Rojas, ML.; Augusto, PED.; Carcel, JA. (2021). Combining ethanol pre-treatment and ultrasound-assisted drying to enhance apple chips by fortification with black carrot anthocyanin. Journal of the Science of Food and Agriculture. 101(5):2078-2089. https://doi.org/10.1002/jsfa.10830

Combining ethanol pre-treatment and ultrasound-assisted drying to enhance apple chips by fortification with black carrot anthocyanin

Running title: Ethanol and ultrasound to enhance apple drying and anthocyanin incorporation

Meliza Lindsay Rojas[1,2,3]; Pedro Esteves Duarte Augusto[3,4]; Juan Andrés Cárcel[1*]

[1]Analysis and Simulation of Agro-food Processes group (ASPA), Food Technology Department, Universitat Politècnica de València (UPV), Valencia, Spain.

[2]Dirección de Investigación y Desarrollo, Universidad Privada del Norte, Trujillo, Peru.

[3]Department of Agri-food Industry, Food and Nutrition (LAN), Luiz de Queiroz College of Agriculture (ESALQ), University of São Paulo (USP), Piracicaba, SP, Brazil.

[4]Food and Nutrition Research Center (NAPAN), University of São Paulo (USP), São Paulo, SP, Brazil.

[*]Corresponding author: Camí de Vera, s/n 46022 Valencia, Spain.
E-mail address: mrojas@usp.br (Rojas, M.L); pedro.ed.augusto@usp.br (Augusto, P.E.D); jcarcel@tal.upv.es (Cárcel, J.A)

Acknowledgements

This work was supported by the São Paulo Research Foundation (FAPESP, Brazil) [project number 2019/05043-6]; the National Council for Scientific and Technological Development (CNPq, Brazil) [P.E.D. Augusto productivity grant number 306557/2017-7]; the Fondo Nacional de Desarrollo Científico, Tecnológico y de Innovación Tecnológica (FONDECYT) from CONCYTEC, Perú [M.L. Rojas Ph.D. scholarship contract number 087-2016-FONDECYT] and the INIA-Spain and the ERDF funds [RTA2015-00060-C04-02].

Conflict of Interest Statement

None.

Abstract

BACKGROUND: An interesting approach to improve dried foods nutritional properties, functionality, and sensorial attributes, is by taking advantage of pre-treatments for incorporating components into the food matrix. Based on this, this work studied the incorporation of black carrot anthocyanins in apple tissue by using ethanol (concentrations 0-300 $mL \cdot L^{-1}$) as a pre-treatment to ultrasound-assisted convective drying. Samples were pre-treated in acidified ethanol solutions, with and without anthocyanins, and then dried (50 °C, 1 $m \cdot s^{-1}$) by convective and US-assisted convective (21.77 kHz, 20.5 $kW \cdot m^{-3}$) drying. Both the drying process improvement and the obtained product properties were studied.

RESULTS: The anthocyanins did not influence the drying kinetics. In contrast, time reduction was >50% by using both ethanol pre-treatments and ultrasound. Ethanol pre-treatments decreased the external resistance to mass transfer, while ultrasound decreased both internal and external resistances. The impregnation increased the anthocyanins (above 947%), which were retained after drying. Colour modifications after pre-treatments and after drying (L*, b*, h° decrease, and a* increase), and antioxidant capacity retention were observed in samples with anthocyanin addition.

CONCLUSION: The results point that ethanol pre-treatments and ultrasound application can accelerate drying, and through the natural colouring incorporation during pre-treatments, the nutritional properties of dried samples were better retained.

Keywords: drying kinetics; food processing; food properties; antioxidant capacity; colour

1. Introduction

One of the main purposes of food drying is preservation. Moreover, the nutritional quality and sensorial characteristics (as colour, texture, and flavour) of dried food are increasingly important. Consequently, emerging drying methods are gaining importance to improve both the drying rate and quality of dried food.

Among the emerging technologies, the high-power ultrasound (US) showed very positive results in terms of drying time reduction and improvement of food properties [1-3]. The associated mechanisms are related to effects on the solid-gas interface and internal food structure. In the solid-gas interface, the acoustic microstreaming, pressure variations or oscillating velocities can contribute to decreasing external resistances to the mass transfer [4-6]. In the food matrix, the structure modifications (cell wall breakdown, creation of microscopic channels) resulting from the acoustic stress ("sponge effect" produced by the cyclical compressions and expansions) or acoustic cavitation in the liquid phase [7-10] promote the water transfer from inside to sample surface. Therefore, the US has demonstrated significant effects in reducing internal and external resistances during drying. Despite this, the effect of the combination with pre-treatments such as the use of ethanol still needs to be studied.

Ethanol pre-treatment provided interesting results enhancing food drying. Different structural modifications were reported, such as changes on cell wall thickness and the air removal from intercellular spaces, which improves the process and product properties [11-15]. Furthermore, during pre-treatments, the entrance of ethanol occurs into the food matrix, forming a mixture with the water of samples. Then, the ethanol properties (such as lower surface tension and higher vapour pressure than those of water), and the modifications of structure and composition in the food matrix promote mechanisms to accelerate drying, such as the Marangoni effect [11, 14].

The influence of ethanol has been studied individually as pre-treatment to convective drying [11, 16-18], US-convective drying [19] and vacuum drying [20], or combined with ultrasound [21] to convective drying. In addition, in the case of infrared drying, ethanol pre-treatments

have been studied combined with vacuum [22] or with ultrasound [12, 23]. However, some combination of technologies with the potential to obtain better processes, for example, as far as we know, the application of pre-treatments with different ethanol concentrations followed by US-assisted convective drying still have not been evaluated.

An interesting option to improve dried foods nutritional properties, functionality, and sensorial attributes, is by taking advantage of the pre-treatments for incorporating interesting components into the food matrix. For example, the iron and carotenoid incorporation during ultrasound pre-treatments to obtain fortified dry apple and pumpkin was studied by Rojas*, et al.* [24], incorporation of calcium lactate and calcium chloride by immersion with/without vacuum pre-treatments in apple by Assis*, et al.* [25] or pineapple snacks by Lima*, et al.* [26]. In addition, some studies evaluated the sample impregnation with highly polyphenolic content natural extracts. Thus, it has been studied the impregnation of beetroot into potato slices [27], anthocyanins from *Garcinia indica* Choisy into watermelon rind [28], roselle extract solution containing sucrose into carrot slice [29], or calcium lactate and black carrot phenolics into ready to eat apple tissues [30]. Particularly, black carrot, a rich source of polyphenolic compounds, can provide an intense and relatively stable red colour to food products due to the presence of anthocyanins with acetylated substituted molecular structure [31]. Moreover, it can improve the food nutritional value by increasing the polyphenolic content and their antioxidant activity.

However, hot air drying can partially degrade the added nutrient, which makes necessary to evaluate alternatives.

Therefore, this work aimed to produce coloured apple chips with enhanced nutritional value by the incorporation of black carrot anthocyanins. The effect of ethanol pre-treatment and ultrasound-assisted convective drying on drying kinetics, colour, anthocyanins and antioxidant activity was evaluated.

2. Material and methods

2.1. Raw material

Apples (cv. Granny smith) were acquired from a local supplier (Valencia, Spain). They were washed, and the flesh part was cut to obtain rectangular-shaped samples of 4 cm length x 2.5 cm width x 0.3 cm height. After that, the raw samples were immersed for 10 min in a solution composed by 20 $g \cdot kg^{-1}$ of ascorbic acid (2%aa) in a rate of 0.4 g of $sample \cdot mL^{-1}$ of solution to prevent browning reactions. Then, samples were pre-treated, and, subsequently, convectively dried (Table 1).

2.2. Black carrot anthocyanins

Experiments were carried out with Black carrot extract powder EV12 (E163) provided by the “Sociedad Española de Colorantes Naturales y Afines (SECNA)” (Valencia, Spain). The powder is produced by spray drying of the extracted and concentrated juice of selected black carrots. It is a natural colouring widely used in the food industry.

2.3. Pre-treatments

Pre-treatments were performed using different ethanol concentrations, with or without colouring addition. For this, acid ethanol solutions (in order to ensure the pH stability and solubility of the colouring) of 0, 15% (150 $mL \cdot L^{-1}$) and 30% (300 $mL \cdot L^{-1}$) v/v were prepared using ethanol (96% v/v) which was diluted in a solution of citric acid (4 $g \cdot L^{-1}$). In this way, the pH of the solutions was maintained in the range of 2.6 - 2.9 at 25 °C. After that, colouring was added (2 $g \cdot L^{-1}$of ethanol acid solution) to carry out the corresponding pre-treatments. The prepared black carrot colouring solutions presented an anthocyanins content of 0.050 ± 0.001 $g \cdot L^{-1}$.

For all pre-treatments, the fresh samples were immersed for 15 min at 25 °C in a proportion of 300 g of $sample \cdot L^{-1}$ of ethanol acid solution (0, 15, or 30%) with or without colouring (Table 1).

2.4. Drying process

Hot-air drying experiments were performed at 50 °C and 1 m·s^{-1} using an ultrasonically assisted dryer, as described by García-Pérez*, et al.* [32]. The convective drying was performed without and with airborne ultrasound energy application (electrical input of 20.5 kW·m^{-3} and frequency of 21.77 kHz). In each drying process, 19 apple slices were randomly placed inside the drying chamber (Figure 1) using a sample holder [33]. Sample weight was automatically recorded each 5 min along the drying time. Drying experiments were stopped when samples showed a variation lower than 0.05 g in the last consecutive three weight measurements. Table 1 shows the code assigned to each pre-treatment with their respective type of drying (convective drying or US-assisted convective drying), then resulting in 12 treatments, which were replicated at least 3 times. The initial and final moisture content was determined by vacuum drying of samples at 70 °C and -0.8 bar (VACIOTEM-T, J.P. SELECTA, S.A., Barcelona) until constant weight.

2.5. Drying kinetics

Three models were applied to describe the apple drying kinetics. The first one was a diffusion model based in Fick's Second Law [33-36] (Eq. 1).

$$\frac{\partial \mathrm{M_{x,t}}}{\partial \mathrm{t}} = \mathrm{D_{eff}} \frac{\partial^2 \mathrm{M_{x,t}}}{\partial \mathrm{x^2}} \quad (1)$$

Where t is the drying time (s); M is the moisture content (kg water·kg^{-1} dry matter); $\boldsymbol{D_{eff}}$ is the moisture effective diffusivity (m^2·s^{-1}), and x is the distance (m) in the direction of the water transport. It is important to highlight the moisture effective diffusivity ($\boldsymbol{D_{eff}}$) is a lumped parameter that represents the global transport phenomena; it includes mechanisms such as molecular diffusion, liquid diffusion through the solid pores, vapour diffusion, capillarity and all other mechanisms that affect mass transport and drying rate [2] - including ultrasound effects (sponge effect, microchannel creations, microstirring) during US-assisted drying.

For modelling purposes, apple samples were considered as an isotropic material exhibiting an infinite symmetric slab behaviour with only one direction of moisture transport [37, 38]. It was assumed a uniform temperature and initial moisture content inside the sample, as well as negligible shrinkage during the process. The moisture effective diffusivity ($\boldsymbol{D_{eff}}$) was considered constant over the process and across the sample. Then, if the moisture content of the solid surface achieves equilibrium when drying process starts ($t > 0; x = L$), it can be assumed the boundary condition expressed in the Eq. (2). Therefore, the movement of the moisture inside the solid controlled the drying process.

$$M(L,t) = M_{eq} \quad (2)$$

Where L is the half-thickness of the sample and M_{eq} is the equilibrium moisture content (kg water·kg^{-1}, dry basis) which was estimated using the desorption isotherm parameters of apple (c.v. Granny Smith). The GAB parameters were obtained from the desorption isotherm reported by Vega-Gálvez*, et al.* [39], which were successfully applied to calculate the M_{eq} of apple samples dried form 45 to 80 °C.

The analytical solution integrated for the sample volume showed in Eq. (3) is the result of this purely diffusive model controlled only by internal resistances (IR-Model) [40].

$$M = M_{eq} + (M_0 - M_{eq})\left[2\sum_{n=0}^{\infty}\frac{1}{\lambda_n^2 L^2}e^{-D_{eff}\lambda_n^2 t}\right] \quad (3)$$

$$\lambda = \frac{(2n+1)\pi}{2L} \quad (4)$$

This IR-Model (Eq. 3) model was considered as a first approach for fitting the experimental results. In another approximation, the external resistance to mass transfer was also considered, by including the boundary conditions of Eq. (2) by Eq. (5) (IER-Model). In this equation (Eq.5), it is shown that the water is transported from inside to sample surface by diffusion ($\boldsymbol{D_{eff}}$), and then water is transferred from the sample surface to the air by convection ($\boldsymbol{h}$).

$$-D_{eff}\rho_d\frac{\partial M(L,t)}{\partial x} = h(a_w(L,t) - \varphi_{air}) \quad (5)$$

Where ρ_d is the density of dry sample (kg dry matter·m^{-3}); $\boldsymbol{h}$ is the convective mass transfer coefficient (kg water·m^{-2}·s^{-1}), a_w is the water activity in the solid surface, and φ_{air} is the relative humidity of drying air. Sorption parameters from the desorption isotherm reported by Vega-Gálvez*, et al.* [39], were used to estimate the relationship between surface water activity (a_w) and average moisture content (M), in function of the drying time (t) and characteristic dimension (L) [41, 42].

Once other mechanisms of mass transfer further than diffusion and convection takes place during drying, the Page empirical model [43] was also used to describe the process (Eq. 6). Simpson*, et al.* [44], using the anomalous diffusion concept and the fractional calculus approach, provided a phenomenological interpretation of the model, where, the drying rate parameter ($\boldsymbol{k}$) is associated with the "diffusion" coefficient and the geometry of the sample, while the dimensionless drying parameter ($\boldsymbol{n}$) is related to food microstructure and the "type of diffusion" ($\boldsymbol{n}$ = 1 pure diffusion, $\boldsymbol{n}$ > 1 super-diffusion and $\boldsymbol{n}$ < 1 sub-diffusion). It means that when $\boldsymbol{n} \neq 1$, another mechanism apart from diffusion is important during the transport of water in the drying process, such as capillarity, matrix relaxation and the "sponge effect" due to ultrasound.

$$\frac{M-M_{eq}}{M_0-M_{eq}} = e^{-k.t^n} \quad (6)$$

The IR-Model (Eq. 3) and Page model (Eq. 6) were fitted to experimental data by identifying $\boldsymbol{D_{eff}}$ (Eq.3), and $\boldsymbol{k}$ *a*nd $\boldsymbol{n}$ (Eq. 6) values that minimize the sum of squared errors (SSE, Eq.7) between the experimental and the predicted values of the moisture content (M) at different drying times. The Generalized Reduced Gradient method implemented in the 'Solver' tool of software Excel 2016 (Microsoft, USA) was used for this purpose.

$$SSE = \sum_{i=1}^{x}((predicted) - (experimental))_i^2 \quad (7)$$

On the other hand, the IER model was solved by applying an implicit finite differences method described by Ortuño*, et al.* [4]. The fitting of this model was carried out by the simultaneous identification of both kinetic parameters, $\boldsymbol{D_{eff}}$ and $\boldsymbol{h}$. The

213 optimization was carried out through the SIMPLEX method available in Matlab (Fmin
214 search function), using the Matlab R2015b (Mathworks, Inc., USA) software.
215
216 **2.6. Total anthocyanins content**
217 The total anthocyanins content of raw samples, pre-treated, and dried samples, was
218 determined according to Giusti and Wrolstad [45] with some modifications. Thus, a first
219 extract was obtained by mixing 4 mL of acidified methanol (10 mL HCL·L^{-1} of methanol
220 (99.8%)) and the sample (~ 3.5 g of raw, fresh or ethanol pre-treated samples, and ~0.5
221 g of ground (coffee grinder, Lauson, 120W, PRC) dried samples). The mixture was
222 homogenized at 8000 r.p.m. with an ultraturrax (D1 25 basic, IKA-WERKE, Germany)
223 for 1 min. Then it was stirred for 20 min and centrifuged at 9167·g (Medifriger B1-5,
224 SELECTA, Barcelona, Spain) for 15 min, being both stages performed at 4 °C. The
225 supernatant was collected and stored in hermetic tubes protected from light. All these
226 operations were repeated 2 times under the same conditions with the remaining pellet
227 (mixed with 4 mL of solvent, centrifuged, and separated). Therefore, a total of 3
228 extractions were carried out (number needed to make the pellet colourless). The 3
229 supernatants were mixed, filtered, the total volume of the extract (mL) was determined
230 and the absorbance at 530 nm was measured. The total anthocyanins content was
231 expressed on cyanidin-3-glucoside equivalents (mg/g dry matter) according to equation
232 Eq. (8). At least nine replicates were performed for each treatment.

233 $$\text{Anthocyanins content}\left(\frac{\text{mg}}{\text{g dry matter}}\right) = \frac{\text{Abs}_{530} \text{ x DF x MW x V}}{\varepsilon \text{ x } m_{dm}} \quad (8)$$

234 Where DF is the dilution factor; MW is the molecular weight of cyanidin-3-glucoside
235 (449.2x10^3 mg·mol^{-1}); V is the volume of the extract (mL) and ε is the molar extinction
236 coefficient in mL·mol^{-1}·cm^{-1} for cyanidin-3-glucoside (34 300x10^3).
237

238 **2.7. Product colour**

239 The instrumental colour of fresh, pre-treated, and dried samples was measured
240 using a spectrophotometer CM-2500d (Konica Minolta, Japan) using a D65° illuminant
241 with an angle of observation of 10°. The CIE (*Commission Internationale d'Eclairage*)
242 colour scale was used, where parameters of L^* (lightness), a^* (green to red) and b^* (blue
243 to yellow) and h° (Hue angle) were obtained. To prevent deformation effects, the samples
244 were placed between two glass plates to obtain flat areas; in addition, the instrument
245 was calibrated to rule out the effect of the glass plates. At least eight readings were
246 obtained for each replicate.

247

248 **2.8. Antioxidant capacity**

249 **2.8.1. Obtaining sample extracts**

250 Sample extracts from raw, pre-treated, and dried samples were performed to assess
251 the antioxidant capacity (AC). Each extract was obtained by mixing 10 mL of ethanol
252 (96%) and the sample (~ 1.2 g of raw, fresh or ethanol pre-treated samples, and ~ 0.2 g
253 of ground (coffee grinder, Lauson, 120W, PRC) dried samples. The mixture was
254 homogenized at 8000 r.p.m. in an ultraturrax (D1 25 basic, IKA-WERKE, Germany) for
255 1 min. Then, the mix was stirred for 20 min using a magnetic stirrer with a stir bar and
256 then centrifuged at 9167·g (Medifriger B1-5, SELECTA, Barcelona, Spain) for 5 min at 4
257 °C. The supernatant was filtered and collected in hermetic glass flasks protected from
258 light, then the obtained extract was stored under refrigeration until analysis. At least three
259 extract replicates were performed for each treatment.

260

261 **2.8.2. Antioxidant capacity (AC)**

262 The ABTS method, described by Vieira*, et al.* [46] with some modifications, was used
263 to evaluate the antioxidant capacity (AC) of samples. The $ABTS^{\bullet+}$ radical was generated
264 according to Re*, et al.* [47] by oxidation of ABTS (2,2′-Azino-bis (3-ethylbenzothiazoline-6-
265 sulfonic acid) diammonium salt) (SIGMA-ALDRICH, Germany) 7mM, with potassium

266 persulphate (SIGMA-ALDRICH, Germany) 2.45 mM (final concentration). The mixture
267 was maintained in dark conditions for 16 h. Ethanol (96% v/v) was used to dilute the
268 $ABTS^{\bullet+}$ radical. Then, the ABTS solution was prepared by fitting their absorbance to
269 0.701 ± 0.003 at 734 nm using a spectrophotometer (Helios gamma UV-Vis
270 spectrophotometer, Thermo electron corporation, USA). For reaction, 2 mL of ABTS
271 solution were used, 50 µL of extract, and 150 µL of ethanol. After performing the reaction,
272 it was left for 20 min in the dark at room temperature and the absorbance was read at
273 734 nm. A calibration curve was performed with solutions of different known
274 concentrations of Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid)
275 (SIGMA-ALDRICH, Germany) 0.5mM (from 10 to 75 µL). The antioxidant capacity was
276 expressed in µg of Trolox/mg dry matter. At least nine replicates were performed for each
277 treatment.
278
279 **2.9. Experimental design and statistical analyses**
280 A completely randomised design (CRD) was conducted. All processes and analyses
281 were performed at least 3 times. The ANOVA test was carried out with a significance
282 level of 5%. To determine statistical differences among means of treatments, Tukey test
283 was used. Statistical analyses were determined using the IBM SPSS Statistics 23
284 software (IBM SPSS, USA).
285
286 **3. Results and discussion**
287 **3.1. Drying kinetics**
288 The effects of three process variables studied in this work, ethanol concentration,
289 colouring addition, and ultrasound application were evaluated in drying kinetics (Figure
290 2). Therefore, drying time of different conditions tested was calculated considering the
291 time required to reach a mass variation lower than 0.05 g in the three last registered
292 weights (0.08 ± 0.02 kg water·kg^{-1} dry matter, final moisture). Drying time reduction was
293 estimated considering the drying of Control samples as reference (Figure 3). In this

294 sense, the US-assisted dried samples showed the highest drying time reductions, being
295 significantly higher ($p<0.05$) than reductions obtained in pre-treated samples dried
296 without US aplication.

297 In addition, Figure 3 shows the ethanol concentration influence was significant only
298 in samples with colouring addition and dried without US application. In these cases,
299 drying time reduction (21 ± 2%) for E30% was greater than the reductions for Cc and
300 E15%c pre-treated samples (Figure 3). The drying time reductions in E30% experiments
301 were similar to those obtained in other products such as Guaco leaves [16], garlic [23], apple
302 [17] or potato [12], pre-treated with greater ethanol concentration solutions (>90% v/v) and
303 shorter times (from 5 s to 3 min). Nonetheless, time reductions above 50% were found
304 during conventional drying of pumpkin [11, 21] and apple samples [19], all pre-treated for
305 longer times (from 15 min to 60 min) by immersion in concentrated ethanol
306 solutions(>90% v/v).

307 The application of US during drying significantly shortened the drying process, its
308 effect overcomes the ethanol pre-treatment effects. In fact, two well-differentiated groups
309 were identified: the US-assisted convective drying process and the convective drying
310 ones (Figure 2.B; 2.D). Thus, drying time in all treatments was reduced from 40% to 60%
311 when was applied US-assisted convective drying (Figure 3). Similar reductions (46.1%)
312 were obtained during US-assisted drying of apple (50 °C, 1 $m \cdot s^{-1}$, 30.8 $kW \cdot m^{-3}$) [48], but
313 also in other products such as kiwifruit (65%) [2], orange peel (45%) [4], or passion fruit peel
314 (48%) [34].

315 To a better comparison between the different conditions tested, models from
316 Equations 3, 5 and 6 were fitted to the experimental drying data, identifying the
317 corresponding parameters (Table 2). In the case of the IR-Model (Eq.3), the low
318 percentage of explained variance (%Var) figures obtained (< 93%) showed a
319 considerable lack of fit of this model. In fact, purely diffusive models were not accurate
320 to simulate the drying kinetics in previous works carried out at similar dying conditions [48,
321 49]. This suggests the water transport was controlled not only by internal resistance but

322 also by the external one, probably due to the limited turbulences produced by the low air
323 velocity (1 $m \cdot s^{-1}$) considered in this study. In any case, the effective diffusivity identified
324 figures indicated an increase of drying kinetics when ultrasound was applied, being
325 increased up to 146% for E30%US (Table 2). Regarding the influence of colouring
326 addition or the ethanolic pre-treatment, no significant differences were found.

327 On the contrary, the fitting of IER-Model, which includes both internal and external
328 mass transfer resistance, provided %Var greater than 98% in every condition tested.
329 Compared to Control samples (C), the US application (CUS) highly increased (288%)
330 the identified $\boldsymbol{D_{eff}}$. In contrast, no effects of ethanol pre-treatment on this parameter were
331 observed. This agrees with the previously reported for apple drying assisted by US [48]
332 and demonstrates that US has an important effect in the internal resistance to mass
333 transfer. This fact is likely related to the alternative compressions and decompressions
334 ("sponge effect") produced by the US waves, which promotes water flow through the
335 intercellular spaces, existing channels and also through new microscopic channels
336 created by the mechanical stress [50, 51]. When ethanol pre-treatment is combined with US
337 application, apparently the $\boldsymbol{D_{eff}}$ value decrease, mainly at the highest ethanol
338 concentration tested (E30%). Consequently, the ethanol pre-treatments could influence
339 other mechanisms of mass transfer that counteract the US effects on $\boldsymbol{D_{eff}}$.

340 Regarding the mass transfer coefficient ($\boldsymbol{h}$), ultrasound application (CUS) increased
341 by 72% the $\boldsymbol{h}$ value when compared to Control (C). This fact can be attributed to pressure
342 variations, oscillating velocities or microstreaming produced by ultrasound at solid-air
343 interface, which reduce the boundary layer thickness and enhance the water transfer [1,
344 4]. In contrast, the ethanol pre-treatment did not significantly affect the $\boldsymbol{h}$ value, probably
345 because the low concentrations of ethanol used. However, the combination of ethanol
346 pre-treatment and ultrasound application during drying intensified the effects of
347 ultrasound. Thus, compared with C experiments, ethanol pre-treatment at highest
348 solution concentration followed by ultrasonically assisted drying (E30%US) increased up

to 134% the $\boldsymbol{h}$ value. It suggests that the ethanol pre-treatment effects (related to ethanol properties, structure and composition modifications), which occurs especially in the sample surface [11-13, 19, 22, 23] leads to modifications in the air-product interface. These modifications could promote the water vaporization when ultrasound was applied.

Finally, the Page model was also fitted to the experimental drying kinetics. Thus, compared to Control experiments, the $\boldsymbol{k}$ parameter value increased with the ethanol pre-treatment while remained similar when US was applied. On the other hand, the $\boldsymbol{n}$ value increased with US application. According to Simpson*, et al.* [44], the $\boldsymbol{n}$ value is related to the "type of diffusion"; attributing a super-diffusive behaviour at values of $\boldsymbol{n}$ greater than 1. In the present study, the highest $\boldsymbol{n}$ value was obtained in experiments which also presented the highest $\boldsymbol{D_{eff}}$ value (US-assisted drying experiments). This reinforces the idea of $\boldsymbol{D_{eff}}$ as a parameter that includes not only the pure diffusion phenomenon but also other mass transfer mechanisms such as the induced by ultrasound application.

Linking the Page Model and IER-Model parameters, it can be suggested that higher $\boldsymbol{n}$ values of US-assisted dried samples could occur when internal mass transfer mechanisms were improved, which was also reflected by the increase of the $\boldsymbol{D_{eff}}$ value. On the other hand, the Page kinetic parameter ($\boldsymbol{k}$) seems to be improved with the ethanol pre-treatment and the external resistance decrease, which was also showed in the increase of the $\boldsymbol{h}$ values from IER-Model fitting.

Regarding the addition of colourant, no influence in experimental drying kinetics was observed neither in the parameters identified of the different models tested.

3.2. Properties of the obtained apple chips

3.3. Total anthocyanins content

After pre-treatments, regarding the fresh samples, the black carrot colouring addition increased the anthocyanins content more than 947±132%. The anthocyanins content was 0.095±0.019 mg·g^{-1} dry matter for Cc, 0.093±0.012 mg·g^{-1} dry matter for E15%c,

and 0.096±0.001 mg·g^{-1} dry matter for E30%c. Independently of the ethanol concentration considered, non-significant influence ($p>0.05$) of ethanol pre-treatments in the anthocyanins content was found (Figure 4).

After drying, the incorporated anthocyanins were completely retained in all pre-treatments, as can be observed in Figure 4. These results are remarkably interesting and reflect the stability of the anthocyanins, which was maintained during both pre-treatments and drying processes. In fact, the anthocyanins from black carrot are known by its stability and they have been used as a model of bioactive substances or to improve product properties. For example, Day*, et al.* [31] incorporated black carrot concentrate in pasta, enhancing functionality and quality or Yılmaz and Ersus Bilek [30] impregnated black carrot extract into ready to eat apple discs, increasing anthocyanins, flavonoid and phenolic content and also antioxidant capacity. Therefore, since the use of black carrot extract could influence not only on the anthocyanins content but also on other product properties, the sample colour and antioxidant capacity were evaluated below.

3.3.1. Product colour

As expected, the changes in colour produced by the addition of colouring were visible to the naked eye (Figure 5), which were quantified by the instrumental colour parameters (Table 3). No significant differences of colour parameters between samples dried with and without US were found (Table 3). Thus, only some representative images of samples dried without US are showed in Figure 5.

The addition of black carrot extract, rich in anthocyanins, changed the apple pulp colour from the white-light green of fresh samples to pink-red colours of impregnated ones. Therefore, compared to fresh material, the lightness (L*) decreased with pre-treatments being this more pronounced in samples with the colouring application and ethanol pre-treatment at 30% (E30%) (Table 3). The L* value is correlated with the characteristics of the sample surface. Therefore, the L* decrease could be a consequence of both the surface tissue modifications caused by ethanol[11, 12, 52], and

composition modifications caused by acidified solution, with ethanol and/or colourant, which enters the sample. After drying, compared to control and uncoloured samples, the measured L* values were significantly lower ($p<0.05$) for all pre-treatments with colouring addition. It means that the coloured samples absorbed more light, and then decreasing the L* values.

Regarding the a* parameter, in the samples with colouring addition the a* increased significantly ($p<0.05$) after pre-treatments, compared to fresh, control and uncoloured samples. After drying, compared to control and uncoloured samples, the same trend was maintained in coloured samples. This is expected, once an increase in a* means a change towards redness colours (Figure 6, Table 3). Moreira and Almohaimeed [27] studied the incorporation of potato slices pre-treated with beetroot extract solution with different concentrations (3, 5, and 7% m/m), with and without vacuum. The chips impregnated with colourant showed lower L* and higher a* value than the other treatments.

On the other hand, compared to fresh and control, the b* values did not change due to pre-treatment with ethanol. However, the colouring addition produced a significant decrease of b* ($p<0.05$), which means the coloured samples were less yellowness. Similarly, after drying, b* values of coloured samples were lower than control and those without colouring, in which their highest b* values mean a trend towards more yellowness colours.

Therefore, the values of a* and b* suggest the sample colours were found between the redness and yellowness tones. To better visualize it, the Hue angle (h°) was calculated (Table 3). Considering that h° values of 0, 90, 180 and 270 represent the maximum values for redness, yellowness, greenness, and blueness hues, respectively[53], it was observed that all h° values were from 17 for coloured samples to 108 for samples without colouring addition. After the pre-treatments and compared to fresh samples, the h° value decreased significantly ($p<0.05$) in all the samples with added colouring. The values show redness hues, while the fresh and uncoloured samples show slightly

greenish yellowness hues. After drying, the trend in treatments was the same as after pre-treatment. Colouring addition treatments showed the lowest h° values, which means that the samples retained a redness hue after drying while the others retained their yellowness hue (Table 3 and Figure 6).

Finally, it is important to mention that the ethanol pre-treatments and ultrasound improved the drying but did not significantly influence the colour of the samples. This would be a good way to obtain a dry product differentiated in terms of colour.

.

3.4. Antioxidant capacity

The antioxidant capacity (AC) was assessed in fresh samples, after pre-treatments in ethanolic solutions and after drying. The antioxidant capacity (AC) of raw apple samples was 7.4 ± 0.7 (μg Trolox·mg^{-1} of dry matter).

The pre-treatment, decreased AC of fresh samples, not founding significant differences ($p>0.05$) among the Control and the different pre-treatment conditions tested (Figure 7). According to previous studies, the compound reduction could be explained to ethanol extraction effects. This fact has been observed in garlic slices, where Feng*, et al.* [23] found a decrease of the allicin content after an ethanolic (75% v/v) pre-treatment for 30min; and also in apple, where Zubernik*, et al.* [17] reported a reduction of the total phenolic content after an ethanolic (96% v/v) pre-treatment for 1-3 min. Nevertheless, as mentioned, even in the Control pre-treatment there was AC reduction, not significantly different from the other pre-treatments, which included ethanol addition (Figure 7). This means that, under the studied conditions, the observed AC reduction cannot only be attributed to the extraction effects of ethanol, but it was an effect of sample surface rinse with all the used solutions, which in this case, could be an important effect because of the small thickness of samples.

Therefore, it could be stated that different factors can influence the extraction effects during ethanol pre-treatments, such as ethanol concentration, time of pre-treatment, temperature, type of compound considered, food matrix and the geometry of

460 the sample. This can explain why not significant effects of the ethanol pre-treatments
461 were observed, in some cases, such as in the carotenoid content in pumpkin [21].
462 After drying, compared to Control, the highest AC was observed in the samples
463 that were pre-treated with colouring without ethanol, and US-assisted drying (CcUS,
464 Figure 8). Regarding the AC of the ethanol pre-treated samples and dried without US, it
465 remained similar than those observed in Control ones, except for E15% pre-treatment
466 which AC was higher. Probably at 15% of ethanol, the modifications due to ethanol were
467 not severe and, in turn, the reduction in drying time was sufficient to preserve its AC.
468 However, in ethanol pre-treated samples without colouring addition, the US application
469 decreased the AC content particularly those treated with the highest ethanol solution
470 concentration (E30%US). These reductions probably mean a combined effect of ethanol
471 pre-treatments with US-assisted drying, in the sample structure [11, 12, 52], then exposing
472 the antioxidant compounds to deteriorating effects of drying.
473 Summarizing, in all the coloured apple samples (Cc, E15%c, E15%cUS, E30%c,
474 E30%cUS) the AC contents were at least like Control or even higher, as is the case of
475 CcUS samples. It means that the addition of colorant allowed to maintain the AC levels,
476 even when using ethanol at the highest concentration(E30%) and US-assisted drying.
477 These results indicated that the combining of ethanol pre-treatment and ultrasound-
478 assisted convective drying permitted the added black carrot anthocyanins to be retained
479 after drying. This procedure could be used to produce apple chips with different colours
480 without deteriorating the nutritional properties.

4. Conclusions

Black carrot extract, rich in anthocyanins, was used to improve apple chips properties (total anthocyanins content, colour, and antioxidant capacity). Different pre-treatments varying ethanol concentrations were evaluated to improve drying with and or without ultrasound. The kinetic parameters identified by modelling suggested that the ultrasound application reduced both internal and external resistance to water transfer. Moreover, a complementary effect of ethanol pre-treatment with ultrasound application was observed, decreasing the external resistance. The total anthocyanins content highly increased with colouring addition and it was retained after drying. The colouring had a significant impact on apple colour parameters, before and after drying, decreasing the lightness and increasing the redness in contrast to samples without colouring, which showed principally an increase in lightness and yellowness. The use of colouring allowed antioxidant capacity retention after drying for all pre-treatments. Therefore, a double purpose was obtained: the ethanol pre-treatment and ultrasound contributed to drying process improvement and the black carrot colouring use contributed to maintaining the product properties.

References

1. Rodríguez Ó, Eim V, Rosselló C, Femenia A, Cárcel JA and Simal S, Application of power ultrasound on the convective drying of fruits and vegetables: effects on quality. *Journal of the Science of Food and Agriculture* **99**:966-966 (2019).
2. Vallespir F, Rodríguez Ó, Cárcel JA, Rosselló C and Simal S, Ultrasound assisted low-temperature drying of kiwifruit: Effects on drying kinetics, bioactive compounds and antioxidant activity. *Journal of the Science of Food and Agriculture* **99**:2901-2909 (2019).
3. Colucci D, Fissore D, Rossello C and Carcel JA, On the effect of ultrasound-assisted atmospheric freeze-drying on the antioxidant properties of eggplant. *Food Research International* **106**:580-588 (2018).
4. Ortuño C, Pérez-Munuera I, Puig A, Riera E and Garcia-Perez JV, Influence of power ultrasound application on mass transport and microstructure of orange peel during hot air drying. *Physics Procedia* **3**:153-159 (2010).
5. Cárcel J, García-Pérez J, Benedito J and Mulet A, Food process innovation through new technologies: Use of ultrasound. *Journal of Food Engineering* **110**:200-207 (2012).
6. De la Fuente-Blanco S, Riera-Franco de Sarabia E, Acosta-Aparicio VM, Blanco-Blanco A and Gallego-Juárez JA, Food drying process by power ultrasound. *Ultrasonics* **44, Supplement**:e523-e527 (2006).
7. Miano AC, Ibarz A and Augusto PED, Mechanisms for improving mass transfer in food with ultrasound technology: Describing the phenomena in two model cases. *Ultrasonics Sonochemistry* **29**:413-419 (2016).
8. Mason TJ, Paniwnyk L and Lorimer JP, The uses of ultrasound in food technology. *Ultrasonics Sonochemistry* **3**:S253-S260 (1996).
9. Corrêa J, Rasia M, Mulet A and Cárcel J, Influence of ultrasound application on both the osmotic pretreatment and subsequent convective drying of pineapple (Ananas comosus). *Innovative Food Science & Emerging Technologies* **41**:284-291 (2017).
10. Nowacka M, Wiktor A, Śledź M, Jurek N and Witrowa-Rajchert D, Drying of ultrasound pretreated apple and its selected physical properties. *Journal of Food Engineering* **113**:427-433 (2012).
11. Rojas ML and Augusto PED, Ethanol pre-treatment improves vegetable drying and rehydration: Kinetics, mechanisms and impact on viscoelastic properties. *Journal of Food Engineering* **233**:17-27 (2018).
12. Rojas ML and Augusto PED, Ethanol and ultrasound pre-treatments to improve infrared drying of potato slices. *Innovative Food Science & Emerging Technologies* **49**:65-75 (2018).
13. Rojas ML, Silveira I and Augusto PED, Improving the infrared drying and rehydration of potato slices using simple approaches: Perforations and ethanol. *Journal of Food Process Engineering* **42**:e13089 (2019).
14. Silva MA, Braga AMP and Santos PHS, Enhancement of fruit drying: the ethanol effect, in *Proceedings of the 18th International Drying Symposium (IDS 2012)*, Ed, Xiamen (2012).
15. Llavata B, García-Pérez JV, Simal S and Cárcel JA, Innovative pre-treatmentS to enhance food DRYING: a current review. *Current Opinion in Food Science* (2019).
16. Silva MG, Celeghini RMS and Silva MA, Effect of ethanol on the drying characteristics and on the coumarin yield of dried guaco leaves (Mikania laevigata SCHULTZ BIP. EX BAKER). *Brazilian Journal of Chemical Engineering* **35**:1095-1104 (2018).
17. Zubernik J, Dadan M, Cichowska J and Witrowa-Rajchert D, The Impact of the Pre-Treatment in Ethanol Solution on the Drying Kinetics and Selected Properties of Convective Dried Apples. *International Journal of Food Engineering* **16**:11 (2019).
18. Corrêa JLG, Braga AMP, Hochheim M and Silva MA, The Influence of Ethanol on the Convective Drying of Unripe, Ripe, and Overripe Bananas. *Drying Technology* **30**:817-826 (2012).
19. Rojas ML, Augusto PED and Cárcel JA, Ethanol pre-treatment to ultrasound-assisted convective drying of apple. *Innovative Food Science & Emerging Technologies* **61**:102328 (2020).

20. Umbelina A, Luiz J, Corrêa G, Letícia Almeida O, Francemir José L and Elias R, The Influence of Ethanol and Vacuum on Okara Drying. (2018).
21. Rojas ML, Silveira I and Augusto PED, Ultrasound and ethanol pre-treatments to improve convective drying: Drying, rehydration and carotenoid content of pumpkin. *Food and Bioproducts Processing* **119**:20-30 (2020).
22. Wang X, Feng Y, Zhou C, Sun Y, Wu B, Yagoub AEA and Aboagarib EAA, Effect of vacuum and ethanol pretreatment on infrared-hot air drying of scallion (Allium fistulosum). *Food Chemistry* **295**:432-440 (2019).
23. Feng Y, Zhou C, ElGasim A. Yagoub A, Sun Y, Owusu-Ansah P, Yu X, Wang X, Xu X, Zhang J and Ren Z, Improvement of the catalytic infrared drying process and quality characteristics of the dried garlic slices by ultrasound-assisted alcohol pretreatment. *LWT* **116**:108577 (2019).
24. Rojas ML, Alvim ID and Augusto PED, Incorporation of microencapsulated hydrophilic and lipophilic nutrients into foods by using ultrasound as a pre-treatment for drying: A prospective study. *Ultrasonics Sonochemistry* **54**:153-161 (2019).
25. Assis FR, Rodrigues LGG, Tribuzi G, de Souza PG, Carciofi BAM and Laurindo JB, Fortified apple (Malus spp., var. Fuji) snacks by vacuum impregnation of calcium lactate and convective drying. *LWT* **113**:108298 (2019).
26. Lima MMd, Tribuzi G, Souza JARd, Souza IGd, Laurindo JB and Carciofi BAM, Vacuum impregnation and drying of calcium-fortified pineapple snacks. *LWT - Food Science and Technology* **72**:501-509 (2016).
27. Moreira RG and Almohaimeed S, Technology for processing of potato chips impregnated with red rootbeet phenolic compounds. *Journal of Food Engineering* **228**:57-68 (2018).
28. Bellary AN, Indiramma AR, Prakash M, Baskaran R and Rastogi NK, Anthocyanin infused watermelon rind and its stability during storage. *Innovative Food Science & Emerging Technologies* **33**:554-562 (2016).
29. Maleki M, Shahidi F, Varidi MJ and Azarpazhooh E, Hot air drying kinetics of novel functional carrot snack: Impregnated using polyphenolic rich osmotic solution with ultrasound pretreatment. *Journal of Food Process Engineering* **43**:e13331 (2020).
30. Yılmaz FM and Ersus Bilek S, Ultrasound-assisted vacuum impregnation on the fortification of fresh-cut apple with calcium and black carrot phenolics. *Ultrasonics Sonochemistry* **48**:509-516 (2018).
31. Day L, Seymour RB, Pitts KF, Konczak I and Lundin L, Incorporation of functional ingredients into foods. *Trends in Food Science & Technology* **20**:388-395 (2009).
32. García-Pérez JV, Cárcel JA, de la Fuente-Blanco S and Riera-Franco de Sarabia E, Ultrasonic drying of foodstuff in a fluidized bed: Parametric study. *Ultrasonics* **44, Supplement**:e539-e543 (2006).
33. Martins MP, Cortés EJ, Eim V, Mulet A and Cárcel JA, Stabilization of apple peel by drying. Influence of temperature and ultrasound application on drying kinetics and product quality. *Drying Technology* **37**:559-568 (2019).
34. do Nascimento EMGC, Mulet A, Ascheri JLR, de Carvalho CWP and Cárcel JA, Effects of high-intensity ultrasound on drying kinetics and antioxidant properties of passion fruit peel. *Journal of Food Engineering* **170**:108-118 (2016).
35. Rodrigues S, Silva LCA, Mulet A, Cárcel JA and Fernandes FAN, Development of dried probiotic apple cubes incorporated with Lactobacillus casei NRRL B-442. *Journal of Functional Foods* **41**:48-54 (2018).
36. Moreno C, Brines C, Mulet A, Rosselló C and Cárcel J, Antioxidant potential of atmospheric freeze-dried apples as affected by ultrasound application and sample surface. *Drying Technology* **35**:957-968 (2017).
37. Erbay Z and Icier F, A Review of Thin Layer Drying of Foods: Theory, Modeling, and Experimental Results. *Critical Reviews in Food Science and Nutrition* **50**:441-464 (2010).

38. Bon J, Rosselló C, Femenia A, Eim V and Simal S, Mathematical Modeling of Drying Kinetics for Apricots: Influence of the External Resistance to Mass Transfer. *Drying Technology* **25**:1829-1835 (2007).
39. Vega-Gálvez A, Miranda M, Bilbao-Sáinz C, Uribe E and Lemus-Mondaca R, Empirical modeling of drying process for apple (Cv. Granny Smith) slices at different air temperatures. *Journal of Food Processing and Preservation* **32**:972-986 (2008).
40. Crank J, *The mathematics of diffusion*. Oxford university press (1979).
41. Cárcel JA, Garcia-Perez JV, Riera E and Mulet A, Improvement of Convective Drying of Carrot by Applying Power Ultrasound—Influence of Mass Load Density. *Drying Technology* **29**:174-182 (2011).
42. Gamboa-Santos J, Montilla A, Cárcel JA, Villamiel M and Garcia-Perez JV, Air-borne ultrasound application in the convective drying of strawberry. *Journal of Food Engineering* **128**:132-139 (2014).
43. Page GE, Factors Influencing the Maximum Rates of Air Drying Shelled Corn in Thin layers, Ed. Purdue University, Ann Arbor (1949).
44. Simpson R, Ramírez C, Nuñez H, Jaques A and Almonacid S, Understanding the success of Page's model and related empirical equations in fitting experimental data of diffusion phenomena in food matrices. *Trends in Food Science & Technology* **62**:194-201 (2017).
45. Giusti MM and Wrolstad RE, Characterization and measurement of anthocyanins by UV-visible spectroscopy. *Current protocols in food analytical chemistry*:F1. 2.1-F1. 2.13 (2001).
46. Vieira FGK, Borges GDSC, Copetti C, Amboni RDDMC, Denardi F and Fett R, Physico-chemical and antioxidant properties of six apple cultivars (Malus domestica Borkh) grown in southern Brazil. *Scientia Horticulturae* **122**:421-425 (2009).
47. Re R, Pellegrini N, Proteggente A, Pannala A, Yang M and Rice-Evans C, Antioxidant activity applying an improved ABTS radical cation decolorization assay. *Free radical biology and medicine* **26**:1231-1237 (1999).
48. Rodríguez Ó, Santacatalina JV, Simal S, Garcia-Perez JV, Femenia A and Rosselló C, Influence of power ultrasound application on drying kinetics of apple and its antioxidant and microstructural properties. *Journal of Food Engineering* **129**:21-29 (2014).
49. García-Pérez JV, Rosselló C, Cárcel JA, De la Fuente S and Mulet A, Effect of Air Temperature on Convective Drying Assisted by High Power Ultrasound. *Defect and Diffusion Forum* **258-260**:563-574 (2007).
50. García-Pérez JV, Cárcel JA, Benedito J and Mulet A, Power Ultrasound Mass Transfer Enhancement in Food Drying. *Food and Bioproducts Processing* **85**:247-254 (2007).
51. Ozuna C, Gómez Álvarez-Arenas T, Riera E, Cárcel JA and Garcia-Perez JV, Influence of material structure on air-borne ultrasonic application in drying. *Ultrasonics Sonochemistry* **21**:1235-1243 (2014).
52. Santos KC, Guedes JS, Rojas ML, Carvalho GR and Augusto PED, Enhancing carrot convective drying by combining ethanol and ultrasound as pre-treatments: Effect on product structure, quality, energy consumption, drying and rehydration kinetics. *Ultrasonics Sonochemistry* **70**:105304 (2021).
53. Purkayastha MD, Nath A, Deka BC and Mahanta CL, Thin layer drying of tomato slices. *Journal of food science and technology* **50**:642-653 (2013).

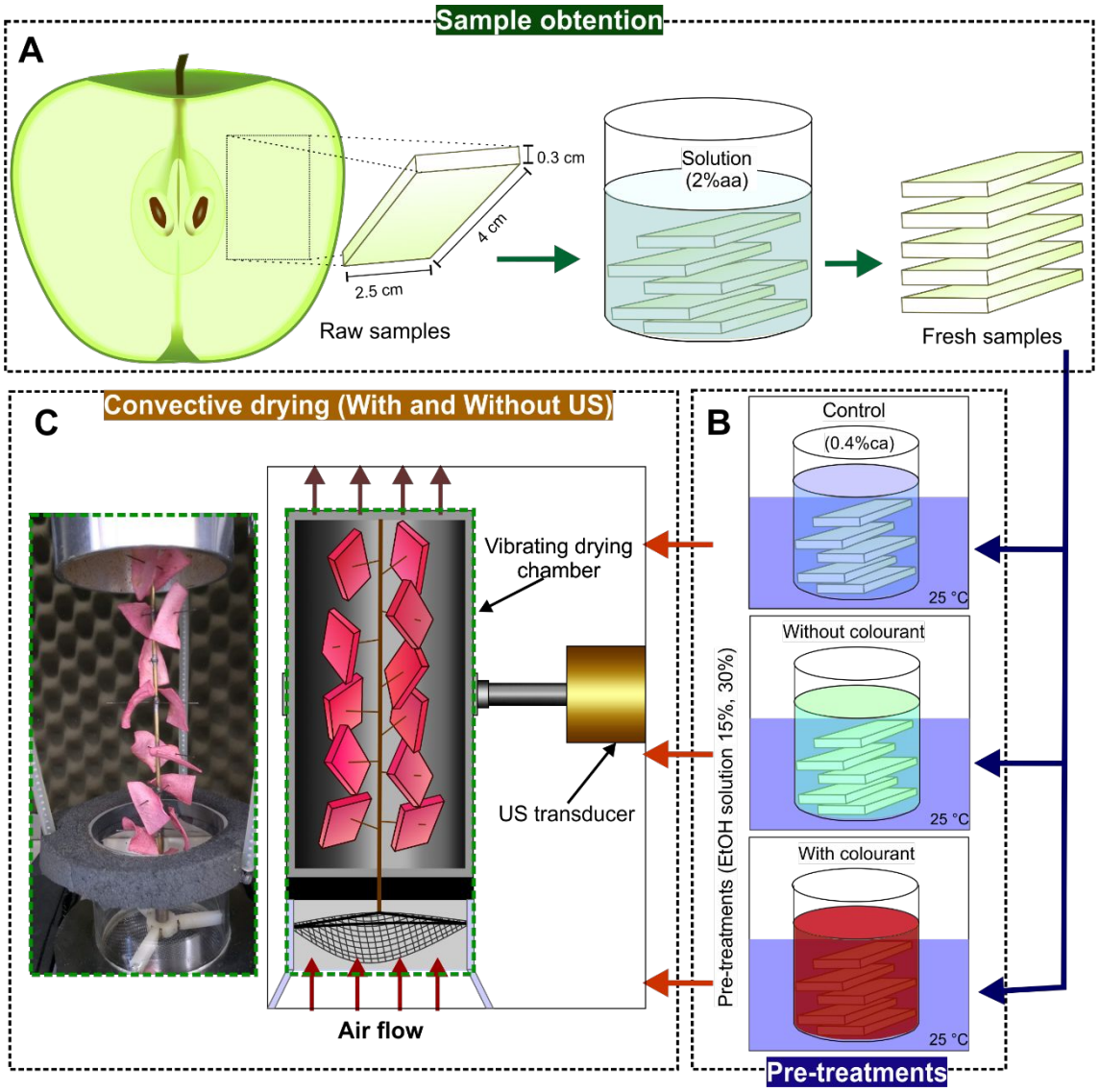

Figure 1. Schematic representation of sample shaping, pre-treatments performed and convective drying.

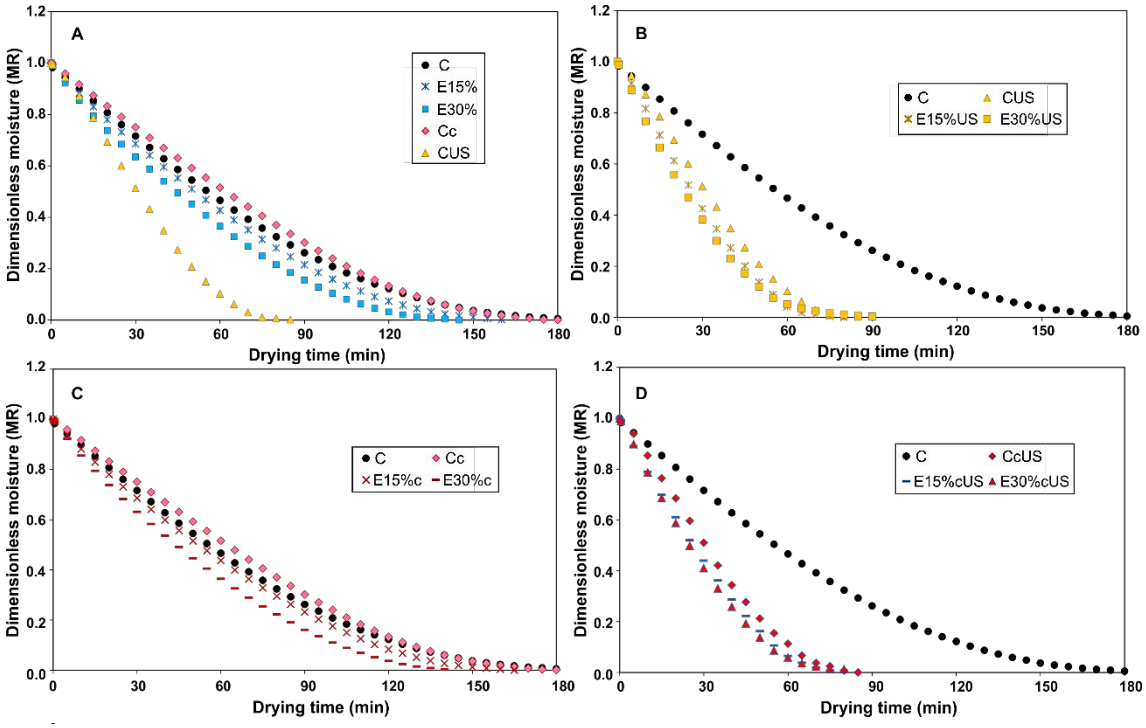

Figure 2. Dimensionless moisture content (MR) evolution during drying (50ºC; 1 $m \cdot s^{-1}$) of apple samples. Regarding the Control (C), A: Curves of pre-treatment with the addition of colouring (Cc), pre-treatments with ethanol (E15% and E30%) and the US-assisted drying (20.5 $kW \cdot m^{-3}$; 21.77 kHz) (CUS). B: Curves for ethanol pre-treatments and US-convective drying (CUS, E15%US, E30%US). C: Curves for ethanol with colouring addition pre-treatments and convective drying (Cc, E25%c, E30%c). D: Curves for ethanol with colouring addition pre-treatments and US-assisted drying (CcUS, E15%cUS, E30%cUS). Each curve is representative of more than three replicates.

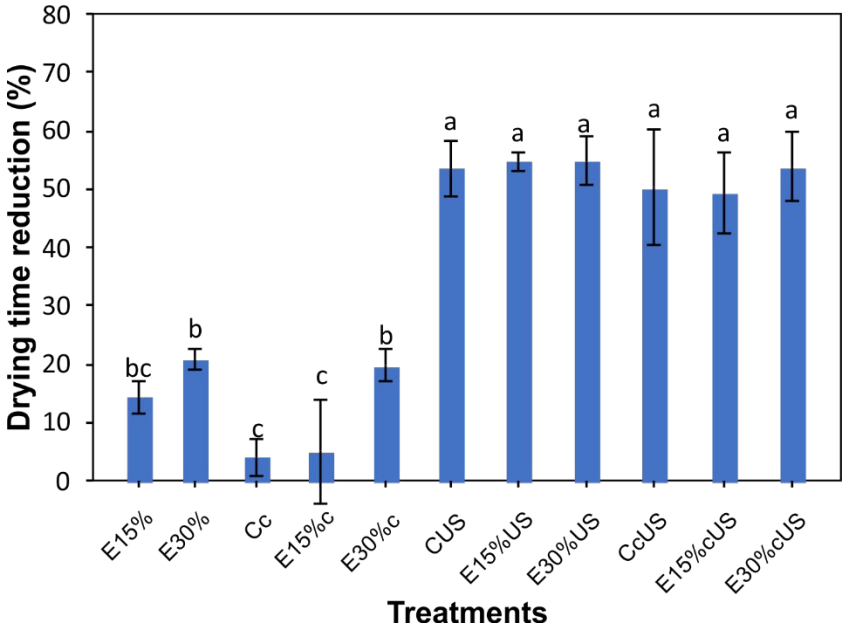

Figure 3. Regarding the Control, Average ± Standard deviation of the drying time reduction (%) produced by colouring addition, and ethanol (E15% and E30 %) pre-treatments applied to convective drying (50 ºC; 1 $m \cdot s^{-1}$) and US-assisted (20.5 $kW \cdot m^{-3}$; 21.77 kHz) drying. Different letters indicate significant differences determined by Tukey test ($p<0.05$).

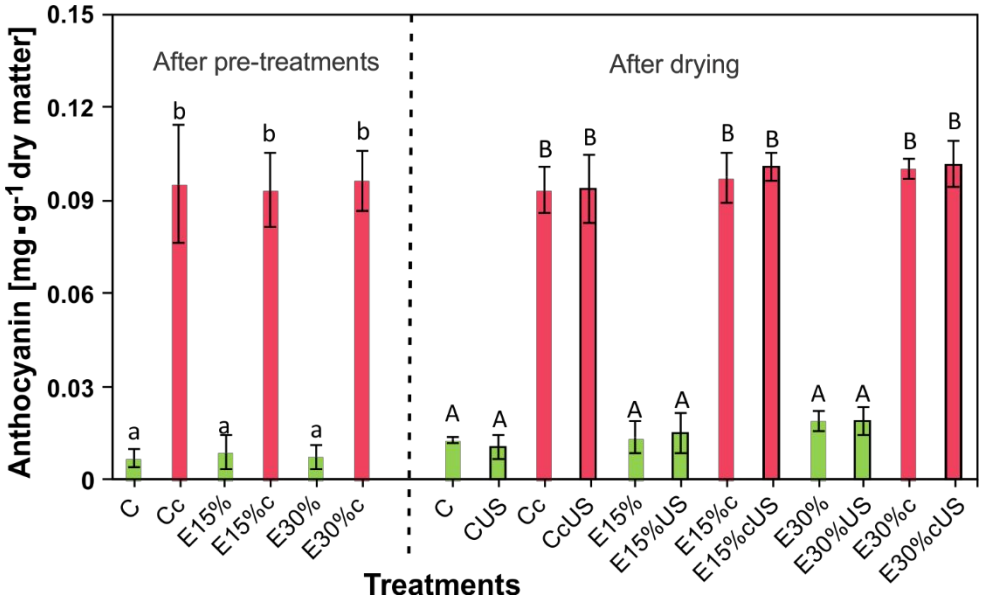

Figure 4. Average ± Standard deviation of the total anthocyanins content of apple samples after pre-treatments and after drying. Different lowercase and uppercase letters indicate significant differences determined by Tukey test ($p<0.05$) before and after drying, respectively

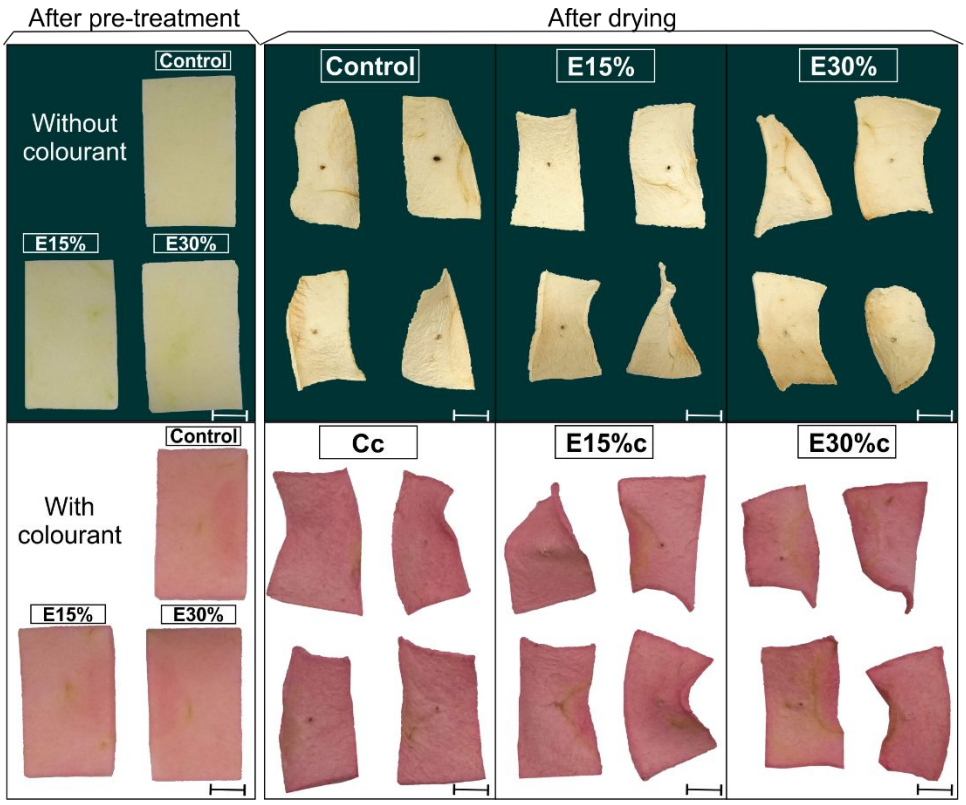

Figure 5. Images (scale bar of 1 cm) of apple samples with and without addition of black carrot colouring after pre-treatments and after drying.

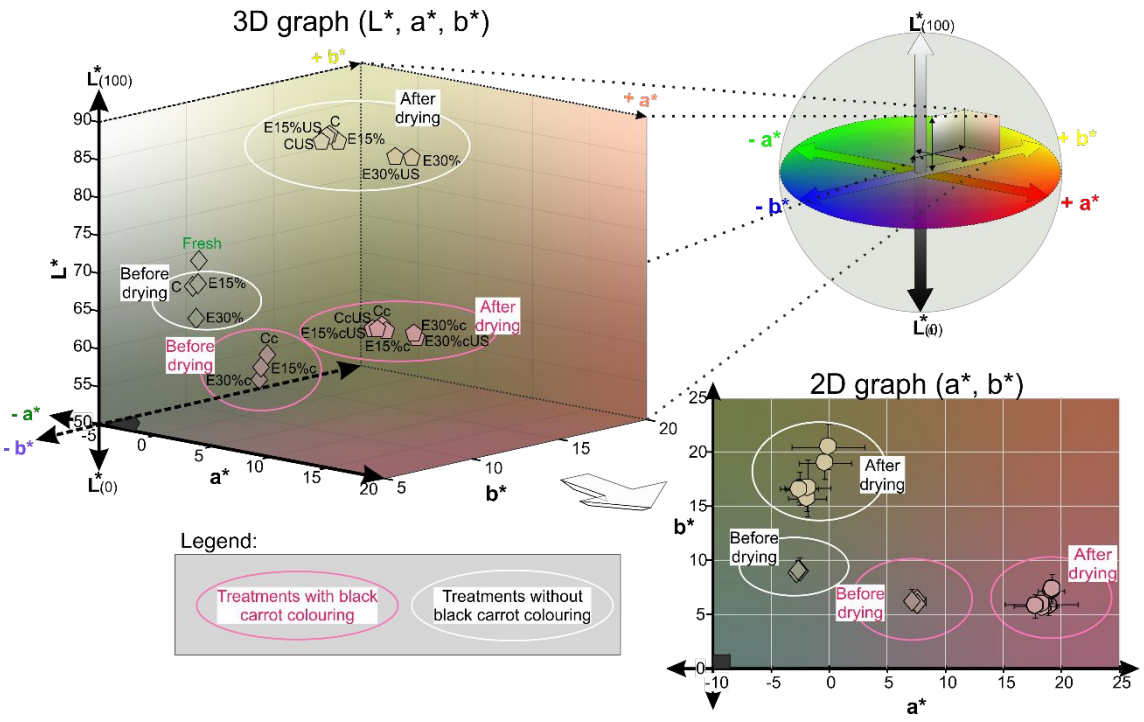

Figure 6. Colour of fresh, pre-treated (before drying) and dried samples represented in a three-dimensional (L*, a* b*) and two-dimensional (a*, b*) plane with an L* value fixed in 50.

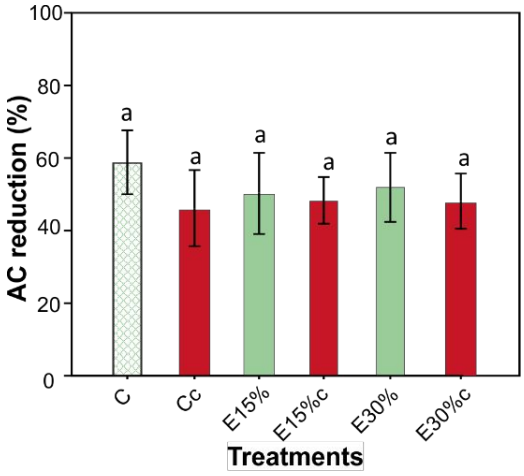

Figure 7. Average ± Standard deviation of the antioxidant capacity reduction (%) after pre-treatments regarding fresh samples. Equal letters indicate non-significant differences determined by Tukey test ($p>0.05$).

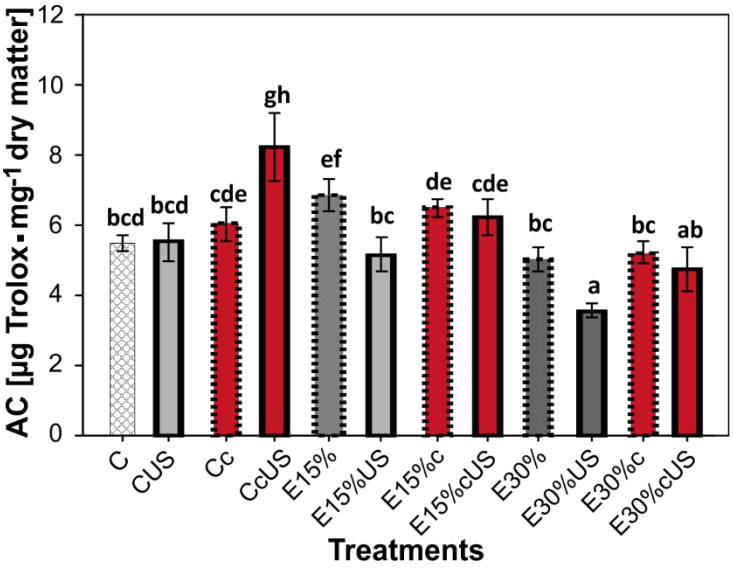

Figure 8. Average ± Standard deviation of the antioxidant capacity after drying of Control and ethanol pre-treated samples with and without addition of black carrot colouring extract. Different letters indicate significant differences determined by Tukey test ($p<0.05$).

Table 1. Pre-treatments of apple samples performed in ethanol solutions with or without black carrot colouring addition and dried with convective and US-assisted convective drying.

Pre-treatment (code)	Description
C	Control samples. Samples immersed in citric acid solution (4 g·L^{-1}) for 15 min at 25 °C, and convective drying.
CUS	Samples immersed in citric acid solution (4 g·L^{-1}) for 15 min at 25 °C, and US-assisted convective drying.
Cc	Samples immersed in citric acid solution (4 g·L^{-1}) with colouring addition (2 g·L^{-1} of acid solution) for 15 min at 25 °C, and convective drying.
CcUS	Samples immersed in citric acid solution (4 g·L^{-1}) with colouring addition (2 g·L^{-1} of acid solution) for 15 min at 25 °C, and US-assisted convective drying.
E15%	Samples immersed in acid ethanol solution (150 mL·L-1, 15% v/v) for 15 min at 25 °C, and convective drying.
E15%US	Samples immersed in acid ethanol solution (150 mL·L-1, 15% v/v) for 15 min at 25 °C, and US-assisted convective drying.
E15%c	Samples immersed in acid ethanol solution (150 mL·L-1, 15% v/v) with colouring addition (2 g·L^{-1} of ethanol acid solution) for 15 min at 25 °C, and convective drying.
E15%cUS	Samples immersed in acid ethanol solution (150 mL·L-1, 15% v/v) with colouring addition (2 g·L^{-1} of ethanol acid solution) for 15 min at 25 °C, and US-assisted convective drying.
E30%	Samples immersed in acid ethanol solution (300 mL·L-1, 30% v/v) for 15 min at 25 °C, and convective drying.
E30%US	Samples immersed in acid ethanol solution (300 mL·L-1, 30% v/v) for 15 min at 25 °C, and US-assisted convective drying.
E30%c	Samples immersed in acid ethanol solution (300 mL·L-1, 30% v/v) with colouring addition (2 g·L^{-1} of acid ethanol solution) for 15 min at 25 °C, and convective drying.
E30%cUS	Samples immersed in acid ethanol solution (300 mL·L-1, 30% v/v) with colouring addition (2 g·L^{-1} of acid ethanol solution) for 15 min at 25 °C, and US-assisted convective drying.

Table 2. Drying kinetics parameters identified for each applied model. Average ± standard deviation. Different letters in the same column indicate significant differences determined by Tukey test ($p<0.05$).

	IR-Model (Eq.3)			IER-Model (Eq.5)				Page Model (Eq.6)			
Treatment	D_{eff} (x 10^{-10}, $m^2 \cdot s^{-1}$)	R^2	%Var	D_{eff} (x 10^{-10}, $m^2 \cdot s^{-1}$)	h (x 10^{-3}, kg water$\cdot m^{-2} \cdot s^{-1}$)	R^2	%Var	k (x 10^{-5}, $1 \cdot s^{-1}$)	n (-)	R^2	%Var
C	1.79 ± 0.15^{a}	≥ 0.97	≥ 87.35	5.13 ± 0.56^{ab}	1.71 ± 0.22^{a}	≥ 0.99	≥ 98.82	0.66 ± 0.09^{abc}	1.44 ± 0.01^{bcd}	≥ 0.98	≥ 97.81
Cc	1.67 ± 0.12^{a}	≥ 0.96	≥ 85.21	6.35 ± 0.39^{ab}	1.43 ± 0.08^{a}	≥ 0.99	≥ 99.82	0.38 ± 0.06^{a}	1.49 ± 0.02^{cde}	≥ 0.99	≥ 99.30
CUS	3.37 ± 0.36^{b}	≥ 0.95	≥ 83.38	19.91 ± 4.85^{d}	2.95 ± 0.27^{b}	≥ 0.99	≥ 99.76	0.56 ± 0.27^{abc}	1.58 ± 0.09^{e}	≥ 0.99	≥ 99.47
CcUS	3.47 ± 0.39^{b}	≥ 0.94	≥ 85.91	17.87 ± 2.69^{cd}	2.92 ± 0.38^{b}	≥ 0.99	≥ 99.91	0.50 ± 0.10^{ab}	1.58 ± 0.03^{e}	≥ 0.99	≥ 99.51
E15%	2.01 ± 0.12^{a}	≥ 0.97	≥ 89.28	4.83 ± 0.69^{a}	2.00 ± 0.19^{a}	≥ 0.99	≥ 98.86	3.46 ± 2.73^{d}	1.29 ± 0.10^{a}	≥ 0.99	≥ 99.04
E15%c	1.86 ± 0.17^{a}	≥ 0.97	≥ 86.05	5.24 ± 0.59^{ab}	1.62 ± 0.01^{a}	≥ 0.99	≥ 99.63	1.35 ± 0.17^{abcd}	1.36 ± 0.02^{abc}	≥ 0.99	≥ 99.37
E15%US	3.85 ± 0.16^{bc}	≥ 0.95	≥ 89.11	14.75 ± 3.10^{cd}	3.25 ± 0.14^{bc}	≥ 0.99	≥ 99.74	0.82 ± 0.05^{abc}	1.54 ± 0.00^{de}	≥ 0.99	≥ 99.23
E15%cUS	4.04 ± 0.11^{bc}	≥ 0.96	≥ 89.11	13.77 ± 2.74^{cd}	3.21 ± 0.33^{b}	≥ 0.99	≥ 99.69	0.67 ± 0.18^{abc}	1.57 ± 0.03^{de}	≥ 0.99	≥ 99.29
E30%	2.18 ± 0.12^{a}	≥ 0.97	≥ 89.35	5.30 ± 0.22^{ab}	2.13 ± 0.28^{a}	≥ 0.99	≥ 99.48	2.68 ± 0.57^{abcd}	1.30 ± 0.02^{ab}	≥ 0.99	≥ 99.31
E30%c	2.16 ± 0.16^{a}	≥ 0.97	≥ 89.10	5.09 ± 0.33^{ab}	1.96 ± 0.02^{a}	≥ 0.99	≥ 99.48	2.43 ± 0.29^{abcd}	1.31 ± 0.01^{ab}	≥ 0.99	≥ 99.30
E30%US	4.40 ± 0.30^{c}	≥ 0.96	≥ 92.10	12.13 ± 1.16^{bc}	4.01 ± 0.37^{c}	≥ 0.99	≥ 99.57	3.12 ± 1.72^{cd}	1.39 ± 0.10^{abc}	≥ 0.99	≥ 99.32
E30%cUS	4.06 ± 0.52^{bc}	≥ 0.96	≥ 89.10	11.60 ± 0.50^{abc}	3.55 ± 0.07^{bc}	≥ 0.99	≥ 99.18	3.07 ± 1.10^{bcd}	1.38 ± 0.04^{abc}	≥ 0.99	≥ 98.87

Table 3. CIE-Lab colour parameters (L*, a*, b* and h°) measured in fresh, pre-treated and dried apple samples. Different uppercase and lowercase letters in the same column indicate significant differences determined by Tukey test ($p<0.05$) before and after drying, respectively.

Treatment		L*	a*	b*	h°
Fresh		70.14 ± 0.82^{D}	-2.71 ± 0.16^{A}	9.24 ± 0.48^{B}	106.37±0.99^{B}
After pre-treatments/ Before drying	C	67.17 ± 1.26^{C}	-2.53 ± 0.41^{A}	9.06 ± 1.25^{B}	105.75±2.74^{B}
	Cc	62.09 ± 1.73^{B}	7.56 ± 0.79^{B}	6.40 ± 0.68^{A}	40.26±3.38^{A}
	E15%	66.86 ± 0.86^{C}	-2.81 ± 0.35^{A}	8.92 ± 0.67^{B}	107.47±1.30^{B}
	E15%c	60.66 ± 2.26^{AB}	7.54 ± 0.80^{B}	6.05 ± 0.55^{A}	38.85±5.13^{A}
	E30%	62.52 ± 1.77^{B}	-2.72 ± 0.26^{A}	9.09 ± 0.84^{B}	106.70±1.61^{B}
	E30%c	58.75 ± 1.81^{A}	7.10 ± 0.64^{B}	6.23 ± 1.10^{A}	41.05±4.99^{A}
After drying	C	83.12 ± 1.38^{b}	-2.56 ± 1.66^{a}	16.61 ± 1.54^{bc}	99.07±6.14^{b}
	Cc	69.44 ± 2.15^{a}	18.29 ± 3.16^{b}	5.96 ± 0.52^{a}	18.41±4.03^{a}
	CUS	82.88 ± 1.62^{b}	-1.89 ± 1.64^{a}	15.69 ± 1.17^{b}	97.00±6.09^{b}
	CcUS	68.89 ± 2.58^{a}	17.77 ± 1.89^{b}	5.79 ± 1.08^{a}	18.15±3.67^{a}
	E15%	82.40 ± 2.48^{b}	-1.84 ± 2.01^{a}	16.64 ± 2.64^{bc}	96.98±7.41^{b}
	E15%c	68.89 ± 0.77^{a}	18.89 ± 1.05^{b}	5.79 ± 0.81^{a}	17.09±2.95^{a}
	E15%US	82.90 ± 0.63^{b}	-2.60 ± 1.14^{a}	16.48 ± 1.01^{bc}	99.05±4.20^{b}
	E15%cUS	69.14 ± 0.96^{a}	18.38 ± 0.71^{b}	5.61 ± 0.60^{a}	17.02±2.27^{a}
	E30%	79.29 ± 4.34^{b}	-0.12 ± 3.14^{a}	20.45 ± 2.09^{c}	90.77±8.33^{b}
	E30%c	67.92 ± 2.27^{a}	19.13 ± 1.18^{b}	7.20 ± 1.03^{a}	20.63±2.98^{a}
	E30%US	79.65 ± 0.75^{b}	-0.37 ± 2.25^{a}	18.94 ± 1.46^{bc}	91.30±6.97^{b}
	E30%cUS	67.22 ± 1.54^{a}	19.19 ± 0.68^{b}	7.35 ± 1.34^{a}	20.93±3.46^{a}