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Combining ultrasound, vacuum and/or ethanol as pretreatments to the convective drying of celery slices

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ABSTRACT

This work studied three emerging approaches to improve the convective drying (50 °C, 0.8 m/s) of celery. Celery slices of 2 mm thick were pretreated for 5 min using ultrasound (32 W/L, 40 kHz), vacuum (75 kPa vacuum pressure) and ethanol (99.8% v/v, as drying accelerator) applied individually or in combination. To evaluate individual effects of ultrasound and vacuum, the treatments were also performed with distilled water or air medium, respectively. Moreover, the cavitational level was characterized in each condition. Drying kinetics was evaluated tending into account the drying time required by each treatment and the Page's model parameters. In addition, microstructural effects and shrinkage were evaluated. As results, ethanol combined with ultrasound significantly improved drying kinetics reducing drying time by around 38%. However, vacuum pretreatment did not affect drying kinetics even in combination with ethanol and/or ultrasound. Microstructural evaluation did not evidence cell disruption, suggesting changes in intercellular spaces, pores and/or cell wall permeability. The use of ethanol and vacuum showed a greater effect on shrinkage after pretreatment and after drying, respectively. In conclusion, at the studied conditions, the drying acceleration by vacuum and ultrasound is lower compared to the effect produced using ethanol.

1. Introduction

Although being an ancient process, there are still many aspects to be improved in food drying. For instance, there is a continuous demand for reducing processing time, energy consumption and costs, as well as increasing product quality. One way to improve this process is to perform pretreatments that changes the food structure or composition, facilitating the water outflow during drying. Some examples of emerging pretreatments are osmotic dehydration, ultrasound, high hydrostatic pressures, pulsed electric fields, ethanol immersion, among others [1].

Ethanol is a simple pre-treatment whose interest are rising recently. This compound acts as a drying accelerator, promoting structural changes [2], both water and ethanol flow due to different mechanisms, such as the Marangoni Effect and osmotic dehydration [3], and influencing the sample temperature during processing [4]. The effect of ethanol could be intensified using other technologies, in combination, such as high power ultrasound and/or vacuum pressures.

High power ultrasound is an emerging pretreatment to improve drying [5]. The fluid cavitation due to ultrasound application is an energetic phenomenon that causes structure disruption, forming new channels and pores inside the food products [6]. This effect improves both mass and heat transfer by many mechanisms as microjets, acoustic stirring, inertial flow, among others [7]. However, the intensity of the effects depends on the processing conditions, the product and the medium through which ultrasound waves travel.

Ultrasound technology is usually applied using water as medium to transmit the mechanical waves to the products, although some studies are applying osmotic solution or ethanol. In this case, ultrasound pretreatment improves the ethanol impregnation into the samples before drying. In fact, recent works demonstrate that ultrasound can improve the drying of vegetables, such as garlic [8], pumpkin [9], apple [10], among others. Besides ultrasound, other technologies can be used to improve ethanol influx, such as using vacuum.

Exposing food to vacuum pressures (lower than atmospheric pressure) can cause the internal fluid to exit from the food matrix, especially occluded gases. When pressure is restored, the surrounded fluid enters the food, filling the spaces that were occupied by the extracted fluids.

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This process is called vacuum impregnation [11]. Therefore, this approach can be also used to increase ethanol influx and improve its effects.

To date, one study has applied vacuum pressure during ethanol immersion of scallion [12], and only two studies using ultrasound in combination with vacuum pressures and ethanol immersion of melon [13] and scallion [14]. However, the study with scallion [14] applied infrared drying, whose mechanisms are different from convective drying – the most common drying process. The study with melon [13] applied convective drying, but using a vegetable with a simple and homogeneous microstructure.

This demonstrates the lack of studies combining emerging technologies to improve the convective drying of food products. To fill this gap, this work studied the combination of ultrasound, vacuum and/or ethanol as pretreatments to improve the convective drying of celery slices, a vegetable with a particular and complex structure. This allowed us to evaluate and describe the associate mechanisms.

2. Material and methods

2.1. Raw material and sample preparation

For this study, celery (*Apium graveolens*) was used, which was obtained from a local supermarket. Primary celery stalks were used by cutting leaves and secondary stalks. They were previously washed using tap water to eliminate any residue. Celery stalks were stored in low-density polyethylene bags under refrigeration (5 ± 0.5 °C) after being used. The storage did not delay>4 days. Before processing, celery stalks were cut into slices of 2.0 ± 0.1 mm using a cutter knife.

2.2. Pretreatments

Ten pretreatments were conducted to evaluate the effect of ethanol and/or ultrasound and/or vacuum, according to Table 1. All of them were performed in the following conditions: 28 ± 0.1 g of sample was placed into a glass flask of 500 mL containing 150 mL of solution and pretreated for 5 min at 25.0 ± 1.0 °C. For some pretreatments, ethanol (99.2% v/v) or distilled water (as control) were used.

For ultrasound pretreatments, the glass flask with the sample was placed at the bottom of an ultrasonic water bath (ACP-120H, MRC, Israel) with 1.5 L of water. Ultrasonic power of 40 kHz frequency was set at 100%, which represents 32 ± 2 W/L of actual volumetric power. It should be mentioned that volumetric power was measured by calorimetric method [15] measured using water without any additional glass flask. In addition, acoustic cavitation was measured by immersing a cavitometer probe (CAV-METER-2, MRC, Israel) in the same position inside the used glass flask containing water or ethanol. This instrument was used to evaluate how the acoustic energy varies when a glass flask, ethanol and/or vacuum pressure is used.

For vacuum application, the glass flask (Kitasato flask) was connected to a vacuum pump according to Fig. 1. The pressure was set to 75 kPa (vacuum pressure). When both approaches (ultrasound and vacuum) were used, a glass flask was immersed in the ultrasonic water bath and connected to a vacuum pump.

Different control pretreatments were performed to evaluate the individual effect of some variables. For instance, ultrasound using water is a control treatment to evaluate only the ultrasound effect. In addition, immersing in distilled water without any other approach was a control treatment to discard the effect of water from the ultrasound effect. Similarly, vacuum treatment using water was used to discard the effect of vacuum from ethanol effect. Finally, vacuum treatment without water (air medium) was used to discard the effect of water from vacuum effect.

Before drying process, the samples were superficially dried with towel paper and their mass was obtained to evaluate any mass gain or loss. The initial moisture (after each pretreatment) was evaluated by using the oven (Memmert UN 75, Germany) method at 105 °C. All experiments were performed three times.

Table 1
List of performed pretreatment. (o) means presence and (x) means absence.

Pretreatment	Medium	Ultrasound	Vacuum
C	x	x	x
V	air	x	o
W	water	x	x
V + W	water	x	o
US + W	water	o	x
V + US + W	water	o	o
OH	ethanol	x	x
V + OH	ethanol	x	o
US + OH	ethanol	o	x
V + US + OH	ethanol	o	o

2.3. Drying processing and kinetics evaluation

Convective drying was performed using a drying oven with air flow (Memmert UF 110 plus, Germany). For this, the pretreated celery slices were spread on a nylon net and placed into the drying oven at 50 °C and 0.8 m/s of air velocity. The mass of the samples was gotten at 5, 10, 15, 25, 35, 45, 60, 80, 100, 120, 150 and 180 min of process. For all treatments, equilibrium moisture content was obtained by assuring, at least, no change of mass between the two last measurements (last 60 min process).

The initial moisture of samples and the equilibrium moisture content (after drying) was obtained using the oven (Memmert UN 75, Germany) method at 105 °C. The moisture content at each drying time was obtained by mass balance using equilibrium moisture content as constant (Equation (1))

$$M_t(\%w.b.) = \frac{[m_f \bullet M_\infty + (m_t - m_f) \times 100]}{m_t} \quad (1)$$

where M_t is the sample moisture in wet basis (% w.b.) after a certain time of drying, m_f is the mass (g) at the end of the drying process, M_∞ is the equilibrium moisture content in wet basis (% w.b.) and m_t is the mass (g) of the sample after a certain time of drying.

Moisture content in wet basis was converted in dry basis (d.b.) using equation (2) in order to study drying kinetics of each treatment. Then, dimensionless moisture (MR) was calculated using equation (3). Where M_∞ is the equilibrium moisture content (d.b.) and M_0 is the initial moisture content of the sample (d.b.).

$$M_t(d.b.) = \frac{M_t(\%w.b.)}{100 - M_t(\%w.b.)} \quad (2)$$

$$MR_t = \frac{M_t - M_\infty}{M_0 - M_\infty} \quad (3)$$

Moisture content as a function of time was modeled using the Page model [16] (Equation (4)). The parameters of this equation were interpreted by Simpson, Ramírez, Nuñez, Jaques and Almonacid [17] for a better explanation of drying kinetics. Parameter "k" is related to the drying rate, while "n" is related to the "type of diffusion" and sample microstructure. Depending on "n" value, mass transfer is considered as pure diffusion ($n = 1$), "sub-diffusion" ($n < 1$) and "super-diffusion" ($n > 1$). Supper-diffusion would indicate that other transfer mechanisms as capillarity and fluid flow are involved.

$$MR_t = exp(-k \bullet t^n) \quad (4)$$

Finally, using equation (4), the drying time to reach moisture of 20% w.b. or 25% d.b. was used [18].

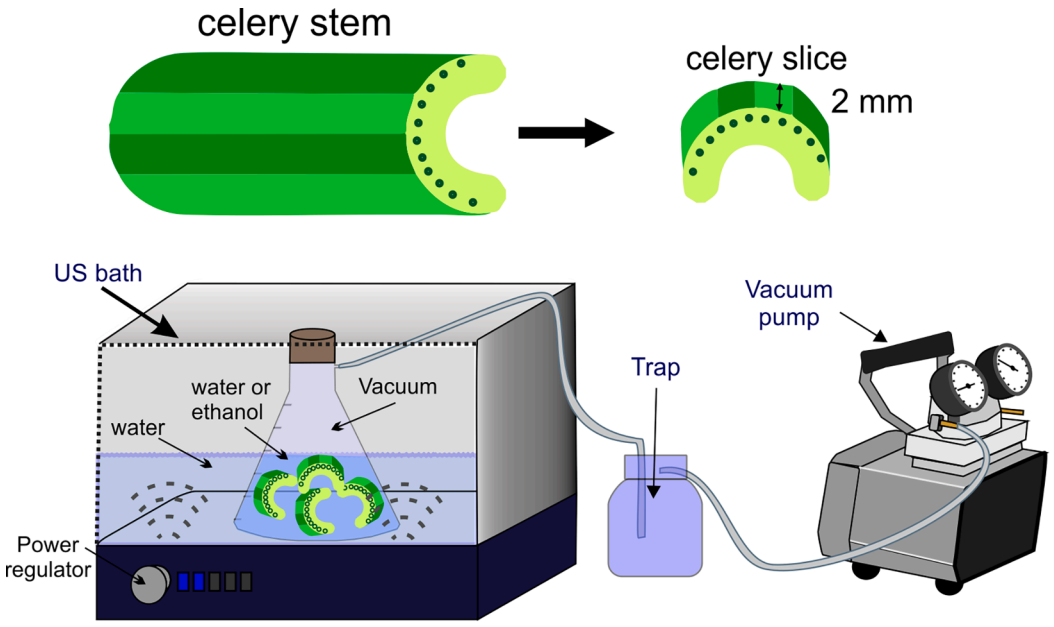

Fig. 1. Schematic representation of experiment setup using ultrasound and/or vacuum and/or ethanol.

2.4. Shrinkage

Shrinkage of samples was studied by measuring the projected area of slices before pretreatment, after pretreatment and at the end of the drying process. For this, around 50 celery slices were placed on a blue surface near to a length reference. The images were obtained by a cellphone camera (Huawei P9 pro model – 64 MP resolution, China) 30 cm of distance from the samples. Then, images were processed using ImageJ software 1.52a version (National Institutes of Health, USA) [19]. First, the measurement scale was set by using the ruler in the photo as a reference using the "set scale" command. Then, the photos were converted to grayscale (8 bits) and binary scale using the "threshold" command. At this point, celery slices should be colored black on a white background. For obtaining slices area, the "analyze particles" command was used, which provide a response window with the area of each slice in the sample.

2.5. Microstructure analysis

The sample microstructure was analyzed using a stereoscopic microscope (AM Scope, USA) coupled to a portable camera of 2.0 megapixels. The samples were stained with 2–3 drops of toluidine blue solution (0.1% in water) and directly observed without any additional cut. Surface cells and different tissues were observed before and after pretreatment.

2.6. Experimental design, regressions and statistical analysis

A completely random design with 3 process replications was performed.

Nonlinear regression was used to find model parameters (Equation (4)) to fit drying kinetics data. For this, a generalized reduced gradient algorithm implemented in the "Solver" tool of Excel 2016 was used.

In addition, variance analysis (ANOVA) was used to verify the significant effect (95% of confidence) of the treatment. In addition, Tukey's test was performed to evaluate differences among levels of the factor (drying kinetics parameters and shrinkage). Statistical analysis was performed using Statistica 7.0 software (Statsoft Inc, USA).

3. Results and discussion

3.1. Acoustic energy transmitted through the medium

When ultrasonic baths are used, the actual energy transmitted to the product is normally measured/characterized considering only water. However, the cavitational energy is influenced not only by the reactor but also by the physical properties of the fluid inside (viscosity, surface tension and vapor pressure), which transmits the energy to the product, as well as by the environment (temperature and pressure).

In the present work, both water and ethanol were used, in pretreatments conducted in both normal and vacuum atmospheres. For this reason, Fig. 2 shows the cavitation energy level of the four pretreatments where ultrasound was used.

First, it can be seen each ultrasonic process result in a specific cavitation level, which probably impacts the level of structural changes in food products, as well as the mechanisms of heat and mass transfer. In fact, when vacuum pressure was used during ultrasonic processing,

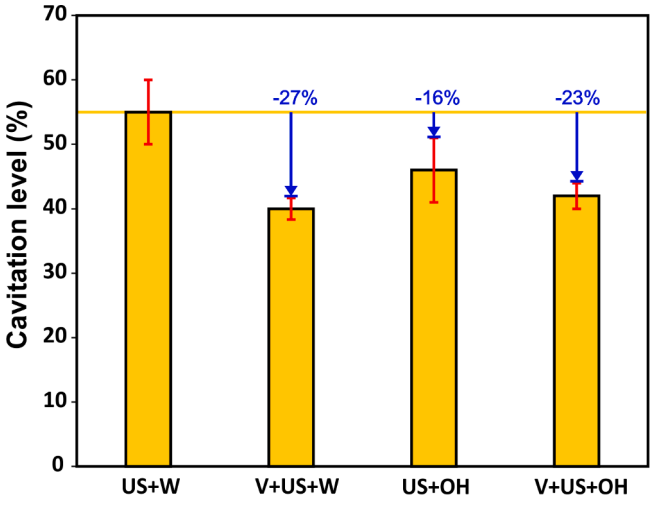

Fig. 2. Cavitation level of different pretreatments. Bars represent the mean, vertical lines standard deviation and down arrows the cavitation reduction comparing with the conventional conditions (US + W).

cavitation decreased almost 27%, indicating less cavitation level reaches the sample, which can reduce ultrasound effects. It also indicates the environment pressure affects ultrasonic cavitation. In fact, Raso, Mañas, Pagán and Sala [20] demonstrated the ultrasound power is increased (with a downward concave behavior) when pressure is increased above atmospheric. Despite the behavior indicated that ultrasound power tends to reduce at lower pressures than atmospheric, this tendency had to be experimentally demonstrated. The present work demonstrated cavitation level reduces when vacuum pressure is applied, but ultrasound power should be evaluated in future works to better discuss this tendency. Regarding acoustic cavitation theory, cavitation bubbles would need lower acoustic energy to implode when absolute pressure is reduced [15]. Consequently, ultrasound would have less effect on the medium and samples.

Concerning using ethanol instead of water as medium, Fig. 2 shows that ethanol reduces cavitation level by almost 16% compared with water medium. This could be due to ethanol presents higher vapor pressure than water. As stated by Mason and Peters [15], when vapor pressure is higher, more vapor is present in medium, cushioning cavitation bubbles collapse. Another possible explanation is that, since ethanol has lower surface tension than water, cavitation bubbles would implode with less energy. In fact, acoustic cavitation is affected by many properties as vapor pressure, surface tension and viscosity [15]. Thereby, a combined effect of that properties would be the cause of the differences in cavitation level, and further studies are needed to better understand each contribution and the impact on biological material.

Finally, when vacuum and ethanol were used in combination, the cavitation level reduction did not demonstrate an additive nor a synergetic effect. This suggested that similar cavitation reduction was observed for V + US + W, US + OH and V + US + OH.

Therefore, each treatment delivered a specific cavitation level to the samples. The impact of each treatment on product structure and drying was then evaluated.

3.2. Microstructure

Fig. 3 shows the microstructure of a celery slice. It demonstrates the complex and heterogeneous structure, which present diverse types of tissues. In fact, celery stem mostly presents parenchyma tissue whose cells have a variation on shape and size varying from isodiametric to prismatic cells [21]. In addition, collenchyma tissue is presented to give mechanical support to the celery stem. Another common tissue on celery stems is the vascular tissue which transports nutrients. Vascular tissue is formed by xylem and phloem vessels, which are similar to tubes that transport fluids by capillarity.

Microstructure demonstrates that celery is not an anisotropic material. Therefore, some considerations for mathematical modeling could not apply, since mass and heat transfer is affected by food structure [22]. For instance, water transport would not be only by diffusion, but also this would be also by capillarity. This should be considered during the process analysis.

Regarding the performed pretreatments, Fig. 4 shows the effect of ultrasound (U + W), vacuum (V), ethanol and vacuum (V + OH) and the combination of ultrasound, vacuum and ethanol (V + US + OH) in celery microstructure. In general, no significant structural change was observed after those pre-treatments. This could be due to the short duration of the pretreatments (5 min), the level of energy involved and/or the resistance of celery tissues, which were not enough to promote cell disruption (cell membrane rupture releasing cytoplasm).

Concerning vacuum, this procedure removes occlude gases in intercellular spaces liberating pathways for water exit [23]. This could not be observed directly in microstructure, especially vacuum application in samples without liquid immersion (water or ethanol), since air can return to the tissues during pressure release. However, when ethanol was used with vacuum and ultrasound (V + US + OH), the identification of cells with defined contours becomes difficult, indicating possible elimination of intercellular air and saturation of ethanol in these spaces.

Despite any evidence of cell disruption was identified, pretreatments could affect intercellular spaces and vascular tissue fluids replacement: air by water or by ethanol. This was observed in the work of Rojas and Augusto [2], where we demonstrated the ethanol influx through xylem vessels – which can improve mass transfer. In fact, only pretreatments where ethanol was involved caused microstructural changes (not related to cell disruption) (Fig. 5). For instance, images evidenced edge flattening caused by cell shrinkage from the epidermis and contiguous parenchymatic tissue. In addition, collenchyma and parenchyma cells were slightly shrunk, where especially the cells of the parenchymal tissue have a wrinkled appearance. On the other hand, no effect of ethanol was evidenced in vascular tissue, whose vascular bundles (xylem and phloem cells) together with collenchyma maintained the shape of ridges in the celery slices after pretreatments. Similar results were reported by Santos, Guedes, Rojas, Carvalho and Augusto [3],

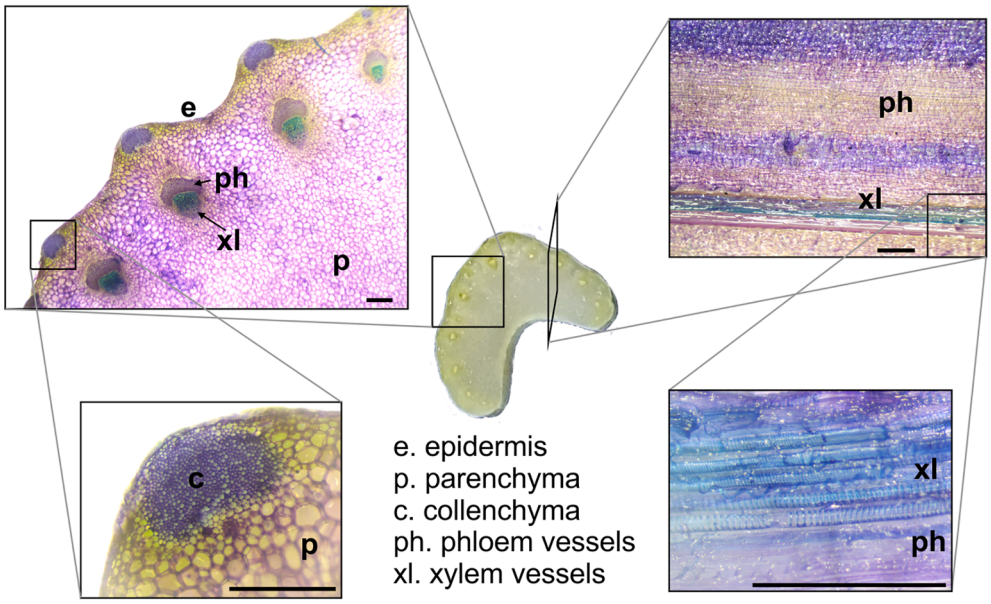

Fig. 3. Microstructure of celery slices. The horizontal bars represent 500 μm.

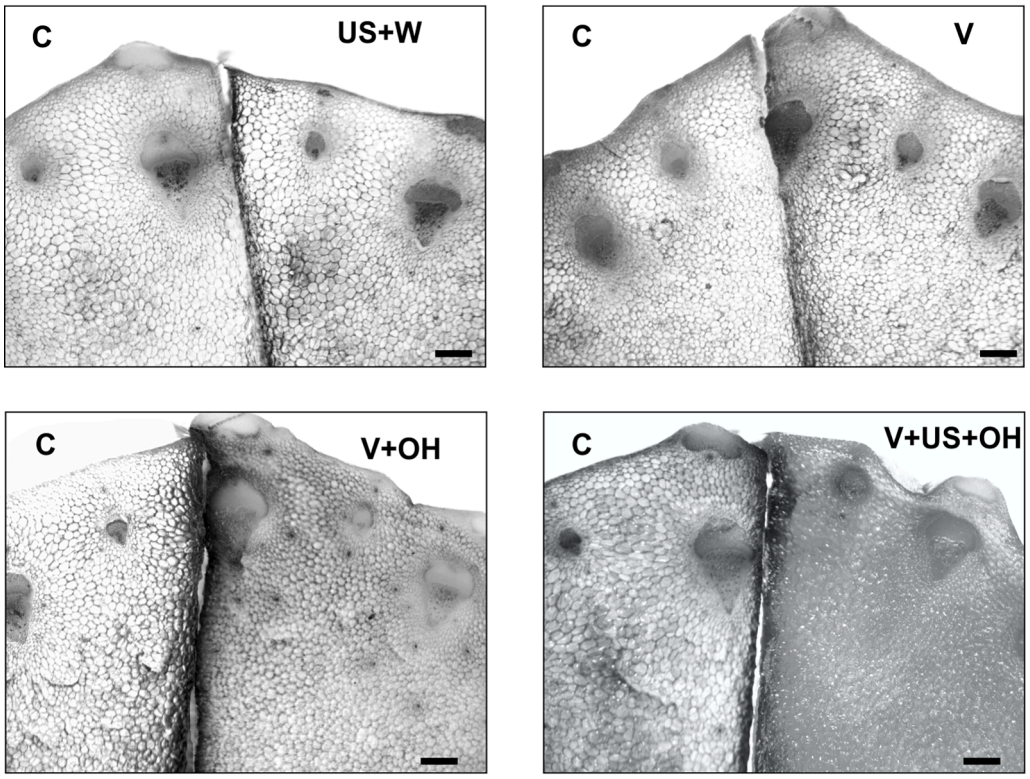

Fig. 4. Sample surface structure, slice halves comparison before (C, control) and after a representative pretreatment (US + W, V, V + OH and V + US + OH). The horizontal bars represent 500 μm.

where vascular tissue of carrot was not affected by ethanol pretreatments.

3.3. Pretreatment effect on mass variation

The pretreatments caused mass changes due to the immersion in water or ethanol and the application of ultrasound and/or vacuum. Fig. 6 reveals that there are three groups of pretreatments: those that did not cause mass variation, those that cause mass increment, and those that caused the mass reduction. The first case was obtained when vacuum (V) was used without immersion media. Although occlude air could be removed during vacuum pressure, total or partial quantity could return to tissue when pressure was recovered. In fact, the mass of air can be considered negligible.

Four pretreatments caused mass gain during pretreatment: W, V + W, US + W and V + US + W. These pretreatments caused a gain of around 0.5% of the mass. In all these treatments water was the medium, thereby water gain was responsible for mass gain. Despite using vacuum, ultrasound or the combination, the water gain was approximately the same, suggesting the negligible effect of ultrasound nor vacuum pressure.

Ultrasound pretreatment with water might cause loss or gain of water [5]. This would depend on pretreatment time since ultrasound mechanisms occurrence are more probable using longer times [24]. For instance, a work reported 1.47% of water gain when pretreatment of 30 min with ultrasound was used and 4.19% of water gain when water without ultrasound was used [25]. Other works reported 9.3% water loss for papaya [26] and 23.2% water loss for pineapple [26] after 30 min of ultrasound pretreatment. This evidenced that ultrasound mechanisms could cause water uptake in shorter pretreatments. However, longer times could cause water loss due to the less water holding capacity of disrupted cells.

On the other hand, four pretreatments caused the mass loss (Fig. 6). These pretreatments have in common the use of ethanol, and the mass variation is the net value between the loss of water with some solutes and the ethanol gain. The water release is partially replaced by ethanol, causing more water movement inside tissues. In fact, the longer the ethanol pretreatment is, the higher the water loss would be [27] until reaching a certain equilibrium. The reduction of mass after ethanol pretreatment was also found for garlic slices [8] and scallion stalk slices [14].

Further, Fig. 6 shows that vacuum did not cause any change in sample mass. Indeed, OH and V + OH pretreatments caused 0.9% of mass loss and US + OH and V + US + OH pretreatments caused 1.2% of mass loss. In these cases, ultrasound increases mass loss even more. This technology increased ethanol influx in the sample, then increasing the loss of water. This happened despite ethanol reduced cavitation level (Fig. 2). Microstructure observation (Fig. 3) did not show evidence of cell disruption when ultrasound was used. Therefore, ethanol influx was probably enhanced by direct effects of ultrasound: inertial flow and sponge effect [28,29]. The effect of vacuum on mass variation could vary in other kind of vegetables or using different ultrasound intensities (power-time).

These short pretreatments can further affect drying kinetics. Despite any change in cell integrity was observed (Fig. 4), intercellular space's structure and composition were changed (Fig. 5), affecting how water is eliminated during air convective drying.

3.4. Drying kinetics

The drying kinetics of celery slices was affected by the performed pretreatments (Fig. 7). Drying curves were suitably fitted by Peleg Model (Equation (4)) for all treatments ($R^2 > 0.99$). In addition, drying curves show a division into three groups: control and treatments that include vacuum and water use (C, V, W, V + W, US + W and V + US + W); treatments without ultrasound in ethanol medium (OH and V + OH); and treatments with ultrasound in ethanol medium (US + OH and V + US + OH). This division can be partially related to mass variation

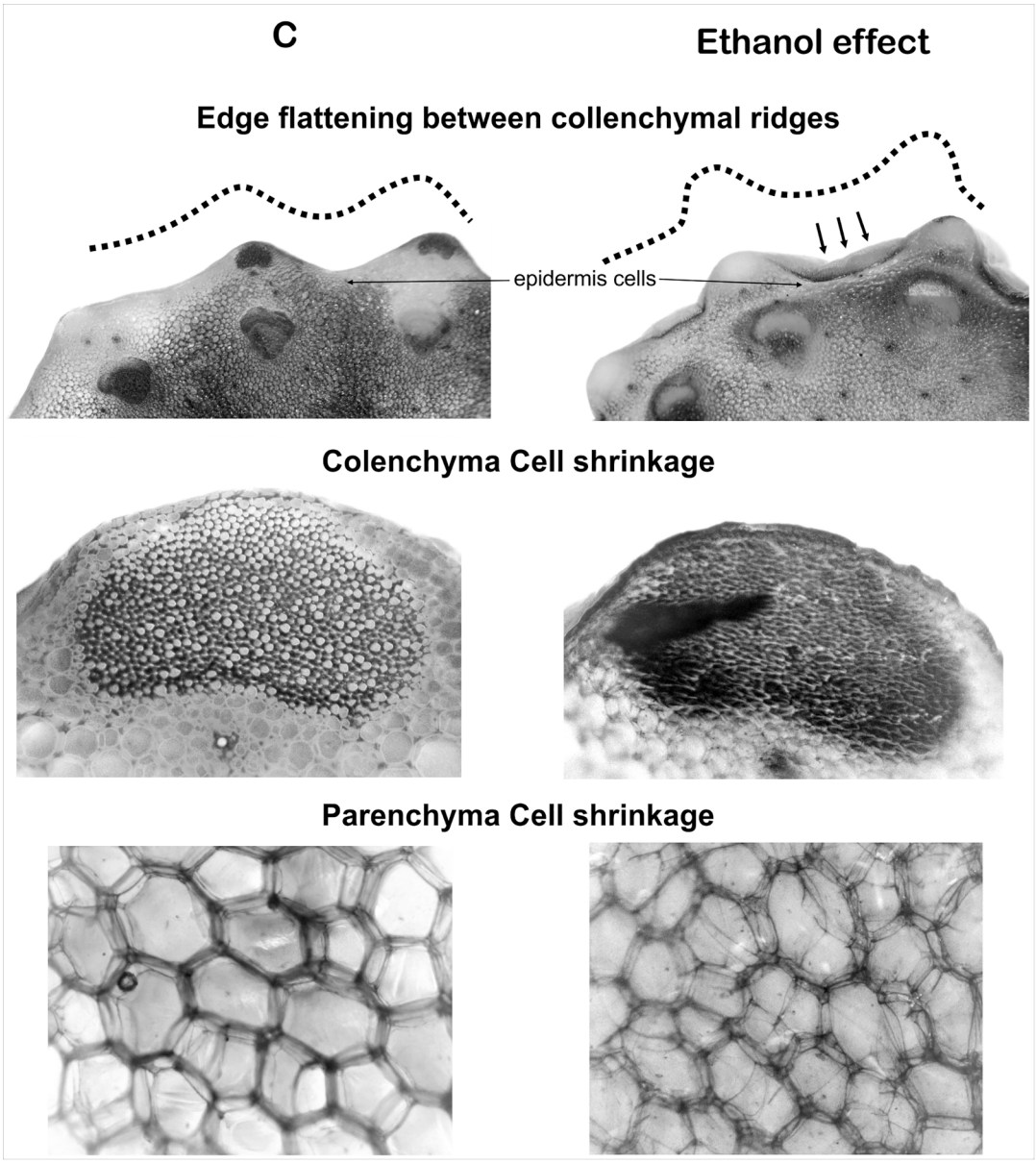

Fig. 5. Shrinkage evidence on samples treated with ethanol. Each pair of images, before (C, control) and after ethanol, were obtained with the same zoom for comparative purposes.

during pretreatment. However, the water gain during pretreatment did not show a significant effect on drying curves, behaving similarly to the control curve.

Regarding drying time (considering reaching 25% d.b.) (Fig. 8 A), it was significantly reduced (~38%) when US + OH and V + US + OH pretreatments were used. Followed by OH and V + OH pretreatments (~28% time reduction), which are statistically similar to the control process. Comparing to other works, drying time was reduced 52% when ethanol pretreatment was used for 30 min in pumpkin [9], 10% when ethanol pretreatment for 15 min in potato was used [30] and 34.5% when ethanol pretreatment for 7.5 min in pineapple slices was used [4]. In fact, besides ethanol promotes Marangoni's flow, ethanol can dissolve some components from the intercellular spaces [27], creating new pathways for water exit. Furthermore, ethanol could extract some components from the cell wall, reducing its thickness without affecting cell general structure; thus, increasing cell wall permeability [3]. These effects on cell membrane and wall can explain the drying time reduction.

Moreover, ultrasound and ethanol presented an additive effect on reducing drying time. As stated before, during pre-treatments ultrasound improves mass transfer (Fig. 6). In addition, ultrasound could improve dissolution of cell wall components by ethanol, unblocking pores. Therefore, during drying, the Marangoni flow effect is more intense than when using ethanol alone. Some recent works have reported drying time reduction when ultrasound was used in combination with ethanol as pretreatment. For instance, drying time was reduced 27.3% for garlic slices using 30 min pretreatment [8], 30% for potato cylinders using 3 min pretreatment [31], 18.3% for apple cylinders using 3 min pretreatment [10] and 56.9% for melon slices using 10 min of pretreatment [13]. Nevertheless, in some cases, ultrasound presented no significant additional effect comparing to ethanol pretreatments [3,9]. In the present work, there is a slightly increment when ultrasound (US + OH) was used compared to ethanol pretreatment (OH).

Regarding the use of vacuum as pretreatment and in combination with ethanol and ultrasound, this approach did not affect drying time. Despite, vacuum can improve ethanol uptake during pretreatment, this was not enough to cause any effect on the subsequent drying, being V + US + OH just as efficient as US + OH in reducing the drying time of celery slices. However, Zhou, Cai, Wang, Feng, Xu, Yagoub, Wahia, Ma

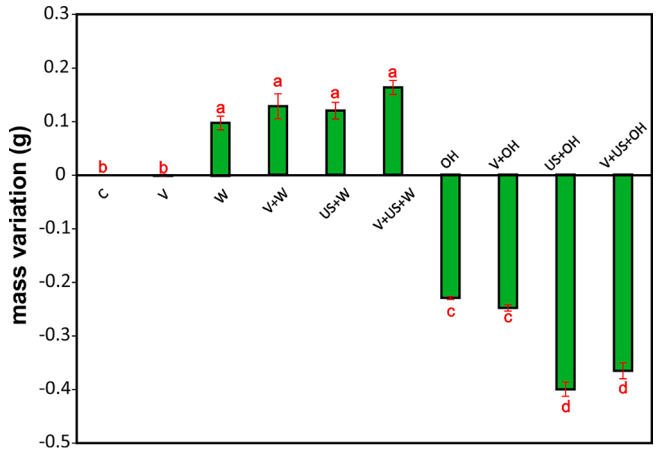

Fig. 6. Mass variation after pretreatment (28 g sample). Bars represent the mean of three replications; vertical lines represent standard deviation and lowercase letters represent Tukey's mean comparison ($p < 0.05$).

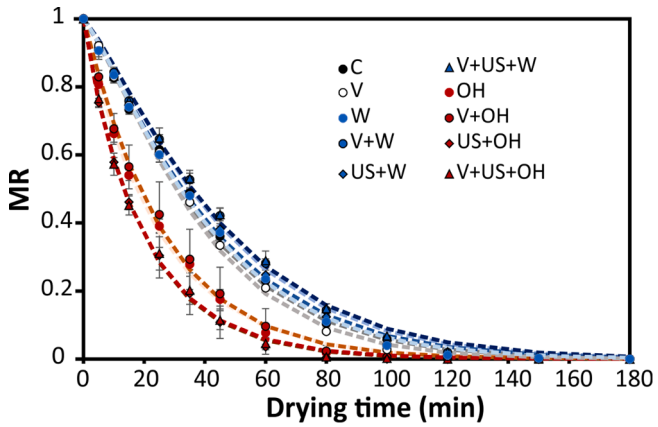

Fig. 7. Drying kinetics of celery slices using different pretreatments. Dots represent the mean of replications; discontinuous lines represent the model fitting (Equation (4)).

and Sun [14] demonstrated 54.5% of infrared drying time reduction for scallion slices using V + US + OH as pretreatment, showing a 15% reduction compared to the US + OH pretreatment (however, pretreatment time to analyze drying time is not clear). It is worth mention infrared drying mechanisms are different from convective drying. In fact, no difference in convective drying time was found using 10 min of pretreatment of US + OH and V + US + OH for melon slices [13]. Therefore, more studies are needed to verify the efficacy of approaches combination (V + US + OH) for different structures, since the few reported works used different drying methods and ultrasound devices.

The drying kinetics parameters were significantly ($p < 0.05$) affected by pretreatments. The dehydration rate (k) for each treatment is in Fig. 8 B. As evidenced in drying kinetics curves (Fig. 6), this parameter was only affected by ethanol and ultrasound application, but not by vacuum. This corroborates the reduction of drying time using ethanol and ultrasound as pretreatments. It is important to observe the individual effect of ultrasound (US + W) did not affect the drying rate. Ultrasound contributed to increasing drying rate only in combination with ethanol (US + OH), with or without vacuum.

The parameter "*n*", which is related to the structure and mechanisms of mass transfer, was significantly reduced when ethanol pretreatments were used (Fig. 8 C). The pretreatments C, V + W, US + W, V + US + W, V and W have an "*n*" value around 1.2, suggesting the water transfer during drying presented a super-diffusive behavior. Therefore, other

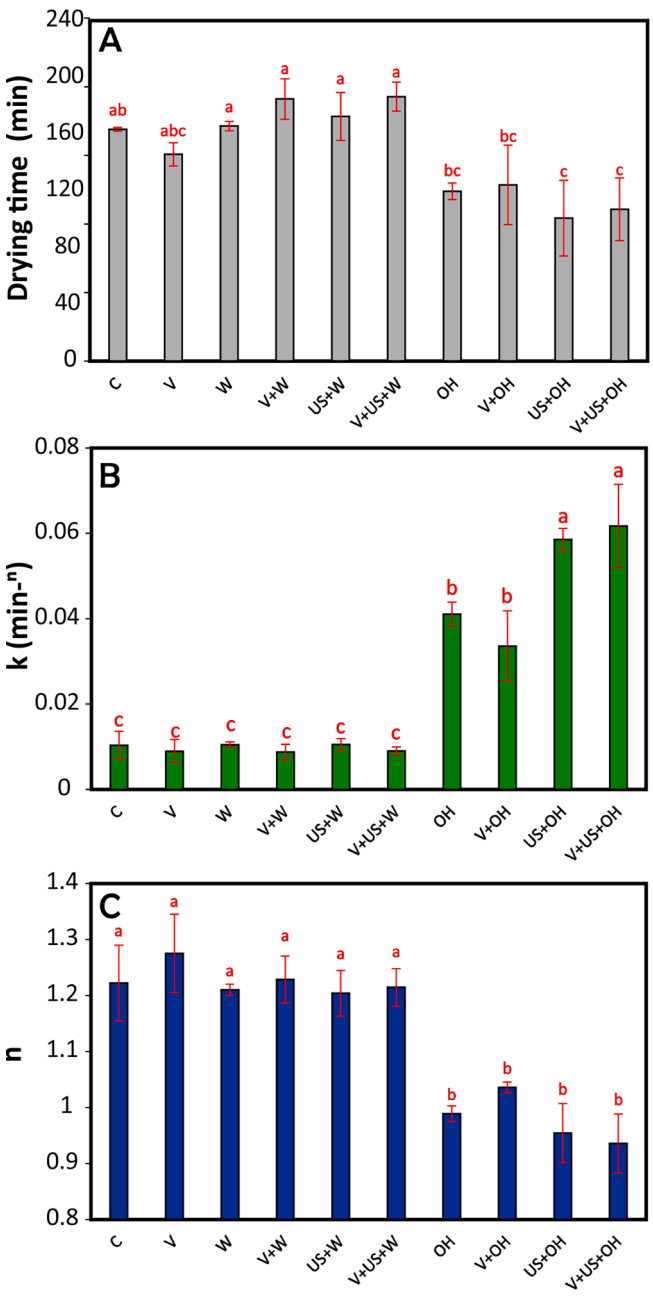

Fig. 8. **A.** Effect of pretreatments on drying time (required time to reach MR = 0.02). **B.** Effect of pretreatments of "*k*" parameter from Equation (4). **C.** Effect of pretreatments on "*n*" parameter from Equation (4). For all, dots represent the mean of replications; vertical lines represent standard deviation and lowercase letters represent Tukeýs comparison test ($p < 0.05$).

mechanisms besides diffusion are important, such as capillarity. In contrast, treatments that include ethanol (OH, V + OH, US + OH and V + US + OH) have "*n*" close to 1.0, which means the water transfer was mainly by diffusion, according to Simpson, Ramírez, Nuñez, Jaques and Almonacid [17] interpretation. These results mean the pretreatments with ethanol change the microstructure and/or composition of celery slices, affecting the mass transfer during drying. As any evidence of cellular disruption was found (Fig. 3) caused by the pretreatment, the change would be in the intercellular spaces and/or cell wall permeability. Then, by shrinkage during pretreatment and then during drying (Fig. 9), the pores could be imploded and closed. Thereby, water had to transfer by diffusion between cell walls since intercellular spaces were less available. Further, cell flattening during ethanol pretreatments

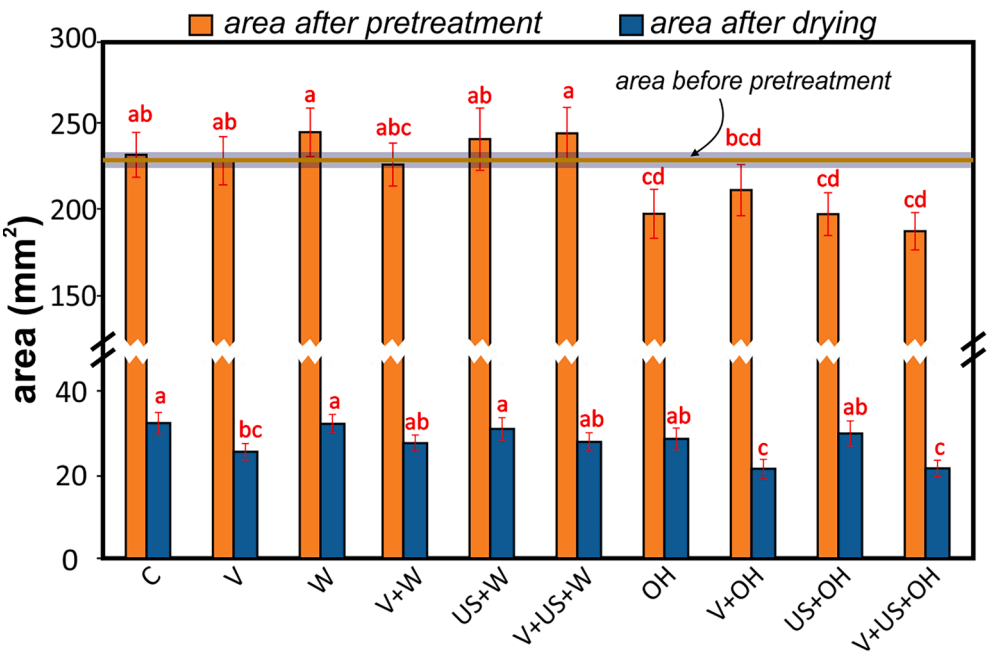

Fig. 9. Projected area of samples after pretreatment and after drying process. Bars represent the mean of 50 slices; vertical lines represent the confidence interval ($p < 0.05$); lowercase letters represent Tukeýs comparison test ($p < 0.05$); the horizontal line represents the mean of projected area of *in natura* celery slices and shade its confidence band ($p < 0.05$).

(Fig. 4) could facilitate intercellular spaces to implode due to changes in their geometry.

3.5. Shrinkage

Fig. 9 shows a significant ($p < 0.05$) shrinkage on celery slices. After pretreatment, a slight area reduction was observed in treatment where ethanol was used (OH, V + OH, US + OH and V + US + OH). This agrees with the mass variation (Fig. 6), where these treatments caused the reduction of mass, and with the structural observation (Fig. 4), where shrunk cells were observed. Comparing to other work, shrinkage due to ethanol pretreatment and its combination with ultrasound was also observed for carrots [3]. In addition, this structural change caused by ethanol pretreatments could match with the discussed reduction on "*n*" parameter value.

Some pretreatments also resulted in shrinkage after drying ($p < 0.05$). In this case, a different behavior was observed. Treatment V + OH and V + US + OH were the samples with more shrinkage. This probably means that despite vacuum did not affect the projected area after pretreatment, its effect was evidenced after drying. In other words, before drying, cells could still keep the integrity of the whole structure, even when intercellular spaces and pores are imploded by low pressure. Maybe, this was helped by mechanical support tissues as collenchyma and vascular. However, during drying, all kinds of tissues collapsed, adding the effect to imploded pores and reducing, even more, the projected area.

3.6. Final considerations

Although adding 5 min of pretreatment to the whole drying process, the drying process of celery slices at 50 °C was reduced around 45 min using the best combination (US + OH). Even, similar levels of shrinkage were obtained compared with a conventional drying process. Furthermore, vacuum was not necessary to use in combination with ultrasound and ethanol in the present work. This suggests that despite that V + US + OH reduced more the drying process than US + OH in infrared drying process of scallion [14], this does not mean that this would be the same for convective drying and/or other foods.

Indeed, future studies should be conducted. For instance, other products should be studied since they present different structures and compositions which can interact differently with the pretreatments. In addition, some dehydrated product properties as nutritional and physical could be studied. Finally, different pretreatment conditions as ultrasound powers, different substances than ethanol, and other vacuum pressures could be considered, as well as different drying conditions.

4. Conclusion

Ethanol, ultrasound and vacuum pretreatments and their combinations affected the drying kinetics of celery slices. No changes in cells integrity were evidenced after pre-treatments, but the results suggest an effect on intercellular spaces, pores and/or vascular tissue composition. Regarding mass variation after pretreatment, drying time and drying kinetics parameter, vacuum application did not demonstrate any effect. However, vacuum seems to be important on sample shrinkage after drying. On the other hand, pretreatment of ethanol with ultrasound was demonstrated to be more efficient for reducing drying time (38%) without reducing sample size after drying more than conventional drying. Finally, as vacuum did not affect the convective drying process, it was not recommended for celery slices since it would generate additional costs. Therefore, other conditions as pretreatment time, ultrasound power, ethanol concentration, vacuum pressure, different food should be considered in future studies.

CRediT authorship contribution statement

Alberto Claudio Miano: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Supervision. **Meliza Lindsay Rojas:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - review & editing, Supervision. **Pedro E.D. Augusto:** Conceptualization, Validation, Data curation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] B. Llavata, J.V. García-Pérez, S. Simal, J.A. Cárcel, Innovative pre-treatments to enhance food drying: a current review, Current Opinion in Food Science 35 (2020) 20–26.
[2] M.L. Rojas, P.E. Augusto, Ethanol pre-treatment improves vegetable drying and rehydration: Kinetics, mechanisms and impact on viscoelastic properties, J. Food Eng. 233 (2018) 17–27.
[3] K.C. Santos, J.S. Guedes, M.L. Rojas, G.R. Carvalho, P.E.D. Augusto, Enhancing carrot convective drying by combining ethanol and ultrasound as pre-treatments: effect on product structure, quality, energy consumption, drying and rehydration kinetics, Ultrason. Sonochem. 70 (2021), 105304.
[4] G.R. Carvalho, A.P. Massarioli, I.D. Alvim, P.E.D. Augusto, Iron-Fortified pineapple chips produced using microencapsulation, Ultrasound and Convective Drying, Food Engineering Reviews, Ethanol, 2020, pp. 1–14.
[5] D. Huang, K. Men, D. Li, T. Wen, Z. Gong, B. Sunden, Z. Wu, Application of ultrasound technology in the drying of food products, Ultrason. Sonochem. 63 (2020), 104950.
[6] J.A. Gallego-Juárez, Basic Principles of Ultrasound, in: M. Villamiel, A. Montilla, J. V. García-Pérez, J.A. Cárcel, J. Benedito (Eds.) Ultrasound in Food Processing, 2017.
[7] M. Villamiel, J.V. Garcia-Perez, A. Montilla, J.A. Carcel, J. Benedito, Ultrasound in food processing: recent advances, Wiley, 2017.
[8] Y. Feng, C. Zhou, A.E.A. Yagoub, Y. Sun, P. Owusu-Ansah, X. Yu, X. Wang, X. Xu, J. Zhang, Z. Ren, Improvement of the catalytic infrared drying process and quality characteristics of the dried garlic slices by ultrasound-assisted alcohol pretreatment, LWT 116 (2019), 108577.
[9] M.L. Rojas, I. Silveira, P.E.D. Augusto, Ultrasound and ethanol pre-treatments to improve convective drying: drying, rehydration and carotenoid content of pumpkin, Food Bioprod. Process. 119 (2020) 20–30.
[10] J. Zubernik, M. Dadan, J. Cichowska, D. Witrowa-Rajchert, The impact of the pre-treatment in ethanol solution on the drying kinetics and selected properties of convective dried apples, Int. J. Food Eng. 16 (2019).
[11] L. Neri, L. Di Biase, G. Sacchetti, C. Di Mattia, V. Santarelli, D. Mastrocola, P. Pittia, Use of vacuum impregnation for the production of high quality fresh-like apple products, J. Food Eng. 179 (2016) 98–108.
[12] X. Wang, Y. Feng, C. Zhou, Y. Sun, B. Wu, A.E.A. Yagoub, E.A.A. Aboagarib, Effect of vacuum and ethanol pretreatment on infrared-hot air drying of scallion (Allium fistulosum), Food Chem. 295 (2019) 432–440.
[13] R.M.C. da Cunha, S.C.R. Brandão, R.A.B. de Medeiros, E.V. da Silva Júnior, J.H. F. da Silva, P.M. Azoubel, Effect of ethanol pretreatment on melon convective drying, Food Chem. 333 (2020), 127502.
[14] C. Zhou, Z. Cai, X. Wang, Y. Feng, X. Xu, A.E.A. Yagoub, H. Wahia, H. Ma, Y. Sun, Effects of tri-frequency ultrasonic vacuum-assisted ethanol pretreatment on infrared drying efficiency, qualities and microbial safety of scallion stalk slices, Drying Technol. (2021) 1–16.
[15] T.J. Mason, D. Peters, Practical sonochemistry: Power ultrasound uses and applications, Horwood Publishing Limited, 2004.
[16] G.E. Page, Factors Influencing the Maximum Rates of Air Drying Shelled Corn in Thin layers, (1949).
[17] R. Simpson, C. Ramírez, H. Nuñez, A. Jaques, S. Almonacid, Understanding the success of Page's model and related empirical equations in fitting experimental data of diffusion phenomena in food matrices, Trends Food Sci. Technol. 62 (2017) 194–201.
[18] X.D. Chen, K.C. Patel, Biological changes during food drying processes, Drying technologies in food processing (2008) 90–109.
[19] J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J.-Y. Tinevez, D.J. White, V. Hartenstein, K. Eliceiri, P. Tomancak, A. Cardona, Fiji: an open-source platform for biological-image analysis, Nat. Methods 9 (7) (2012) 676–682.
[20] J. Raso, P. Mañas, R. Pagán, F.J. Sala, Influence of different factors on the output power transferred into medium by ultrasound, Ultrason. Sonochem. 5 (4) (1999) 157–162.
[21] O. Leroux, Collenchyma: a versatile mechanical tissue with dynamic cell walls, Ann. Bot. 110 (2012) 1083–1098.
[22] M.U.H. Joardder, C. Kumar, M.A. Karim, Food structure: Its formation and relationships with other properties, Crit. Rev. Food Sci. Nutr. 57 (6) (2017) 1190–1205.
[23] X. Shi, P. Fito, A. Chiralt, Influence of vacuum treatment on mass transfer during osmotic dehydration of fruits, Food Res. Int. 28 (1995) 445–454.
[24] A.C. Miano, M.L. Rojas, P.E.D. Augusto, Structural changes caused by ultrasound pretreatment: Direct and indirect demonstration in potato cylinders, Ultrason. Sonochem. (2018).
[25] A. Fijalkowska, M. Nowacka, A. Wiktor, M. Sledz, D. Witrowa-Rajchert, Ultrasound as a pretreatment method to improve drying kinetics and sensory properties of dried apple, J. Food Process Eng 39 (2016) 256–265.
[26] F.A.N. Fernandes, F.I.P. Oliveira, S. Rodrigues, Use of ultrasound for dehydration of papayas, Food Bioprocess Technol. 1 (4) (2008) 339–345.
[27] T. Funebo, L. Ahrne, F. Prothon, S. Kidman, M. Langton, C. Skjoldebrand, Microwave and convective dehydration of ethanol treated and frozen apple–physical properties and drying kinetics, Int. J. Food Sci. Technol. 37 (6) (2002) 603–614.
[28] T. Patero, P.E.D. Augusto, Ultrasound (US) enhances the hydration of sorghum (Sorghum bicolor) grains, Ultrason. Sonochem. 23 (2015) 11–15.
[29] J.D. Floros, H. Liang, Acoustically assisted diffusion through membranes and biomaterials, Food Technology 48 (1994) 79–84.
[30] M.L. Rojas, I. Silveira, P.E.D. Augusto, Improving the infrared drying and rehydration of potato slices using simple approaches: Perforations and ethanol, J. Food Process Eng 42 (5) (2019), https://doi.org/10.1111/jfpe.v42.510.1111/jfpe.13089.
[31] M.L. Rojas, P.E.D. Augusto, Ethanol and ultrasound pre-treatments to improve infrared drying of potato slices, Innovative Food Sci. Emerg. Technol. 49 (2018) 65–75.