and the Approximation of diffusion models. They presented randomness, normality and homoscedasticity of the residuals, providing the highest R^2_{adj} (1.000) and the lowest χ^2 values, having originated excellent fits.

In conclusion, the main objectives of this study were attained and give a first insight into the comprehension of the effects of convective, microwave, and freeze-drying on orange peel. Regarding the application of dried orange peel, it may be transformed in flour, or in slices, cubes or different geometrical features, and further incorporated as an ingredient in many types of foods such as cakes, biscuits, or bread, enriching their content in phenolic compounds and total antioxidant activity, therefore creating a value-added product. Concerning future studies on dried orange peel, it would be interesting to focus on dietary fibers and other nutritional properties. Sensorial analysis of food products with dried orange peel and determination of their physical properties, like texture, would also be interesting.

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References

Alibas, I. (2009). Microwave, vacuum, and air drying characteristics of collard leaves. *Drying Technology, 27*(11), 1266–1273. htpps://doi.org/10.1080/07373930903267773.

AOAC INTERNATIONAL Official Methods of Analysis (2002) 16th Ed., AOAC INTERNATIONAL, Gaithersburg, MD, USA, Official Method 984.25 - 1984.

Bejar, A. K., Kechaou, N., & Mihoubi, N. B. (2002). Effect of microwave treatment on physical and functional properties of orange *(Citrus Sinensis)* peel and leaves. *Journal of Food Processing & Technology*, *2*(2). htpps://doi.org/10.4172/2157-7110.1000109.

Buera, M.P., Lozano, R.D., & Petriella, C. (1986). Definition of colour in the non enzymatic browning process. *Die Farbe*, *32*(33), 318-322.

Egbuonu, A., & Osuji, C. (2016). Proximate compositions and antibacterial activity of *Citrus sinensis* (sweet orange) peel and seed extracts. *European Journal of Medicinal Plants, 12*(3), 1–7. htpps://doi.org/10.9734/EJMP/2016/24122.

Erdem, T., Karaaslan, S., Öztekin, S., Şahan, Z., & Çiftçi, H. (2014). Microwave drying of orange peels and its mathematical models. *Journal of Agricultural Machinery Science, 10*(4), 329–333.

FAO (2010). Dried fruit. Fruit processing toolkit. *Food and Agriculture Organization of the United Nations*, 2–3, htpps://doi.org/10.1017/S002081830000607X.

Foust, A.S., Wenzel, L.A., Clump, C.W., Maus, L. & Andersen, L.B. (Eds.). (1980). Simultaneous Heat and Mass Transfer-Drying. In *Principles of Unit Operations*, John Wiley & Sons, Singapore.

Fundo, J. F., Miller, F. A., Garcia, E., Santos, J. R., Silva, C. L. M., & Brandão, T. R. S. (2018). Physicochemical characteristics, bioactive compounds and antioxidant activity in juice, pulp, peel and seeds of *Cantaloupe* melon. *Journal of Food Measurement and Characterization*, *12*(1), 292–300. htpps://doi.org/10.1007/s11694-017-9640-0.

Guerrero, S., Alzamora, S. M., & Gerschenson, L. N. (1996). Optimization of a combined factors technology for preserving banana puree to minimize color changes using response surface methodology. *Journal of Food Engineering*, *28*, 307-322.

Hammond, D. A. (2007). Analysis of Soft Drinks and Fruit Juices. In P. R. Ashursts (Ed.), *Chemistry and Technology of Soft Drinks and Fruit Juices* (2nd ed., pp. 236-278). Oxford, Willey.

Hiri, N. M., Ioannou, I., & Ghoul, M. (2015). Proximate chemical composition of orange peel and variation of phenols and antioxidant activity during convective air drying. *Journal of New Sciences, Agriculture and Biotechnology*, *9*(9), 881–890.

Ihns, R., Diamante, L. M., Savage, G. P., & Vanhanen, L. (2011). Effect of temperature on the drying characteristics, colour, antioxidant and beta-carotene contents of two apricot varieties. *International Journal of Food Science and Technology*, *46*(2), 275–283. htpps://doi.org/0.1111/j.1365-2621.2010.02506.x.

İncedayi, B., Tamer, C. E., Sinir, G. Ö., Suna, S., & Çopur, Ö. U. (2016). Impact of different drying parameters on color, β-carotene, antioxidant activity and minerals of apricot *(Prunus armeniaca L.). Food Science and Technology, 36*(1), 171–178. htpps://doi.org/10.1590/1678-457X.0086.

İzli, G. (2017). Total phenolics, antioxidant capacity, colour and drying characteristics of date fruit dried with different methods. *Food Science and Technology, 37*(1), 139–147. htpps://doi.org/10.1590/1678-457x.14516.

Kamiloglu, S., Toydemir, G., Boyacioglu, D., Beekwilder, J., Hall, R. D., & Capanoglu, E. (2016). A Review on the effect of drying on antioxidant potential of fruits and vegetables.

Critical Reviews in Food Science and Nutrition, 56, 110–129. htpps://doi.org/10.1080/10408398.2015.1045969.

Korus, A. (2011) Effect of preliminary processing, method of drying and storage temperature on the level of antioxidants in kale (*Brassica oleracea L. var. acephala)* leaves. *LWT - Food Science and Technology, 44*(8), 1711-1716, https://doi.org/10.1016/j.lwt.2011.03.014.

Kucuk, H., Midilli, A., Kilic, A., & Dincer, I. (2014). A review on thin-layer drying-curve equations. *Drying Technology*, *32*(7), 757-773.

Maltini, E., Torreggiani, D., Venir, E., & Bertolo, G. (2003). Water activity and the preservation of plant foods. *Food Chemistry*, *82*(1), 79–86. htpps://doi.org/10.1016/S0308-8146(02)00581-2.

Mazza, G., & Le Maguer, M. (1980). Dehydration of onion: some theoretical and practical considerations. *Journal of Food Technology, 15*(2), 181-194.

Mundada, M., Hathan, B. S. & Maske, S. (2010). Convective dehydration kinetics of osmotically pretreated pomegranate arils. *Biosystems Engineering*, *107*(4), 307–316. htpps://doi.org/10.1016/j.biosystemseng.2010.09.002.

Nijhuis, H. H., Torringa, H. M., Muresan, S., Yuksel, D., Leguijt, C., & Kloek, W. (1998). Approaches to improving the quality of dried fruit and vegetables. *Trends in Food Science & Technology*, *9*(1), 13–20. htpps://doi.org/10.1016/S0924-2244(97)00007-1

Nindo, C. I., Sun, T., Wang, S. W., Tang, J., & Powers, J. R. (2003) Evaluation of drying technologies for retention of physical quality and antioxidants in asparagus (*Asparagus officinalis, L.*). *Lebensmittel-Wissenschaft Und-Technologie - Food Science Technology, 36*(5), 507–516. htpps://doi.org/10.1016/s0023-6438(03)00046-x.

Obafaye, R. O., & Omoba, O. S. (2018). Orange peel flour: A potential source of antioxidant and dietary fiber in pearl-millet biscuit. *Journal of Food Biochemistry,* 1–8. htpps://doi.org/10.1111/jfbc.12523.

Okpala, L. C., & Akpu, M. N. (2014). Effect of orange peel flour on the quality characteristics of breads. *British Journal of Applied Science & Technology*, *4*(5), 823–830.

Oliveira, S. M., Brandão, T. R. S., & Silva, C. L. M. (2015a). Influence of drying processes and pretreatments on nutritional and bioactive characteristics of dried vegetables: A review. *Food Engineering Reviews, 8*(2), 134–163. htpps://doi.org/10.1007/s12393-015-9124-0.

Oliveira, S. M., Ramos, I. N., Brandão, T. R. S., & Silva, C. L. M. (2015b). Effect of air-drying temperature on the quality and bioactive characteristics of dried galega kale *(Brassica oleracea L. var. Acephala). Journal of Food Processing and Preservation*, *39*(6), 2485–

2496. htpps://doi.org/10.1111/jfpp.12498.
Onwude, D. I., Hashim, N., Janius, R. B., Nawi, N. M., Abdan, K. (2016). Modeling the thin layer drying of fruits and vegetables: a review. *Comprehensive Reviews in Food Science and Food Safety, 15*(3), 599-618.
Pragati, S., & Preeti, B. (2014). Technological revolution in drying of fruit and vegetables. *International Journal of Science and Research, 3*(10), 705-711.
Que, F., Mao, L., Fang, X., & Wu, T. (2008) Comparison of hot air drying and freeze-drying on the physicochemical properties and antioxidant activities of pumpkin (*Cucurbita moschata Duch.*) flours. *International Journal of Food Science and Technology, 43*(7), 1195–1201. htpps://doi.org/10.1111/j.1365-2621.2007.01590.x
Rahman, N. F. A., Shamsudin, R., Ismail, A., Shah, N. N., & Varith, J. (2018). Effects of drying methods on total phenolic contents and antioxidant capacity of the pomelo *(Citrus grandis (L.) Osbeck)* peels. *Innovative Food Science & Emerging Technologies*, 50, 217–225. htpps://doi.org/10.1016/j.ifset.2018.01.009.
Ramos, N., Brandão, T. R. S., & Silva, C. L. M. (2014). Effect of pre-treatments on solar drying kinetics of red seedless grapes *(cv. Monukka). International Journal of Food Studies*, 3, 239–247. htpps://doi.org/10.7455/ijfs/3.2.2014.a9.
Ronoh, E. K., Kanali, C. L., Mailutha, J. T., & Shitanda, D. (2009). Modeling thin layer drying of amaranth seeds under open sun and natural convection solar tent dryer. *Agricultural Engineering International: the CIGR Ejournal*, 1420, XI.
Sagar, V. R., & Suresh Kumar, P. (2010). Recent advances in drying and dehydration of fruits and vegetables: A review. *Journal of Food Science and Technology*, *47*(1), 15–26. htpps://doi.org/10.1007/s13197-010-0010-8.
Slama, R. B., & Combarnous, M. (2011). Study of orange peels dryings kinetics and development of a solar dryer by forced convection. *Solar Energy, 85*(3), 570–578. htpps://doi.org/10.1016/j.solener.2011.01.001.
Toĝrul, I. T., & Pehlivan, D. (2004). Modelling of thin layer drying kinetics of some fruits under open-air sun drying process. *Journal of Food Engineering, 65*(3), 413–425. htpps://doi.org/10.1016/j.jfoodeng.2004.02.001.
Yaldiz, O., Ertekin, C., & Uzun, H. I. (2001). Mathematical modeling of thin layer solar drying of sultana grapes. *Energy, 26*(5), 457–465. htpps://doi.org/10.1016/S0360-5442(01)00018-4.2
Yang, J., Chen, J. F., Zhao, Y. Y., & Mao, L. C. (2010). Effects of drying processes on the antioxidant properties in sweet potatoes. *Agricultural Sciences in China*, *9*(10), 1522-1529.

https://doi.org/10.1016/S1671-2927(09)60246-7.