UNIVERSIDADE FEDERAL DE LAVRAS

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EMERGING TECHNOLOGIES TO IMPROVE FOOD DRYING:
ETHANOL, FREEZING, PULSED ELECTRIC FIELD AND ULTRASOUND APPLIED TO DEKOPON AND ORANGE PEEL

LAVRAS - MG
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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós Graduação em Ciência dos Alimentos, área de concentração em Ciência dos Alimentos, para a obtenção do título de Doutor.

Prof. Dr. Jefferson Luiz Gomes Corrêa
Orientador

Prof. Dr. Juan Andrés Carcel
Coorientador

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LAVRAS – MG

2020

Á Deus.

Aos meus amados pais, Ronaldo Elias e Maria de Lourdes.

A toda minha família.

A todas as pessoas que marcaram essa trajetória.

DEDICO

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“Sempre faça tudo com muito amor e com muita fé em Deus, que um dia você chega lá. De alguma maneira você chega.”

Ayrton Senna

RESUMO GERAL

Os frutos cítricos são de grande importância para a alimentação humana bem como para a industrialização e desenvolver tecnologias que visam melhorar sua conservação e criar alternativas para o reaproveitamento dos subprodutos destes frutos oriundos da cadeia produtiva agroindustrial é de extrema importância no eixo ambiental e tecnológico. Portanto, este trabalho tem com objetivo estudar as influências de técnicas de secagem bem como da aplicação de pré-tratamentos na desidratação de dekopon (*Citrus retiulata "Shinarui"*) e de cascas de laranja (*Citrus sinensis*). No primeiro artigo foram estudados os efeitos do etanol como pré-tratamento à secagem convectiva (50 e 70 °C; 2,0 m/s) de fatias de dekopon, sendo observadas reduções no tempo de secagem e na diferença total de cor, maiores retenções de compostos fenólicos e ácido ascórbico e melhor capacidade antioxidante com o pré-tratamento. O segundo artigo trata dos efeitos da secagem convectiva (50 °C) e da liofilização a pressão atmosférica (-10 °C) assistida por ultrassom (US; 20,5 kW/m³) em casca de laranja cv. Valência Late. US reduziu significativamente o tempo de secagem, e o processo a 50 °C apresentou melhores resultados das propriedades tecnológicas do resíduo insolúvel em álcool (capacidade de retenção de água e óleo e capacidade de inchamento). No terceiro artigo, foi avaliada a influência de campos elétricos pulsados (PEF – 200 e 600 µs) e US durante a secagem de casca de laranja (50 °C). Menores tempos de secagem e alterações na coloração das amostras secas foram obtidos com aplicação de US e PEF 200 µs, respectivamente. Todos os tratamentos com PEF apresentaram porcentagem semelhante de ácido ascórbico, e apenas a 600 µs produziu redução na retenção de atividade antioxidante. O efeito combinado das técnicas apresentou aumento significativo na retenção de compostos fenólicos. O quarto artigo estuda a influência de PEF na cinética de secagem de casca de laranja e nos parâmetros do modelo matemático utilizado. A aplicação de US bem como o seu efeito associado com PEF promoveram redução no tempo de secagem. O coeficiente D_e foi maior nos experimentos com US e na combinação com PEF. O último artigo debate a influência do congelamento (lento e rápido) e US na cinética de secagem de casca de laranja e nos parâmetros do modelo matemático. As aplicações de US bem como o seu efeito combinado com congelamento promoveram redução no tempo de secagem. O coeficiente D_e foi estatisticamente maior no experimento com US comparado ao controle.

Palavras chave: Frutos cítricos. Subprodutos. Intensificação da secagem. Pré-tratamentos.

GENERAL ABSTRACT

Citrus fruits are of great importance for human consumption as well as for industrialization and to develop technologies that aim to improve their conservation and creating alternatives for the reuse of by-products of these fruits from the agro-industrial productive chain is of extreme importance in the environmental and technological axis. Therefore, this work aims to study the influence of drying techniques as well as the application of pretreatments in dehydration of dekopon (*Citrus retiulata "Shinarui"*) and orange peels (*Citrus sinensis*). In the first article, the effects of ethanol as a pretreatment to convective drying (50 and 70 °C; 2.0 m/s) of dekopon slices were studied, with reductions in drying time and total color difference, greater retention of phenolic compounds and ascorbic acid and better antioxidant capacity with ethanol application. The second article deals with the effects of convective drying (50 °C) and atmospheric freeze-drying (-10 °C) assisted by ultrasound (US; 20.5 kW/m³) on orange peel cv. Valencia Late. US significantly reduced the drying time, and drying at 50 °C showed better results of the technological properties of the alcohol insoluble residue (water and oil retention capacity and swelling capacity). In the third article, the influence of pulsed electric fields (PEF - 200 and 600 µs) and US during the drying of orange peel (50 °C) was evaluated. Shorter drying times and changes in the color of the dry samples were obtained with the application of US and PEF 200 µs, respectively. All treatments with PEF showed a similar percentage of ascorbic acid, and only at 600 µs produced a reduction in the retention of antioxidant activity. The combined effect of the techniques showed a significant increase in the retention of phenolic compounds. The fourth article studies the influence of PEF on the drying kinetics of orange peel and the parameters of the mathematical model that was used. The application of US as well as its effect associated with PEF reduced the drying time. The D_e coefficient was higher in the US experiments and in the combination between US and PEF. The last article discusses the influence of freezing (slow and fast) and US on the drying kinetics of orange peel and on the parameters of the mathematical model. US applications as well as their effect combined with freezing reduced the drying time. The D_e coefficient was statistically higher in the US experiment compared to the control.

Keywords: Citrus fruits. By-products. Drying intensification. Pretreatments.

RESUMEN GENERAL

Los frutos cítricos son de gran importancia para el consumo humano así como para la industrialización y desarrollar tecnologías que apunten a mejorar su conservación y crear alternativas para la reutilización de subproductos de estos frutos de la cadena productiva agroindustrial es de suma importancia en la eje ambiental y tecnológico. Por lo tanto, este trabajo tiene como objetivo estudiar la influencia de las técnicas de secado así como la aplicación de pretratamientos en la deshidratación de dekopon (*Citrus retiulata “Shinarui”*) y piel de naranja (*Citrus sinensis*). En el primer artículo se estudiaron los efectos del etanol como pretratamiento al secado convectivo (50 y 70 °C; 2,0 m/s) de rodajas de dekopon, con reducciones en el tiempo de secado y diferencia de color total, mayor retención de compuestos ácido fenólico y ascórbico y mejor capacidad antioxidante con aplicación de etanol. El segundo artículo trata sobre los efectos del secado por convección (50 °C) y el secado por congelación a presión atmosférica (-10 °C) asistido por ultrasonidos (US; 20,5 kW/m³) sobre la piel de naranja cv. València Late. US redujo significativamente el tiempo de secado y el secado a 50 °C mostró mejores resultados de las propiedades tecnológicas del residuo insoluble en alcohol (capacidad de retención de agua y óleo y capacidad de hinchamiento). En el tercer artículo se evaluó la influencia de campos eléctricos pulsados (PEF - 200 y 600 µs) y US durante el secado de piel de naranja (50 °C). Se obtuvieron tiempo de secado más cortos y cambios en el color de las muestras secas con la aplicación de US y PEF 200 µs, respectivamente. Todos los tratamientos con PEF mostraron un porcentaje similar de ácido ascórbico, y solo 600 µs produjeron una reducción en la retención de la actividad antioxidante. El efecto combinado de las técnicas mostró un aumento significativo en la retención de compuestos fenólicos. El cuarto artículo estudia la influencia del PEF en la cinética de secado de la piel de naranja y los parámetros del modelo matemático utilizado. La aplicación de US así como su efecto asociado con PEF redujo el tiempo de secado. El coeficiente D_e fue más alto en los experimentos de US y en la combinación con PEF. El último artículo discute la influencia de la congelación (lenta y rápida) y la US en la cinética de secado de la piel de naranja y en los parámetros del modelo matemático. Las aplicaciones de US, así como su efecto combinado con la congelación, redujeron el tiempo de secado. El coeficiente D_e fue estadísticamente más alto en el experimento de US en comparación con el control.

Palabras clave: Frutas cítricas. Subproductos. Intensificación del secado. Pretratamientos.

RESUM GENERAL

Els fruits cítrics són de gran importància per al consum humà així com per a la industrialització i desenvolupar tecnologies que apunten a millorar la seua conservació i crear alternatives per a la reutilització de subproductes d'aquests fruits de la cadena productiva agroindustrial és de summa importància en l'eix ambiental i tecnològic. Per tant, aquest treball té com a objectiu estudiar la influència de les tècniques d'assecat així com l'aplicació de pretractaments en la deshidratació de dekopon (*Citrus retiulata “Shinarui”*) i pell de taronja (*Citrus sinensis*). En el primer article es van estudiar els efectes de l'etanol com a pretractament a l'assecat convectivo (50 i 70 °C; 2,0 m/s) de rodanxes de dekopon, amb reduccions en el temps d'assecat i diferència de color total, major retenció de compostos àcid fenòlic i ascòrbic i millor capacitat antioxidant amb aplicació d'etanol. El segon article tracta sobre els efectes de l'assecat per convecció (50 °C) i l'assecat per congelació a pressió atmosfèrica (-10 °C) assistit per ultrasons (US; 20,5 kW/m³) sobre la pell de taronja cv. València Late. US va reduir significativament el temps d'assecat i l'assecat a 50 °C va mostrar millors resultats de les propietats tecnològiques del residu insoluble en alcohol (capacitat de retenció d'aigua i oli i capacitat d'inflament). En el tercer article es va avaluar la influència de camps elèctrics premuts (PEF - 200 i 600 µs) i US durant l'assecat de pell de taronja (50 °C). Es van obtindre temps d'assecat més curts i canvis en el color de les mostres seques amb l'aplicació de US i PEF 200 µs, respectivament. Tots els tractaments amb PEF van mostrar un percentatge similar d'àcid ascòrbic, i només 600 µs van produir una reducció en la retenció de l'activitat antioxidant. L'efecte combinat de les tècniques va mostrar un augment significatiu en la retenció de compostos fenòlics. El quart article estudia la influència del PEF en la cinètica d'assecat de la pell de taronja i els paràmetres del model matemàtic utilitzat. L'aplicació de US així com el seu efecte associat amb PEF va reduir el temps d'assecat. El coeficient D_e va ser més alt en els experiments de US i en la combinació amb PEF. L'últim article discuteix la influència de la congelació (lenta i ràpida) i la US en la cinètica d'assecat de la pell de taronja i en els paràmetres del model matemàtic. Les aplicacions de US, així com el seu efecte combinat amb la congelació, van reduir el temps d'assecat. El coeficient D_e va ser estadísticament més alt en l'experiment de US en comparació amb el control.

Paraules clau: Fruites cítriques. Subproductes. Intensificació de l'assecat. Pretractaments.

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AFD	Atmospheric freeze-drying
AIR	Alcohol insoluble residues and/or Air drying
EP	Ethanol pretreatment
FRC	Fat retention capacity
HTD	High temperature drying
MTD	Convective drying at moderate temperature
US	Power ultrasound
N50	Non-pretreated samples dried at 50 °C
N70	Non-pretreated samples dried at 70 °C
P50	Pretreated samples dried at 50 °C
P70	Pretreated samples dried at 70 °C
PID	Proportional-Integral-Derivate
SC	Swelling capacity
WRC	Water retention capacity
HAD	Hot air drying
HAD-US	Ultrasound assisted at hot air drying
HAD-200 µs	Hot air drying with pulsed electric field at 200 µs
HAD-600 µs	Hot air drying with pulsed electric field at 600 µs
VAR	Variance explained
AIR-US	Ultrasound assisted at air drying
SF	Slow Freezing
FF	Fast Freezing
MRE	Mean relative error

LISTA DE SÍMBOLOS

W_p	Local moisture content
D_e	Effective diffusivity
K	Mass transfer coefficient
t	Time
x	Direction of the water transport
Ψ	Dimensionless moisture content
α	Parameter of the Weibull model
β	Parameter of the Weibull model
U	Voltage
L	Electrode distance
d.m	Dry matter

SUMÁRIO

FIRST PART

GENERAL INTRODUCTION

The use of fruits and vegetables in human diet is essential to maintain the health. The consumption in adequate quantities is associated with the prevention of several diseases. It also contributes to prevention of obesity. Due to these benefits, the world population has been increasingly striving to incorporate such foods into their daily diet.

In general, the fruits have a diversified composition of nutrients. They are sources of phenolic compounds, antioxidants, ascorbic acid, fibers and minerals. Such characteristics can be found, even in the external parts of the fruits (peels). Because of this, several studies have been developed with the objective of promoting more fruit consumption and the most appropriate processing techniques.

Among the fruits produced and commercialized worldwide, we can highlight citrus fruits. This group is characterized, mainly, by their high content of vitamin C and by other substances that benefit in the regulation of the physiological functions of the human organism. Orange, lemon, pineapple, grape, kiwi, strawberry, among others, are citrus fruits, in addition to several hybrids, such as dekopon.

On an industrial scale citrus are widely used in the production of juices because of their sensory attributes such as aroma, flavor and color, beyond the nutritional potential these fruits present. The use of the citrus fruits by the juice industry generates a high production of waste that mostly consists of the peel. The external part of the fruits may have nutritional properties and industrial applications that need to be widely explored adding values to these by-products.

In addition, citrus fruits have high moisture content which can be an aggravating factor in the loss of post-harvest quality. Conservation techniques can be applied to increase the shelf life, add value to products and by-products and be used as a way to offer a diversity of products throughout the year.

The drying process is an alternative for preserving fruits and vegetables that has the characteristic of providing products to the consumer market regardless of seasonality. Drying promotes reduction of moisture content and water activity which minimize the reactions of degradation and action of microorganisms, providing longer shelf life. However, this process can cause undesirable physical, chemical, nutritional and sensory changes when compared to the fresh product, especially when for thermolabile substances. Therefore, it is necessary to study and apply alternative processes to conventional drying that can minimize the effects generated during processing, increasing the sensory and nutritional quality of the final product without minimizing the stability of the product. Among these possibilities, we can highlight the use of ethanol, PEF (pulsed electric field) and freezing techniques as pretreatment to drying. Moreover, several studies are carried out with the use of high-power ultrasound and freeze drying. These techniques can influence the improvement of drying processes, reducing energy consumption and impacting on the quality of the processed product.

1. THEORETICAL REFERENCE

1.1.Citrus fruits

The consumption of fruits and vegetables has grown over the years, mainly due to studies that emphasize the importance of daily intake of these products in human health. A balanced diet that includes fruits and vegetables can have beneficial effects on the human organism and prevent cardiovascular diseases, obesity and diabetes, since these products are sources of essential nutrients for the operation of the organism such as vitamins, antioxidants, phenolic compounds, fibers and other substances (ALISSA; FERNS, 2017).

The type of fruits that are most consumed is the citrus, highlighting its nutritional properties (considerable concentration of secondary metabolites) that promote health benefits. Citrus include fruits such as orange, mandarin, lime, lemon and others (SATARI; KARIMI, 2018). In addition, different hybrids of citrus are found as a result of natural or artificial crossbreeding (SINGH et al., 2020), such as dekopon.

Some countries like Brazil and Spain appear as one of the great economic potential in the production and marketing of fruit and may also highlight China, United States, Mexico and India (SATARI; KARIMI, 2018). The latest survey conducted by the Food and Agriculture Organization of the United Nations estimated that worldwide production of citrus exceeded 124 million tons (FAO, 2017).

In the human diet, citrus are beneficial because they present high levels of bioactive components and antioxidant capacity (SINGH et al., 2020). These fruits have high concentrations of carotenoids, that are responsible for the external color and the pulp, the content and composition of which influence their commercial quality (MA et al., 2015). Furthermore, phenolic compounds, especially flavonoids, comprise the group of bioactive components of citrus with a broad spectrum of activity, including promising pharmaceutical properties to human health (WANG et al., 2017; WANG et al., 2019). Ascorbic acid, also called vitamin C, is among the main vitamins found in fruits, with citrus fruits being the main sources of this compound (MAGWAZA et al., 2017). The set of nutrients present in citrus fruits is the main reason of their studies and commercialization.

Based on the characteristics of citrus fruits and their nutritional composition, there is a vast demand for these fruits in industrial production of juice. It is estimated that about 23 million tons of fruit produced in the world are intended for processing (FAO, 2017). Besides, during juice processing, an enormous amount of waste is generated, especially with regard to the external part of the fruits.

Several studies have confirmed the presence of polyphenols, vitamins, minerals, dietary fibers, essential oils and carotenoids on the peels of citrus (RAFIQ et al., 2018). Phenolic compounds, dietary fibers with technological applications were found in orange peels by Carme Garau et al. (2007) and Bejar; Kechaou; Mihoubi (2011). Passion fruit peel presents phenolic compounds with considered antioxidant activity (NASCIMENTO et al., 2016). Lemon peel presents phenolic compounds and flavonoids (NESRINE et al., 2015). Apple peel presents ascorbic acid, phenolic compounds and antioxidant activity (MARTINS et al., 2018). It is therefore evident the importance of citrus fruit that exhibit in its entirety for human consumption, economic potential and the same processing is increasingly being required the improvement of the studies that involve the production of citrus chain.

1.1.1. Dekopon

Dekopon is an exotic fruit and its consumption has increased in many countries due to their sensory, nutritional properties and therapeutic value (SANTOS; DE AQUINO SANTANA, 2019). Dekopon (*Citrus retiulata “Shinarui”*) is a citrus fruit, hybrid of Kiyomi tangor (*Citrus uses Markov. x Citrus sinensis Osb*.) and ponkan (*Citrus reticulata Blanco*), developed by the Fruit and Vegetable Experimental Station of the Japanese Ministry of Forestry and Fishery in 1972. It is currently produced in the southern part of Japan and in Korea (UMANO; HAGI; SHIBAMOTO, 2002). Due to the origin of the fruit, its aroma is similar to orange and it has an average dimension of 7.5-8.8 cm, it weights from 200 to 250g with a considerable amount of juice (UMANO; HAGI; SHIBAMOTO, 2002).

Dekopon is a citrus fruit with potential commercial value due to its attractive and pleasant aroma. The pulp of this fruit is juicy and tastes good, it has a sweet aroma (CHOI, 2003). The fruit has nutritional compounds characteristic of citrus fruits that play important roles in human metabolism, such as flavonoids, limonoids and coumarins. In addition to the pulp, the peel and the flower of the fruit have essential oils with anti-inflammatory effect (HAN et al., 2010; HERATH et al., 2016). Due to its characteristics, dekopon has great potential in the juice industry as well as in the proper use of the peel for the production of herbal medicines. Moreover, as the vast majority of fruits and vegetables, dekopon can have excellent food matrix to be used in dehydration processes generating a new product option to the consumer market.

Although the fruit has several nutritional properties and sensory aspects of high value and interest for its consumption, it is still little explored in the field of science, being found a small number of scientific articles about the fruit. Thus, one of the objectives of including dekopon in the present work is to prove its properties and increase the supply of scientific data about the fruit in order to contribute a little more to the scientific literature, especially with regard to the process of dehydration of dekopon.

1.1.2. Orange

Fruits are sensorially attractive foods, due to color, shape, flavor and aroma, and with a high nutritional value, mainly minerals, vitamins and other bioactive compounds. Among citrus fruits, we can highlight the orange (*Citrus sinensis*) which is widely produced and consumed all over the world (TOPUZ et al., 2005).

The origin of this fruit is contradictory. However, there is a greater acceptance that the orange was found first in Malaysia, China. Over the years, orange was spreaded throughout the world, reaching Europe during the Middle Ages, being brought to the American continent during colonization. The consumption and orange cultivation were quickly encouraged because at that time it was believed that the fruit could be an antidote to scurvy, a disease caused by vitamin C deficiency, very common in the period of navigation (OKINO DELGADO; FLEURI, 2016).

Currently, according to the latest study on the production of citrus fruits carried out by Food and Agriculture Organization of the United Nations, orange production worldwide was over 66 million tons. Brazil and the United States are the major producers of orange juice in the world and account for about 90% of all world production (FAO, 2017). However, there is a difference between the countries since the North Americans consume almost all production and in Brazil there is a preference for the consumption of fresh fruit and for this reason the production of concentrated juice is mostly destined for export, mainly to countries in the Europe (OKINO DELGADO; FLEURI, 2016).

There is a great variety of oranges that are cultivated in Brazil and they are classified by the harvest period (early, intermediate, late). The species *Citrus sinensis (L.) Osbeck* is the most cultivated in Brazil and United States for the juice producing industry. Among the varieties of these species, Pera is the most relevant, as it has an excellent adaptation to climate factors, cultural practices and other characteristics of the field. However, estimates are that about 45-60% of the total weight of the fruit is turned into juice, while the remainder is considered a by-product (OKINO DELGADO; FLEURI, 2016).

Citriculture is also featured in European countries like Spain, the Comunidad Valenciana is one of the main regions in the country that produces orange (SANJUÁN et al., 2005). In addition to the significant production of orange index in Spain, it is also a significant place in the export parameter of fresh fruit, and global leadership. Spanish citrus production exceeded 7 million tons, more than half of it was orange (ALCON et al., 2019). Studies indicate that Spain is one of the global potentials in citrus growing due to its geographical location being close to the main importing countries of fruits and vegetables, the climate and production area are favorable to the cultivation of citrus fruits. In addition, the reach of extremely wide varieties and with a well-distributed calendar making it possible to make available several varieties of fruits during the year, such as, for example, clementine and "Valencia" (ALCON et al., 2019).

As already mentioned, the consumption of fruits and vegetables should be part of a balanced diet, since they provide a wide variety of vitamins, minerals, fibers and other biologically active nutrients. Considering this aspect, orange is widely appreciated for its biochemical composition rich in secondary metabolites such as proteins, amines, carbohydrates, organic acids, phenolic and aromatic compounds, minerals and vitamins. All these characteristics plus the sensory properties increase the value of the fruit in both fresh and processed foods (OKINO DELGADO; FLEURI, 2016).

Orange has a high content of vitamin C, characteristic of citruses. Ascorbic acid acts as an antioxidant, with great efficacy and low toxicity, being involved in vital biological activities (collagen synthesis, neurotransmitters, steroid hormones, among others), also showing a positive effect in reducing the risk of cardiovascular diseases and cancer (GIRONÉS-VILAPLANA; MORENO; GARCÍA-VIGUERA, 2014; DE ANCOS et al., 2017). Several authors mention vitamin C concentrations in orange, De Ancos et al., (2017) found 121.06 mg ascorbic acid/100 g in dried product. In addition, Ywassaki; Canniatti-Brazaca, (2011) conducted a study with seven different varieties of orange and obtained a range of 37.26 to 70.10 mg ascorbic acid/100g sample fresh, also being found by Fallico et al. (2017).

An important factor when it comes to vitamin C in foods is that it is a very sensitive substance under various process conditions being used as indicator of nutritional value of processed as well as on the effects of processing on quality of the product (AGUILAR et al., 2017). Therefore, the choice of the best processing conditions in order to provide the lowest possible degradation to the product is vital.

Oranges have a significant concentration of phenolic compounds and others bioactive substances. De Ancos et al. (2017) found significant amounts of phenolics, flavonoids and antioxidant activity in two different orange varieties. Other substances such as carotenoids are found in several varieties of orange according to Rodrigo et al. (2015).

Due to high world production of orange came the need of industrialization of this fruit and most of it is destined to juice industry. It is estimated that approximately 96% of world production of the fruit are used for juice industry (FREIRE et al., 2016). However, during juice production it generates an accumulation of by-products, such as peel, seeds, cell and membrane residues that represent approximately half of the fruit weight (KHAN et al., 2010). These orange by-products are usually processed for animal feed production or are discarded directly. Such by-products are highly rich in bioactive compounds (phenolic, flavonoids, limonoids, and carotenoids), vitamin C and above all, fiber that can be widely used in the food industry (HERNÁNDEZ-CARRANZA et al., 2016; LI et al., 2017).

1.1.3. Orange peel

Fruit processing has increased considerably in the last few decades due to studies pointing out the importance of including these vegetables in the human diet, especially with regard to disease prevention. The industrialization of fruits generates an enormous volume of waste and by-products with a high biochemical and chemical demand, which makes it feasible to recognize the valorization of the by-products and the minimization of their waste (FAVA et al., 2013). Moreover, fruits by-products have a high nutritional value, being an excellent alternative source of protein, sugars, lipids, as well as other aromatic and aliphatic complex compounds. This characteristic emphasizes that the by-products are abundant sources and with a reduced cost and they can present a high added value for the pharmaceutical, food and other industrial sectors (FAVA et al., 2013).

Orange peel has been widely studied not only for its high production worldwide, but mainly for its nutritional diversity. The orange peel has a high concentration of phenolic compounds (mainly quercitrin, rutin and quecetin) and flavonoids. These bioactive compounds have an excellent capacity for eliminating the 2,2′-azino-bis diamonium salt (3-ethylbenzothiazoline-6-sulfonic acid) diamonium (ABTS); reducing ferric antioxidant properties (FRAP) and radical scavenging capacity 2,2-diphenyl-1-picryl-hydrazyl (DPPH), being an excellent alternative in the development of functional products (ADIAMO et al., 2018).

Evaluating the composition of orange peels Omoba et al. (2015) found several phenolic compounds and flavonoids at different maturation stages. Moreover, it was proven that the orange peel provides antioxidant capacity. Confirming the presence of bioactive compounds in orange peel Hernández-Carranza et al. (2016) found phenolic compounds (514 mg of GAE/100 g dry weight), flavonoids (656 mg of catechin/100 g dry weight) and a significant antioxidant capacity (720 mg of Trolox/100 g dry weight and 5.2 mM Fe^{2+} /100 g dry weight). Corroborating the other studies, different types of extraction of phenolic compounds in orange peels were tested and nine compounds were found (Gallic Acid; Narirutin; Naringin; Hesperidin; Ellagic Acid; Naringenin; Hesperitin; Diosmetin; Tangeritin). Furthermore antioxidant capacity were observed by DPPH and FRAP method (BARRALES et al., 2018).

Another nutrient that is part of the composition of citrus fruits, especially in orange is vitamin C. The presence of ascorbic acid makes it a product of nutritional interest because the substance plays important roles in human food. The orange peel has considerable concentration of this compound which further increases the interest in research and development of products and reduces the negative effects of organic waste disposal on the environment (TEIXEIRA et al., 2020). During the study of seven orange varieties it was observed in the peel fruit a variation of 37.26 a 60.63 mg of ascorbic acid/100 g (YWASSAKI; CANNIATTI-BRAZACA, 2011). Restating the presence of vitamin C in orange peel, similar results were found during a study of Montero-Calderon et al. (2019) (53.78 mg of ascorbic acid/ 100 g of orange peel). In addition, high concentrations of vitamin C were observed in orange peels -cultivated in Brazil, corroborating the data previously presented and reaffirming the presence of this compound in the orange by-product (DE MORAES BARROS; DE CASTRO FERREIRA; GENOVESE, 2012).

Moreover, to the compounds mentioned, the nutritional value of the orange by-products, especially the peel, is even higher and more diversified due to the high content of dietary fiber. Recently, dietary fiber has attracted the interest of researchers, industry and consumers due to the benefits it can provide when included in the human diet. There are reports of reduced blood lipids and glucose and the risk of cardiovascular disease, colorectal cancer, increased satiety and gastrointestinal immunity (WANG et al., 2015). The dietary fibers of the orange peel have technological properties of high interest to the industrial ones due to their solubility, water and oil retention capacity as well as expansion capacity, among other advantages. Such properties depend on the portions of the fractions found in the fiber (soluble dietary fiber and insoluble dietary fiber) (TEJADA-ORTIGOZA et al., 2018).

During the study of the fiber properties of these by-products, a content of 53.43 g/100 g dry matter was observed in the orange peel cv.Valencia and the soluble fraction was 7.17 g/100 g dry matter and insoluble 46.16 g/100g dry matter. Also, the water and oil absorption capacities of the extracted fibers were observed (TEJADA-ORTIGOZA et al., 2018). The application of this by-product presents an enormous variety due to the characteristics and the composition of the fibers Crizel et al. (2013) observed a high level of total dietary fiber and an ideal portion between soluble and insoluble fibers with high water and oil retention, being tested with efficiency in the replacement of fat in ice cream processing. Moreover, Liu et al. (2017) developed and studied various methods of dehydration of orange peel and demonstrated that the functional effects of extracted fiber product may have industrial applicability in the development of health-promoting products. In general, studies involving the use of by-products due to dietary fibers indicate benefits to human health as well as technological advantages in search of improvements in the development of new products.

As previously mentioned, the offer of the by-product is extensive and its applications in human food as well. However, it is necessary to carry out the processing of the fruit peel in an effective way to guarantee product stability. We know that fruits and vegetables have a huge post-harvest loss due to their characteristics and this also happens with by-products. The high moisture content and water activity of orange peels can trigger undesirable enzymatic and biochemical changes as well as the development of deteriorating microorganisms, conforming Bejar; Mihoubi; Kechaou (2012) that found 2.97 kg water/kg orange peel (dry matter) and water activity value of 0.95. The high water content in fresh orange by-products was also mentioned by several other authors, among them Manjarres-Pinzon; Cortes-Rodriguez; Rodríguez-Sandoval (2013) and Tamer et al. (2016).

In view of the above, on the high supply of these by-products provided by the large scale of orange production and industrialization worldwide, as well as on the nutritional values of high interest and benefit to human health and the technological properties that orange peels can provide, it becomes evident the importance and the need for further processing techniques that -ensure the product stability, nutritional quality, sensory and industrial application. Therefore, developing studies of different drying techniques combined with pretreatment applications can generate a stable final product, with a good nutritional value, sensorially accepted and with technological properties of interest.

1.2.Drying techniques

The drying food process is a very old and widely used technique for food conservation. It is also a unitary operation applied to the industry in many food matrices. The various drying techniques are based on reducing the water content of the food to obtain a product with a safety water activity that minimizes the possibility of deterioration and increase the stability of the food.

Among the drying methods, some aspects have to be pointed. Initially, it is necessary to understand the impacts of processing on quality attributes and how the product will be used by the consumer. In addition, it is essential to evaluate the costs of the process (equipment, process time, energy consumption, among others) and the environmental impacts caused by the technique, as it is essential to produce a stable food, with nutritional appeal, sensorially attractive and economically viable.

1.2.1. Hot air drying convective

Convective drying reduces the moisture content of the wet solid by evaporating the water. Air flow and temperature is applied, transferring energy to the product, thus causing the phenomenon of water evaporation. The drying technique in question has been applied since antiquity and has been improved over the years.

The energy of the air stream is transferred by convection to the product and into the tissues by diffusion, increasing the internal temperature, thus causing water to evaporate. The moisture is transferred from the solid surface to the drying air by convection and from its inside to surface by diffusion and capillarity (FERNANDO; LOW; AHMAD, 2011; CASTRO; MAYORGA; MORENO, 2018).

The velocity of the process is related to mechanisms involved in the process of reducing the moisture content of the product. The elimination of water present on the surface of the material is conditioned to some factors: temperature, humidity and velocity of the air, surface of the solid exposed to the air flow and pressure. In addition, the exit of internal water to the surface is dependent on the porosity of the solid and the water content. Therefore, the drying rate can be determined by an internal or external resistance or by both resistances, which can influence the process time (MULET, 1994; FERNANDO; LOW; AHMAD, 2011; GARCIA-PEREZ et al., 2012).

During the drying process, therefore, we identified the simultaneous heat and mass transfers between the product and the drying air. The evolution of these transfers can be divided into three periods, as shown in Figure 1.

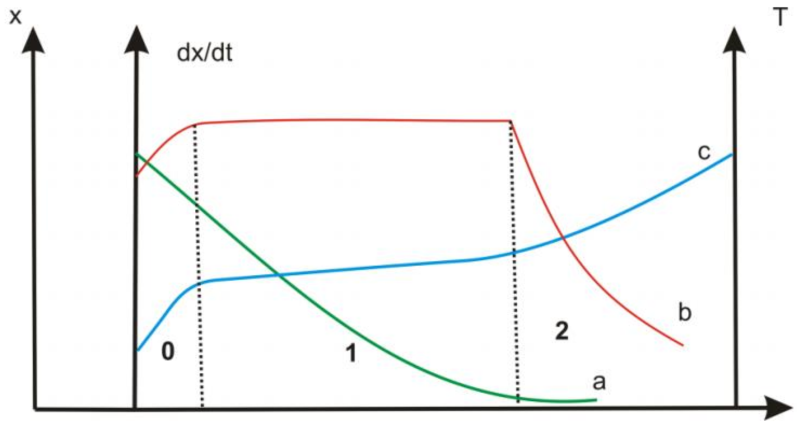

Figure 1 - Evolution of time (t), product water content (X), temperature (T) and drying rate (dX/dt); (a) evolution of moisture content, (b) drying kinetics and (c) product temperature evolution

Source: PARK et al. (2007).

Curve (a) represents the decrease in the moisture content of the product (X) in relation to the time (t) during the drying process; (b) shows the velocity or drying rate of the product (dX / dt), that is, the change in humidity of the product by time, in relation to the evolution of time (t); (c) is the variation of the sample temperature (T) with time (t).

The classification of the three periods is related to the variation of the velocity of the drying process:

Increasing drying rate or induction period (0): It is assumed period of adapting the product process conditions wherein the solid heated by increasing the temperature of the interface and consequently increasing the evaporation rate of water on the surface of the product (GARCIA-PÉREZ, 2007; PARK et al., 2007).

Constant rate period (1): Characterized by the rapid movement of water inside the product due to the amount of water available, providing saturation conditions on the surface. The velocity of the process is now controlled by the evaporation of water and its transfer from the surface of the material to the surrounding medium, the transfer of water being carried out by diffusion through the solid/air interphase. As a result, the drying velocity is constant and the end of the period occurs when the water migration from the interior to the surface cannot compensate for the evaporation rate of surface water. Generally the critical humidity values of the food are close to the values of the initial moisture content so that the period of constant velocity in food is very short or nonexistent (GARCIA-PÉREZ, 2007; PARK et al., 2007).

Decreasing rate period (2): The surface of the solid loses saturation, reducing the velocity of drying, generating dry areas. In saturated areas the drying rate will occur at the same velocity as in the period of constant velocity and in dry areas it will decrease, as the overall velocity will decrease. Drying continues until it reaches equilibrium moisture. In this period the influence of the properties of the external phase on the velocity of the process decreases, while the importance of the movement of water inside the product increases, being a limiting factor (GARCIA-PÉREZ, 2007; PARK et al., 2007).

During the drying process, the transport of moisture inside the solid can occur through several mass transfer mechanisms, according to Mujumdar (2006):

Liquid diffusion: occurs when the solid with moisture is at a temperature lower than the boiling point of the liquid.

Vapor diffusion: when there is vaporization of the liquid within the material.

Knudsen diffusion: it is the mechanism resulting from drying processes at low temperatures and pressure.

Surface diffusion: it is one of the possible options during the drying process. However, it has not been proven yet.

Hydrostatic pressure: it occurs at a time when the rates of internal vaporization exceed the rate of vapor transport from the solid to the surroundings.

It is important to note that moisture transport within the solid can also occur due to the combination of the mentioned factors and that the physical structure of the product is subject to changes throughout the process and changes in the transfer mechanisms can also occur (MUJUMDAR, 2006).

Drying food and biological materials is a wide area that concentrates several experimental and theoretical researches in order to determine and estimate the parameters of the process and moisture transfer. In order to provide better control over the operation, precise models are used to simulate the drying curves under different operating conditions. Various complex models of heat and mass transfer have been developed for various foods. However, the drying requires practical simplified models tested by experimental data that have the ability to provide better solutions to the process without performing experimental tests in the actual system (BEZERRA et al., 2015; DE MELLO JR et al., 2019).

The mathematical models applied to the drying of fruits and vegetables can be classified as semi-theoretical, using the concept of thin layer and theoretical models that are based on the fundamental physics of the drying process. The semi-theoretical models represent an excellent tool for modeling the kinetics of these products, though, due to the advance of the availability of the numerical calculation the theoretical models are also being developed (CASTRO; MAYORGA; MORENO, 2018).

The complexity of the physical phenomena and the transport mechanisms that describe the migration of water during drying operations does not allow the use of excessively simplified models. The diffusional model is commonly used and it was formulated by Lewis (1921) and later developed by Sherwood (1929). Through Fick's Law and a microscopic balance of material in a controlled volume, the equation that governs mass transfer is obtained for sample slab, assuming that the material is homogeneous and isotropic and that the effective diffusivity (D_e) is constant (Equation 1) (GARCIA-PEREZ et al., 2012a).

$$\frac{\partial W_p(x,t)}{\partial t} = D_e\left(\frac{\partial^2 W_p(x,t)}{\partial x^2}\right) \tag{1}$$

where W_p is the local moisture content, D_e is the average effective moisture diffusivity, t is the time, and x is the characteristic direction of the water transport.

The diffusive models are, for the most part, simple to solve and present the ability to provide reasonable results. A great disadvantage consists of assumptions attached to each process aiming to solve the model. In general, it is used as an effective diffusion that includes the effects related to kinetics, phenomena that are known and unknown (GARCIA-PÉREZ, 2007). Thus, one of the models widely used in several studies on the modeling of drying processes for food and biological materials is the Weibull model (PÉREZ-WON et al., 2016).

The Weibull model represents the distribution of resistance to material rupture, describing the behavior of systems or events with variability, such as drying air (PÉREZ-WON et al., 2016). This model has been used to model the drying kinetics of different foods, for example, coroba (CORZO et al., 2008), pepino fruit (URIBE et al., 2011), eggplant (GARCÍA-PÉREZ et al., 2011), cherry tomatoes (FERNANDES et al., 2016), blueberries (YU; JIN; XIAO, 2017), apple (DALMAU et al., 2017) and yam tubers (JU et al., 2018). Equation 2 describes the Weibull model.

$$\Psi = \exp\left(-\left(\frac{t}{\beta}\right)^{\alpha}\right) \tag{2}$$

where Ψ is the dimensionless moisture content, and α and β are the parameters of the Weibull model. Parameter α is the form factor and represents a solid behavior index, the higher its value, the lower the initial velocity of the drying process. If it is greater than 1, it predicts process downtime and if it is equal to unity, the model presents first-order kinetics.

In addition, parameter β is related to the process kinetics, being inversely related to the drying rate. This parameter includes the effects that cause variations in the drying process, such as temperature, air velocity and even the application of ultrasound.

The convective drying process, despite being widely used and studied as an excellent way to obtain stable products, it is necessary to take into account the impacts that the process can bring with regard to maintaining the sensory and nutritional characteristics of the product as well as the cost of operation and the possible environmental impacts caused by the technique (MAISNAM et al., 2017). Focused on reducing the environmental impact of the process of dehydration or use of pre-treatments and additional energy sources are alternatives of great interest in the attempt to increase the velocity of the process to achieve less than environmental impact onthe quality of the final product (MICHALCZYK; MACURA; MATUSZAK, 2009; JUNQUEIRA et al., 2017; YU; JIN; XIAO, 2017; CÁRCEL et al., 2018; ROJAS; AUGUSTO, 2018; DE MELLO JR et al., 2019).

1.2.2. Atmospheric freeze drying (AFD)

The freeze-drying process of biological matrices is one of the best ways of reducing moisture and obtaining a stable product with high quality, since at very low temperature there is a reduction in deteriorative reactions. The process is based on the removal of water through sublimation (SAGAR; SURESH, 2010).

Freeze-drying process can occur under vacuum or at atmospheric pressure. Vacuum freeze drying (VFD) occurs at low temperatures and pressure, removing ice in the form of sublimation. The process consists inthree main steps (freezing, primary and secondary drying), with freezing being the critical step that influences the quality of the final products (HARGUINDEGUY; FISSORE, 2020).

Atmospheric freeze-drying (AFD) had its efficiency verified based on the principle that the removal of water is determined by the vapor pressure gradient and not by the absolute pressure of the system. The energy cost is considerably reduced compared to VFD, although there are some limitations, such as the long drying time (WOLF; GIBERT, 1990; HARGUINDEGUY; FISSORE, 2020). AFD drying process consists in applying a stream of dried and cold air to a frozen product. The temperature used is between -10 ° C and the initial freezing point of the product providing a better quality product when compared to drying with hot air (COLUCCI et al., 2017).

The AFD process has been used to drying various food products such as carrot (GARCIA-PEREZ et al., 2012b), apple (BRINES et al., 2015; SANTACATALINA et al., 2015), codfish (SANTACATALINA et al., 2016) and kiwifruit (VALLESPIR et al., 2019a).

AFD can be applied in fluidized and fixed bed and the characteristics of the final product are very similar to VFD with a lower cost. In addition, AFD products have less color and shrinkage changes and greater rehydration capacity when compared to hot air processes (CLAUSSEN et al., 2007).

However, the AFD process has low vapor diffusivity at atmospheric pressure, being controlled by the internal resistance to mass transfer, making it a long drying process. Therefore, increasing the mass transfer rate without reducing the quality of the products obtained by AFD is highly beneficial (SANTACATALINA et al., 2015).

1.3.Technology and pretreatment applied to convective drying

Convective drying processes have some important limitations and have been studied by the scientific community in order to minimize impacts. Among the main limitations we can highlight the low velocity of the process and the – quality loss in the product during to drying. Low drying rate is even more evident when low temperatures are applied (AFD) (CLAUSSEN et al., 2007; SANTACATALINA et al., 2015; MUSIELAK; MIERZWA; KROEHNKE, 2016; MORENO et al., 2017).

In addition, the convective drying processes can cause some sensory (color and aroma), nutritional and physical properties changes, for example, in the shrinkage of the material and can significantly modify the diffusion coefficients, influencing the drying rate (MAYOR; SERENO, 2004; CORRÊA et al., 2011; CORRÊA et al., 2012).

Therefore, the use of new technologies that provide additional energy to the process as well as the application of pretreatments to convective drying can minimize or even solve some limitations. It is noteworthy that the combination of technologies and previous treatments need to combine reduction of energy costs to the final product quality maintenance.

1.3.1. High power ultrasound

Drying process ultrasound assisted, at low and high temperature, has the ability to promote an increase in the drying rate due to acoustic energy of high intensity and low frequency. The waves have a low thermal effect and are even more suitable for application in thermolabile materials. Although, with great potential, ultrasound waves increasingly require studies in order to optimize processes and verify the effects on the quality of the final product (GALLEGO-JUAREZ et al., 2007).

Sound is an oscillation of matter that has the ability to propagate in the form of a mechanical wave. Mechanical waves can be propagated in solids being classified as elastic, while those propagated in fluids are called acoustic waves. Therefore, due to the need for material propagation medium, sound waves cannot be propagated in a vacuum, differing, for example, from electromagnetic waves (MUSIELAK; MIERZWA; KROEHNKE, 2016).

Ultrasound are acoustic elastic waves with a wave range of 20 kHz up to frequencies associated with wavelengths compatible with intermolecular distances (approximately 10^{12} Hz). Ultrasound waves are short (lengths around centimeters and nanometers) produced by specific technological sources and applied in the industrial, medical and environmental fields, and the use of ultrasound was preceded by animals (bats and dolphins) that use waves as form of guidance and communication (GALLEGO-JUÁREZ et al., 2017).

Ultrasonic waves are produced by a vibrating system so that the vibratory movement of this system communicates with the particles around it generating oscillation and energy communication in an oscillatory way to the surrounding particles. The propagation of ultrasound in a medium can be classified as longitudinal (compressional) and transversal (shear) being defined according to the nature of the medium and the characteristics of vibration generation (GALLEGO-JUÁREZ et al., 2017).

The longitudinal waves oscillate in the same direction of propagation, while the - transversal waves are characterized by the vibration of particles in a direction perpendicular to that of propagation. Ultrasonic waves come in both forms or with a combination of the two types (MUSIELAK; MIERZWA; KROEHNKE, 2016; GALLEGO-JUÁREZ et al., 2017).

In the same way that any kind of waves, ultrasonic are characterized by several parameters, of which the frequency (f; Hz), acoustic velocity (v; m/s), wavelength (λ; m), amplitude (A; m), intensity (I; W/m²), acoustic power (P; W), acoustic impedance (Z; MRayl) and attenuation (MASON; PANIWNYK; LORIMER, 1996; MUSIELAK; MIERZWA; KROEHNKE, 2016; GALLEGO-JUÁREZ et al., 2017) .

Frequency and intensity parameters are used to classify ultrasonic waves and define their possible applications. Therefore, based on these parameters, we have low intensity, high frequency or signal ultrasound that present intensity below 1 W/cm² and frequency in the range between 100 kHz and 20 MHz (MASON; PANIWNYK; LORIMER, 1996; CHANDRAPALA, 2015). The application of the low intensity ultrasound technique is defined by the changes that the wave undergoes when passing through a material. The velocity and attenuation are two parameters that can be used to evaluate the applicability of the technique because they vary depending on the physical properties of the medium (AWAD et al., 2012). Low frequency and high frequency ultrasound has been widely used in the food industry with the ability to provide a rapid, accurate, and non-destructive method, evaluating the properties of food during the production process (CHANDRAPALA, 2015). Therefore, this technique has been used in several studies such as cheese processing (BENEDITO et al., 2002), evaluation of physical parameters of animal fat during storage (SANTACATALINA; CORONA; BENEDITO, 2011), microbial growth (YU; CHEN; CAO, 2012; DAI et al., 2017) and other applications.

On the other hand, high intensity, low frequency or power ultrasounds are those with intensities -higher than 1W/cm² and frequency between 20 and 100 kHz, being applied in order to cause changes in the products or processes used (SANTACATALINA; CORONA; BENEDITO, 2011; PICO, 2013; GALLEGO-JUÁREZ et al., 2017). In the present study we used high-power ultrasound technique and therefore aspects related to this technique are discussed.

1.3.1.1. High power ultrasound effects

The propagation of the power ultrasound waves depends on the medium (liquid, solid, gas) that they propagate. The effects produced by the magnitude are also influenced by the medium, the process variables (temperature, pressure, intensity) and the characteristics of the product to be studied (CÁRCEL et al., 2011; GARCIA-PEREZ et al., 2012b).

In general, ultrasound produces successive compression and decompression in the medium. In liquids, the appearance of cavitation bubbles resulting from attractive forces exerted by a rarefaction cycle can be observed at the moment when the ultrasonic energy reaches a certain limit. Such cavitation bubbles are formed due to the gaseous nuclei existing in the medium and can maintain a steady increasing and decreasing size, resulting in a stable cavitation that promotes microagitation of the medium. Cavitation bubbles can assume an unstable size and explode (unstable cavitation), releasing a large amount of energy and producing mechanical (turbulence) and thermal (temperature increase) effects. The collapse of the bubbles when they occur near a solid surface, results in a stream of liquid (microjet) striking the surface of the solid. This process may promote an increase in the transfer of matter between liquid and solid, but it can change the surface structure of the solid. Therefore, due to the relative simplicity of the ultrasound process in a liquid medium, its use becomes more frequent than in other media (SORIA; VILLAMIEL, 2010; CÁRCEL; BENEDITO; MULET, 2012).

The application of high power ultrasound waves in a gaseous medium presents an important challenge of obtaining an efficient transmission of acoustic waves at high frequencies due to the incompatibility of the acoustic impedance between transducers and gas, as well as the high ultrasonic attenuation in gaseous media. On the other hand, the efficiency of the application of this process can produce intense effects on the interfaces (pressure variations or microstirring), reducing the thickness of the boundary layer, which can directly influence the mass transfer mechanisms (CÁRCEL et al., 2007a; CÁRCEL; BENEDITO; MULET, 2012).

In a solid medium, the sponge effect generated by the successive compressions and expansions originated from the application of ultrasound waves occurs. The sponge effect promotes the release of liquid from the inner part of the particle to the solid surface and the entry of external fluid. The forces involved in it can be greater than the surface tension, that keeps the water molecules internalized in the capillaries of the material, generating microscopic channels, which promotes greater transfer of matter. In addition, effects on viscosity, surface tension, as well as on the deformation of the solid structure can occur (CÁRCEL; BENEDITO; MULET, 2012).

The application of high intensity ultrasound is presented as an effective alternative to enhance the mass transfer and heat shortens the processing time not only for drying at high temperature, but also at lower temperature (MARTINS et al., 2018).

1.3.1.2. Generation of high power ultrasound and application in convective drying

In general, ultrasound production consists in converting any type of energy into acoustic energy through an ultrasonic transducer. The most used conversion is electric energy in ultrasonic. An ultrasound generation system consists of a generator, transducer and emitter. The generator has the function of supplying energy to the system, so that the transducer that needs to be a vibrating body performs the conversion of the high frequency electrical signal into mechanical vibrations and the emitter transmits the acoustic energy produced through the transducer. The main types of electric transducers are piezoelectric, magnetostrictive, capacitive or electrostatic and electromagnetic (CÁRCEL; BENEDITO; MULET, 2012; (MUSIELAK; MIERZWA; KROEHNKE, 2016).

Piezoelectric transducers are the most commonly used in ultrasound and are based on the piezoelectric effect of some crystal. The effect is generated when a pressure is exerted on the crystal that generates a charge of opposite direction on each side of it, but of equal items. The reverse effects occur after the application of an equal but opposite charge on both sides of the ridges that contract or expand depending on the polarity of the charges. With a possible application of alternating electric current of high frequency, it can promote alternating change in size of the material and consequently a vibration. This vibration generates a mechanical wave that at an appropriate frequency is named as an ultrasonic wave. These transducers have the ability to deliver high power across the entire frequency range and have very high electrical energy conversion factors. However, its main limitation is the gradual aging that ceramics suffer with the time of exposure to work and depolarization when subjected to high temperatures (FUENTE-BLANCO et al., 2006; CÁRCEL; BENEDITO; MULET, 2012; GALLEGO-JUÁREZ et al., 2017).

Magnetostrictive transducers use the magnetostriction effect produced in ferromagnetic materials (iron, nickel and cobalt and cubic ferrites), that alternate the dimension under the application of a magnetic field. Capacitive or electrostatic are flat capacitors in which one electrode is an extremely thin membrane very close to the other rigid electrode. Electromagnetic transducers make use of the interaction of the magnetic field of a permanent magnet and the alternating electric current in a moving coil in order to convert electrical oscillations into ultrasonic waves. Finally, mechanical transducers are used only as transmitters and generally produce high amplitude vibrations with limited use (GALLEGO-JUÁREZ et al., 2017).

Power ultrasound application systems can be grouped into two important types according to the medium, the liquid and gaseous media. For liquid application, ultrasonic baths (indirect sonication) and the probe (direct sonication) type system are commonly used. The use of ultrasonic bath has been proven in the osmotic dehydration as pretreatment of strawberries freeze dried (GARCIA-NOGUERA et al., 2012), and tomato (CORRÊA et al., 2015), influence of mass transfer in apple immersed in the sucrose solution (CÁRCEL et al., 2007b), extraction of nutritional compounds (SUN et al., 2015; VALLESPIR et al., 2019) and other applications. In turn, direct sonication has been used in processes of enzymatic inactivation of fruit juice (AGUILAR et al., 2017), osmotic dehydration as a pretreatment for drying guava and banana slices (KEK; CHIN; YUSOF, 2013; FARHANINEJAD et al., 2017), extraction of plant and vegetable compounds (KEK; CHIN; YUSOF, 2013) among so many other applications.

In a gaseous medium, the application of high-power ultrasound is extremely more complex than in liquid media, since the transmission of acoustic energy becomes difficult due to the great difference in impedances between the systems emitting ultrasonic waves and the gases. In addition, the high acoustic absorption of gases becomes another limiting factor, and it is necessary to achieve an impedance adaptation between the emitter and the air, large amplitudes of vibration and a high energy concentration (GALLEGO-JUÁREZ et al., 1999).

The systems used for the application of ultrasonic waves in gaseous media are the emitters of stepped, rectangular or circular plates, as well as the emitters of vibrating cylinder, designed by the Power Ultrasound Group (ITEFI, CSIC), as shown in Figure 2.

Figure 2 - Cylindrical drying chamber used for the application of ultrasound without direct contact between the emitter and the food.
Source: Author (2020).

Figure 2 shows an ultrasonic emitter, in which the walls of its cylindrical drying chamber itself vibrate and radiate the acoustic energy in the medium, generating an acoustic field inside the samples to be dried (CÁRCEL et al., 2011).

High-power ultrasound has been considered an efficient alternative to intensify the processes of convective drying by different food products. The application of ultrasound can reduce the resistance to internal mass transport (sponge effect, creation of microchannels, among others) and external (microstreaming at interfaces). In addition, it can promote some microcracks in the external part of the product, facilitating the transport of water from the internal part to the air-product interface. The combination of all these factors can contribute to a significant reduction in drying time and even a reduction in the temperature ranges applied to the process (CÁRCEL et al., 2018).

Several studies corroborate the theory mentioned above regarding the reduction of drying time for food products, as show Table 1.

Table 1 - Effect of the application of power ultrasound on the drying kinetics of different products under different process conditions.

Product	Drying conditions	Reducing in drying time	Reference
Eggplant	40 °C; 1 m/s	72%	García-Pérez et al., (2011)
Apple	-10, -5, 0, 5, 10 °C; 2 m/s	77 % at -10 °C and around 60% at others conditions	Santacatalina et al. (2014)
Desalted codfish	-10, 0, 10 °C; 2 m/s	60, 16 and 29% at -10, 0 and 10 °C, respectively	Santacatalina et al. (2016)
Passion fruit peel	40, 50, 60, 70 °C; 1 m/s	60, 49, 38 and 28% at 40, 50, 60 and 70 °C, respectively	Nascimento et al. (2016)
Pineapple	40 and 70 °C; 1m/s	35% at 40 °C and 34% at 70 °C	Corrêa et al. (2017)
Red pepper	30, 50, 70 °C; 1 m/s	62 and 32% at 50 and 70 °C, respectively	Cárcel et al. (2018)
Kiwifruit	5, 10, 15 °C; 0.1 - 2.0 m/s	62, 65 and 55% at 5, 10 and 15 °C, respectively	Vallespir et al. (2019)

In addition to the studies mentioned in Table 1, several other cases have been developed and in some of them it can be observed that the temperature and velocity of the drying air as well as the acoustic power can affect the effects of ultrasonic waves. High temperatures generate a large amount of thermal energy in the system, which can mask the effects produced by ultrasound, showing that at low temperatures the process can be even more interesting. Additionally, there is evidence that the low velocity of the drying air (≤4 m/s) provides the best effects of ultrasonic waves, since an increase in the air flow can generate turbulences that affect the acoustic field, reducing its intensity. Finally, the acoustic power also has a positive relationship with the drying rate, and the increase in power promotes an intensification of the drying process (CÁRCEL et al., 2007a; SABAREZ; GALLEGO-JUAREZ; RIERA, 2012; RODRÍGUEZ et al., 2014).

In -addition to the effect on drying kinetics, the use of power ultrasound can directly influence the quality of dried products. The application of ultrasonic waves improved the retention of vitamins and carotenoids in tomatoes (FERNANDES et al., 2016), as well as, in one of the conditions evaluated, it was efficient in improving the retention of the content of polyphenols and flavonoids during apple drying (RODRÍGUEZ et al., 2014). However, in other studies, the effects on the quality of the final product can be negatively affected according to the process parameters, for example, in the drying of apple (MORENO et al., 2017), apple peel (MARTINS et al., 2018), and red pepper (CÁRCEL et al., 2018). These presented data indicate that the combination of the power ultrasound parameters and the different drying conditions need to be well studied in order to maintain the quality of the final product.

1.3.2. Ethanol impregnation pretreatment

The pretreatment of fruits and vegetables before the drying process acts to effectively increase the drying rate, to improve and preserve the quality of the final product in nutritional and sensory terms. Food infiltration treatment refers to the complete immersion of the samples in specific solutions under controlled temperature conditions and using the natural semi-permeability of the cell membrane to develop the water transfer from the product to the solution in order to reduce the initial content moisture (CORRÊA et al., 2012; WANG et al., 2019a).

Ethanol as a solution can also accelerate the drying rate. Ethanol is an organic solvent and its use can dissolve compounds in the cell wall of the food, increasing the permeability of the structure and consequently accelerating mass transfers during drying. In addition, there are reports in the literature that the efficiency of using ethanol as pretreatment is related to surface tension (FUNEBO et al., 2002; ROJAS; AUGUSTO, 2018), because of this it can create a relationship with the Marangoni effect. The movements of liquids resulting from unbalanced surface tension give rise to an important surface phenomenon (Marangoni effect) which is based on the fact that the generated surface tension gradient naturally induces the liquid to move from low surface tension regions to regions high surface tension (HU et al., 2007). Adding, ethanol is widely used because it has rapid penetration characteristics, easy evaporation and does not present chemical residues and becomes harmless, in small concentrations to human health (HAIYAN et al., 2016).

The effects of the application of ethanol as a pretreatment in drying food has been observed by several studies previously carried out with respect to process time and changes in the properties and quality of the final product. Funebo et al. (2002) found during the convective drying of the apple that the rehydration capacity of the samples was improved with the use of pretreatment and the shrinkage was reduced. During the drying of guaco leaves, effects on the reduction of the process time after application of 99.5% ethanol as a pretreatment were reported, as well as a reduction in the loss of the compound of medicinal interest (coumarin) (HU et al., 2007).

In drying pretreated with ethanol in eggplant slices were observed reduction in drying time and a significant reduction in the effects of varying the color of samples (HAIYAN et al., 2016). Similar results related to drying time have been found during the drying apple slices, and furthermore, it was observed that the tissues of the pretreated samples were less hygroscopic which enables the maintenance of a texture characteristic of dried apple (ZUBERNIK et al., 2019).

Therefore, according to the results mentioned regarding the application of ethanol as pretreatment to convective drying processes, it is feasible to develop further studies using this technique in order to reduce the drying time and obtain quality products.

1.3.3. Freezing pretreatment

Convective drying processes of fruits and vegetables present the inconvenience of the long exposure time of the product and the high energy demand. Freezing is a very popular technique used to preserve the quality and safety of fresh food. However, freezing can be applied as a pretreatment to drying processes. The freezing of samples before the drying process has the potential to reduce the processing time by increasing the drying rate of various foods (JUNQUEIRA et al., 2017; VALLESPIR et al., 2019b). Freezing process of the samples causes a disorder in the structural tissues of the food matrix, thus resulting in the improvement of mass transfer in the process drying (ESHTIAGHI; STUTE; KNOW, 1994; LEWICKI, 2006).

During freezing the change in the physical state of the water generates a variety of stress mechanisms in the tissues. Volumetric change of water can occur for conversion to ice, distribution of ice within tissues and size of formed crystals (VAN BUGGENHOUT et al., 2006). Slow freezing, in general, has the ability to generate large crystals in the extracellular region of food, which from a structural point of view, can affect the quality of products after thawing, as it promotes softening of tissues, increased loss drip, decreased retention capacity and water sensitivity, among other factors (LI; ZHU; SUN, 2018). On the other hand, fast freezing prevents water from flowing from the tissues to the outside of the food, as occurs in slow freezing, and this generates the formation of small ice crystals incorporated in the structure of cell walls (NOWAK et al., 2016). The difference between the two types of freezing is in the size of the crystals and the amount of them formed, and the fast freezing process has the ability to form numerous nuclei. Such difference may have a direct influence on the drying of fruits and vegetables, as mentioned by Junqueira et al. (2017) who described that the fast freezing of apples promoted a slight increase in the drying rate compared to slow freezing, possibly due to the more open structure of the food that the fast freezing promotes. Another factor related to product quality, Van Buggenhout et al. (2006) demonstrated that rapid freezing caused fewer landings in the texture of carrots compared to slow freezing, due to the reduction of cell wall damage.

The effects of freezing samples as pretreatment to convective drying processes have been reported in the literature by Vallespir et al. (2018) and proved that the freezing prior to drying of beetroot, apple and eggplant provided a reduction in drying time of up to 34 %.

However, some effects on product quality, such as changes in color, were more intensified after freezing, due to greater exposure to drying process. Another study shows that the application of pretreatment by freezing beetroot and eggplant promoted reductions in drying time by up to 32% compared to non-pretreated samples (VALLESPIR et al., 2019b).

For that reason, the combination of food freezing, mainly fruits and vegetables with convective drying, can present important results with respect to the behavior of the matrix throughout the drying process, referring to the process time and the final quality parameters inherent. In addition, it can be seen that the characteristics of each product and the type of freezing can influence and need to be evaluated in a specific and even more detailed way.

1.3.4. Pulsed electric field (PEF) pretreatment

The various convective drying methods have some disadvantages such as high processing times, energy costs and some possible changes in the quality of the final product, as mentioned above in other points. These factors must always be minimized and, therefore, the development of techniques that assist in this step has been increasingly discussed and studied. One approach to solve these disadvantages is the pulsed electric field technology (PEF).

PEF is a non-thermal technique that has a variety of applications and can be applied according to the purpose of the food processing industry. Such a technique can be used in the treatment of microorganisms aiming to improve the quality of food, extraction of high value compounds, enzymatic inactivation and pre-treatment to dry food process (YOGESH, 2016). The pioneering of the technique was conducted in the 1960s by the Doevenspeck, responsible for patenting the method of food disintegration from the application of high voltage waves (WITROWA-RAJCHERT et al., 2014).

1.3.4.1. Principle of PEF

The application of PEF consists in the use of electric pulses with intensity in the range of 10 to 80 kV/cm. The process is dependent on the number of pulses emitted to the product, which is maintained between two electrodes The electrodes have a specific space between them, called the chamber treatment space (SYED et al., 2017).

During the PEF process, high voltage is applied to the system and the electric field can be emitted in different ways, such as exponentially decaying waves, bipolar waves or oscillatory pulses. Regarding temperature, PEF can be conducted at ambient temperature, sub-ambient or above-ambient temperature (SYED et al., 2017).

The operating mechanism of PEF technology consists in providing pulsed energy to the product that is placed between two electrodes by limiting the treatment chamber. The system has a pulse generator for the production of high voltage pulses, a treatment chamber that accommodates the product to be treated and that remains associated with the control and monitoring device. Therefore, the food is placed in the treatment chamber, immersed in a solution with the capacity to conduct energy, coupled to two electrodes that are isolated from each other by a non-conductive material, receiving the high electrical pulses, transferring to the product that suffers a force per unit of load that has the capacity to promote changes in its structure the product (Figure 3) (WOUTERS; ALVAREZ; RASO, 2001; SYED et al., 2017).

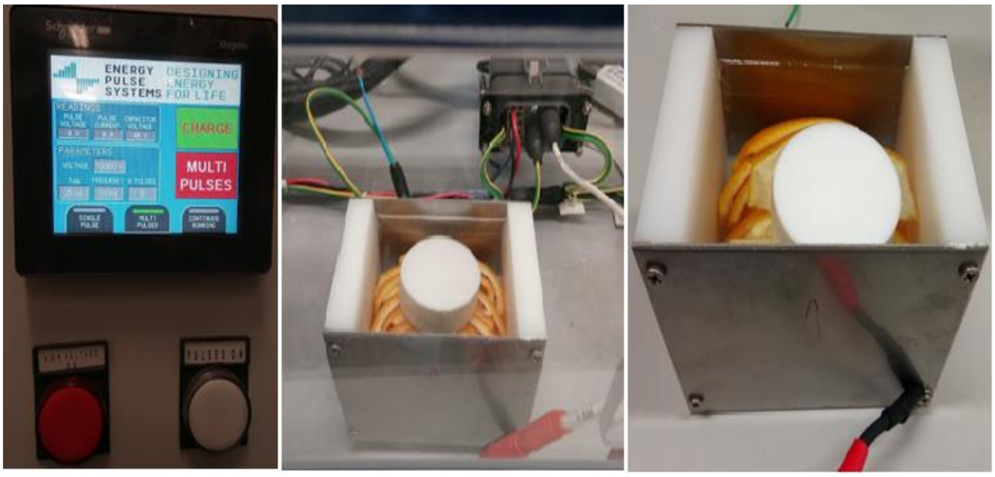

Figure 3 – Operation system and chamber treatment of PEF.
Source: Author (2020).

As well as other techniques applied to food industry, the PEF has some process control parameter settings that exerts influence directly on the effects of the material. Electric field strength (E), treatment time (t), number or pulses (n), pulse repetition frequency (f) and other parameters are important for the PEF process.

The intensity of the electric field refers to the intensity of the field in the treatment chamber during the PEF process, being dependent on the applied voltage between the electrodes, geometry of the treatment chamber and the spatial distribution of the dielectric properties of the material present between the electrodes. For the configuration of electrodes on parallel plates, the homogeneous electric field is considered, and in this way, the intensity of the electric field can be measured according to Equation 3 (RASO et al., 2016).

$$E = \frac{U}{L} \tag{3}$$

where U is the voltage measured across the electrodes and L is the electrode distance.

Treatment time refers to the number of pulses applied multiplied by the duration of each pulse (Equation 4) (RASO et al., 2016).

$$t = n \cdot \tau \tag{4}$$

where τ depends on the pulse shape. The pulse shapes usually in PEF treatments are either exponential or square-wave pulses, unipolar or bipolar (RASO et al., 2016). The frequency can be defined by the number of pulses applied per unit of time and is called Hz (number of pulses/s). Specifying the pulse frequency is one of the main factors in the process, because it is through this parameter that it is possible to determine the amount of electrical energy supplied per unit of time to the product under treatment, which in turn can generate an increase in temperature of the process caused by the Joule effect (RASO et al., 2016).

In general, the definitions of the PEF parameters are dependent on each objective and may have variations based on this principle. For example, the intensity of the electric field used is lower when the process object is connected to the improvement of heat and/or mass transfer and higher when the PEF acts as a conservation technique. In addition, the application of PEF applied in the processes of heat and mass transfer are considered as pre-treatment and this includes the drying processes (WITROWA-RAJCHERT et al., 2014).

1.3.4.2. PEF application in food processing

The food industry has been developing more and more every day and the applied processes to meet the demands of productivity and quality of the final product. Many processes, especially the thermal ones, ensure product stability. However, they can affect the chemical, nutritional and sensory composition of food. For this reason, the development of techniques that aim to optimize food production processes making them increasingly safe and economically viable has become an exponential need.

PEF can be applied in order to inactivate microorganisms and ensure the quality of food products. Wouters; Alvarez; Raso (2001) shows that the electromechanical compression and tension induced by the electric field causes pore formation in the membrane (electroporation) generating a local instability of microorganisms, which could be one of the effects of the microbial PEF inactivation. Another study by Wyk; Silva; Farid (2019) proves the effectiveness of applying PEF in the inactivation of *Brettanomyces bruxellensis*, which is a great challenge and concern as they have the ability to deteriorate wines worldwide. Corroborating the microorganism inactivation theory with the application of PEF (WALTER et al., 2016) demonstrated the efficiency of the treatment in inactivating UHT milk-spoiling microorganisms. As well as the works mentioned, it is possible to find several others in the literature reaffirming the efficiency of the PEF as pretreatment.

Additionally, studies prove the efficiency of PEF as pretreatment of several industrial processes with the aim of inactivating enzymes with the potential to reduce the quality of various products. Mendes-Oliveira; Jin; Campanella (2020) demonstrated the efficiency of PEF in inactivating polyphenol oxidase in apple juice and in addition, there was evidence of improvement in the lightness of the juice and in maintaining the fresh-like flavor. Another example of enzymatic inactivation with the application of PEF in apple juice was confirmed by Wibowo et al. (2019), which verified the inactivation of polyphenol oxidase, peroxidase and pectin methylesterase. In addition, the beneficial effect of PEF on the inactivation of enzymes in tomato products has been proven by improving the quality of the products (ANDREOU et al., 2016).

Another positive point of the application of PEF as pretreatment to industrial processes concerns the benefits promoted in the processes of extraction of compounds. Polikovsky et al. (2016) found out that the PEF enabled the increase in the extraction of macroalgae proteins with functional properties. Furthermore, PEF positively affected the extraction of phenolic and flavonoid compounds as well as the antioxidant activity of the compounds originating from onion treated with PEF (LIU; ZENG; NGADI, 2018).

Due to the high energy consumption and the possible loss of quality of the dried products, the PEF technique can be applied as a pretreatment to the drying processes in order to optimize and reduce quality losses on the final product . The literature presents a serie of PEF studies as pre-treatment for drying and Rizvi Alam et al. (2018) demonstrated that the process time was reduced, mainly at 50 and 60 ° C and Wiktor et al. (2016) also verified a reduction in the processing time of carrot samples pretreated with PEF. An important point to note is that the effects of PFE during drying by convection have a greater effect on the drying speed at moderate temperatures for some products (RIZVI ALAM et al., 2018). Corroborating this theory the effects of PEF were observed by Liu et al. (2018) for drying potatoes and drying blueberries (YU; JIN; XIAO, 2017) .

The freeze-drying processes can also have reduced times with the application of PEF, although with less intensity than compared to hot air drying convective. During the drying of the apple it was observed that the effect of electroporation caused the process time to be twice as fast in the pretreated samples (LAMMERSKITTEN et al., 2019).

Besides the advantages presented concerning the reduction of the drying time, using PEF has influence on quality parameters of products and such influences can vary according to the parameters of PEF and drying process, and according to the characteristic of each food. Analyzing, Rizvi Alam et al. (2018) found out that the PEF promoted a change in the color of the analyzed samples, and in the carrot samples there was a significant reduction in lightness values (L *) compared with untreated samples, while parsnips pretreated products showed a significant increase in yellowness values (b). In addition, it was possible to verify the reduction in the luminosity values in dried carrot samples by up to 25.3% in comparison with the untreated samples, being also observed a direct influence on the ΔE of pretreated samples (WIKTOR et al., 2016). Electroporation can influence on the bioactive compounds in food. During the drying of carrots and parsnips, reductions in the levels of carotenoids and development of the Maillard reaction were observed (FRATIANNI et al., 2019). On the other hand, the use of PEF promoted an increase in β-carotene in dehydrated apricots at 45 ° C (HUANG et al., 2019).

Recently, few studies have been found in the literature that demonstrates the effectiveness of applying PEF followed by ultrasound-assisted drying (LLAVATA et al., 2020). The combination of the two technologies can have effects in reducing the drying time, as described by Wiktor et al. (2019) and Wiktor; Witrowa-Rajchert, (2020). Although the results are promising, the amount of research developed on the subject is still small and it needs to be further investigated in order to understand the effects of the association of these technologies applied to the drying process as well as the influences on the quality of the products.

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SECOND PART – ARTICLES

Manuscripts are formatted according to the requirements of each scientific journal.

ARTICLE 1 - Article submitted to the Journal Heat and Mass Transfer

PROCESS AND QUALITY ASPECTS OF CONVECTIVE DRYING OF DEKOPON WITH APPLICATION OF ETHANOL IN THE SURFACE AS PRETREATMENT

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Abstract

Dekopon is an exoctic citrus fruit, by cross between Kiyomi (*Citrus uses* Markov. x *Citrus sinensis* Osbeck) and Ponkan (*Citrus reticulata* Blanco). The influence of ethanol pretreatment (EP) and temperature in the drying time and quality of dekopon slices were studied. Drying at 50 and 70 °C and 2.0 $m.s^{-1}$ with (P50 and P70) and without EP (N50 and N70), was performed. The EP application and air temperature shortened drying time. The lowest total color difference were observed for P50 and P70 (10.02 ± 1.05^b and 11.01 ± 4.55^b, respectively). P50 experiment presented the highest retention of total phenolics compounds (67% of the fresh fruit content). The P50 experiment showed the highest ascorbic acid content (2026.21 ± 71.55^c), statistically different to that of fresh dekopon (2495.68 ± 93.71^a). Regarding the antioxidant capacity (IC_{50}), P50 and P70 presented more preservation of antioxidant capacity comparated to pretreatments without ethanol application (2.71 ± 0.03^c and 3.40 ± 0.05^d $mg.ml^{-1}$, respectively). It was 1.98 ± 0.19^a $mg.ml^{-1}$ for the fresh fruit. Therefore, ethanol application is recommended for obtaining a shortened time dried dekopon with low color alteration and high retention of nutritional components by convective drying.

Keywords: Citrus fruit; dried product; reduction time; quality preservation

1. Introduction

The consumption of citrus fruits is important for human health as they contain vitamins, minerals, and dietary fiber. Such compounds are essential for normal growth and development, and nutritional well-being [1]. Dekopon (*Citrus reticulata "Shinarui"*), a citrus fruit, is a cross between Kiyomi (*Citrus uses* Markov. x *Citrus sinensis* Osbeck) and Ponkan (*Citrus reticulata* Blanco). Its commercial value is due to its sweet taste and pleasant aroma [2].

Vitamin C is an important vitamin in plant foods, consisting of ascorbic acid and dehydroascorbic acid. It is also used in food preparation and processing. The vitamin not only prevents certain diseases but also plays the role of a biological antioxidant [3]. Furthermore, most of the beneficial properties of fruits and vegetables have been attributed to bioactive compounds, commonly named as phytochemicals. Among these are the phenolic compounds that have been extensively studied due to their diverse health benefits [4].

In general, fruits and vegetables have high moisture content and, consequently, have a reduced post-harvest shelf life. In this context, drying techniques are applied to improve the shelf life as well as to increase the market value of the products [5]. The convective method is one of the most common food drying methods. However, the products are affected by processing conditions such as temperature, relative humidity, air velocity, and physical and chemical parameters [6]. Thus, the process of drying should be examined closely by taking into account, the degradation of nutritional compounds, oxidative damage, loss of flavor, browning, and shrinkage [7].

Temperature and time are the most important variables affecting vitamin C degradation in thermal processes [8, 9]. The high sensibility of this nutrient to heat determines its retention in the drying process and is dependent on the temperature and time parameters [3]. Moreover, drying could lead to activation of oxidative enzymes, such as polyphenol oxidase and peroxidase, which results in the loss of phenolic compounds [10].

Drying processes, especially conventional ones, present several advantages and disadvantages when used in vegetable processing. The excessive time of exposure of the product to the drying conditions can generate a degradation of the quality due to the large exposure to temperature. In addition, conventional methods are characterized by high energy consumption [11]. In order to minimize the degradation of foods exposed to the drying process as well high energy consumption, pretreatments such as, osmotic dehydration [12] , ultrasound-assisted drying [13], pulsed vacuum osmotic dehydration [14], application of ethanol on fruits, and addition of ethanol to the drying atmosphere [15], have been used.

The use of ethanol promotes a less pronounced volatile loss, intense water evaporation, higher drying rates, lesser color degradation, and higher vitamin C retention [16] Moreover, [15], during convective drying of pumpkin with the use of ethanol as pretreatment obtained a significant reduction in drying time, as well as observed by [17] in drying of apple. In addition, the use of ethanol as a pre-treatment to dry food is shown to be viable because ethanol presents rapid penetration, easy evaporation, does not leave chemical residues and is harmless to human health in small quantities [18].

Although dekopon presents great sensory and nutritional characteristics, there is a lack of studies about this product, mainly regarding to the maintenance of dekopon nutrients in drying process. Therefore, this work aimed to (i) investigate the effects of ethanol and the drying temperature in reducing the convective drying time of dekopon slices and (ii) examine the influence of ethanol and the drying temperature on color parameters, retention of phenolic compounds, vitamin C content, and antioxidant activity.

2. Materials and methods

2.1. Sample preparation

Dekopon fruits (*Citrus reticulata "Shinarui"*) were purchased in the local market (Lavras, MG state, Brazil). The fruits were selected by size and uniformity in the samples and stored at 7 °C (±2 °C) until the beginning of each experiment. The fruits were washed and sanitized with sodium hypochlorite solution. The epicarp was removed manually and the pulp was sliced into a disk shape (60.54±1.12 x 3.27±0.32 mm, diameter x thickness) using a cutter and a stainless-steel knife. The initial dimensions of the slices were verified with a digital caliper (Western, DC-60 model, Zhejiang, China).

2.2. Experimental conditions

The experiments were performed in a 2 × 2 factorial design at two air temperatures (50 and 70 °C). The non-pretreated samples (N50 and N70) were submitted directly to the drying process. The treated samples (P50 and P70) were immersed in 95% (v/v) ethanol for 10 s [19]. The concentration ethanol was study previously by [20]. The samples were placed in a petri dish and completely immersed with ethanol generating a 1:1 (w/w) ratio of sample/ethanol.

2.3. Convective drying

Convective drying was performed in a tunnel dryer (Eco Engenharia Educacional, MD018 model, Brazil) (Fig.1) at 50 °C or 70 °C with an air velocity of 2.0 m s^{-1}. The air velocity was monitored by a anemometer (Akso, AK833 model, Brazil).

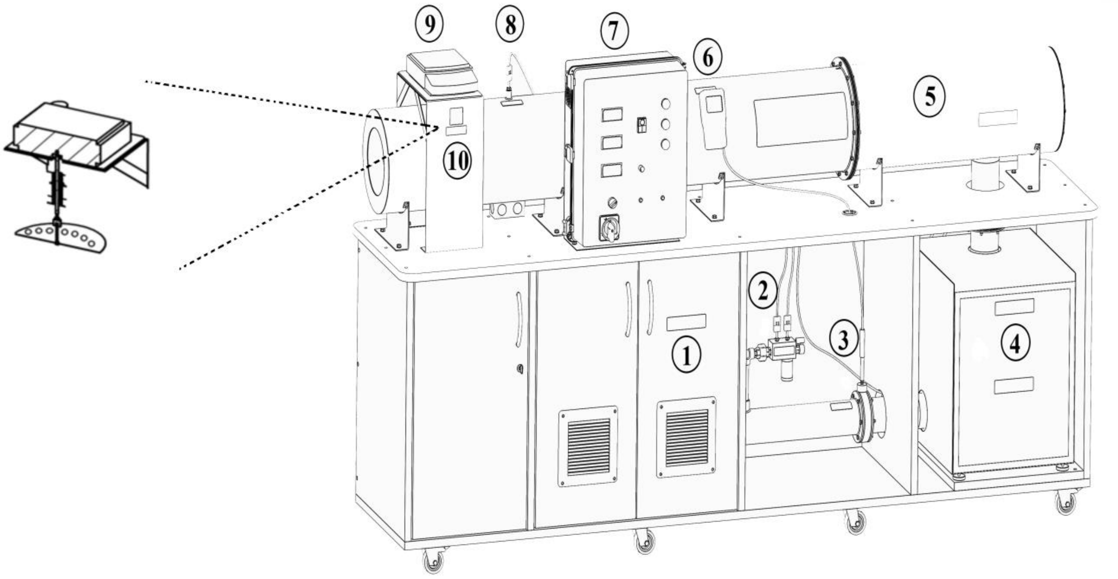

Fig. 1. Diagram of the tunnel dryer by Eco Engenharia Educacional (MD018 model, Brazil): 1-centrifugal fan site; 2-digital psychometer; 3-thermocouple; 4-box with electrical resistances; 5-air tunnel; 6-digital anemometer; 7-electrical system panel; 8-temperature sensor; 9-digital scale; 10-sample holder coupled to the digital scale.

In each experiment, 145.11 ± 5.86 g of fresh fruits were dried. The process was performed until an average final moisture content of 0.23 ± 0.05 kg H_2O kg^{-1} d.b was reached. The mass variation of samples during the drying process was monitored using a digital scale (Marte Científica, AD33000 model, Brazil) (accuracy ± 0.01 g) coupled to a sample holder which evaluated the drying evolution with time. All the experiments were carried out in triplicates, and the moisture content of the dried dekopon was determined in a vacuum oven at 70 °C according to the [21] standard method 934.06. The water activity determination was performed in a hygrometer (Aqualab, 3-TE model, Decagon Devices, Inc., Pullman, WA, USA). The analyses were performed in triplicates.

2.4. Color

The color parameters of fresh and dried dekopon were measured using a colorimeter (Minolta, Model CR-400, Osaka, Japan). The CIELAB coordinate system was used and the parameters L^*, a^*, and b^* were evaluated with a D65 illuminant [7]. The total color difference (ΔE) was calculated according to Eq. (1) [22].

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

where L^* indicates lightness (100 for white to 0 for black), a^* indicates red when positive and green when negative, and b^* indicates yellow when positive and blue when negative. The subscript ‘0’ refers to the fresh fruit color.

2.5.Determination of total phenolic compounds

The total phenolic content was quantified using an adaptation of the Folin-Ciocalteu method (Waterhouse, 2002). Quantification was performed by a spectrophotometer (Varian, Cary 50 Probe) at 750 nm, and the results were expressed in mg of gallic acid /100 g of d.m..

2.6.Determination of ascorbic acid by HPLC

Ascorbic acid extraction was performed according to the methodology described by Barcia et al. (2010), with minor modifications. Approximately 10 g of sample was weighed to which 30 mL of metaphosphoric acid solution (4.5%) in ultrapure water was added and allowed to stand for 1 h in an amber bottle. The sample was subsequently filtered using a filter paper, and the supernatant was centrifuged at 7000 rpm for 10 minutes and transferred into a 1.5 mL vial. This was placed in an ultrasound bath (Unique brand, Model USC 2850 A, Indaiatuba, Brazil) for 30 minutes. A high-performance liquid chromatograph (HPLC, Shimadzu, LC-20AT) equipped with a UV detector (Shimadzu, SPD-20A) was used to determine the ascorbic acid content in the samples according to Vinci, Botrè, & Mele (1995) with modifications. The separation was carried out using a Phenomenex 5 µm C18 column (250 x 4.6 mm), thermostated at 30 °C. The mobile phase was an aqueous solution of 0.15% (v/v) acetic acid with a flow rate of 1.0 mL min^{-1}. The detection was performed at 254 nm. The peak of ascorbic acid was identified by its retention time compared to standard solutions. The analytical curve was obtained from the chromatogram of standards measuring the peak areas of ascorbic acid at the same separation conditions as that applied to the samples. Standard ascorbic acid concentrations ranged from 1 to 600 mg L^{-1}.

2.7.Determination of antioxidant activity

Fruit extracts for total phenolics and antioxidant activity measured in methanol extract analysis were prepared according to [26] with some modifications. For the extraction, 2.5 g of the fruit were weighed and 20 ml of 50% methanol were added. After homogenization ultraturrax, the mixture was allowed to stand for 60 minutes at room temperature. After, the contents were centrifuged at $1.5x10^4$ rpm/15 min, the supernatant transferred to a 50 ml volumetric flask. From the residue of the first extraction, 20 ml of 70% acetone was added. The mixture was homogenized and left to stand for 60 min at room temperature. After resting, there was a new centrifugation at $1.5x10^4$ rpm/15 min. The supernatant was transferred to the volumetric flask containing the first supernatant and the volume was made up to 50 ml with distilled water.

The total antioxidant activity was assessed using the DPPH (1,1-diphenyl-2-picrylhydrazyl) radical-scavenging assay according to [27] and was expressed as inhibitory concentration IC_{50}. The IC_{50} is the concentration of an antioxidant at which 50% inhibition of free radical activity is observed.

2.8.Statistical analyses

All analytical determinations were performed in triplicates. Parameter values are expressed as the mean ± standard deviation. The results were analyzed using analysis of variance (ANOVA) and the Tukey test at 5% significance to compare the mean values. The statistical analyses were performed using Statistic (Statsoft, Tulsa, OK, USA).

3. Results and discussion

3.1. Experimental convective drying

Fig. 2 shows the drying curves of non-pretreated and pretreated dekopon samples during convective drying.

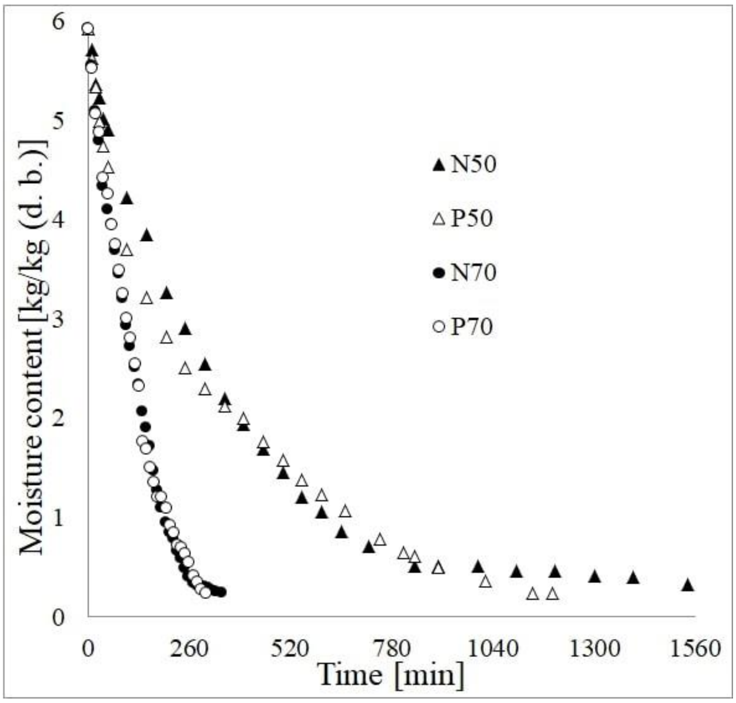

Fig. 2. Drying kinetics of dekopon slices at 2.0 m.s^{-1} in the different air temperatures and use of ethanol pretreatments (P means treated samples, N means non-pretreated samples, 50 and 70 corresponds to the temperature of 50 °C and 70 °C, respectively).

To reach a final moisture content of 0.23 ± 0.05 kg H_2O kg^{-1} d.m. at 50 °C, the non-treated sample N50 took 1540.00 ± 0.83^a min while the treated sample P50 reached the same condition in 1193.33 ± 0.64^b min ($p < 0.05$). The time taken by P50 was shorter by 22.50%. At 70 °C, it was not possible to verify a significant difference in the drying time between treated and non-treated samples, P70 and N70 (300.33 ± 0.95^c and 343.33 ± 0.91^c min), respectively. The use of ethanol in the samples before the drying process can create flow channels and pores of water from the internal part to the surface in the cell matrix, which provides a higher drying rate [28]. However, there was a reduction in processing time by 12.50% for P70. Previously study [16] reported that the application of ethanol on the surface of banana allowed higher diffusivity during convective drying, thus reducing the drying time. Thus, ethanol on the sample was probably solubilized in the aqueous solution of the sample (water and sugar), resulting in a new liquid phase. Ethanol presents a hydroxyl part which forms hydrogen bonds with water. Therefore, a mixture of the two substances in any proportion, results in a miscible solution. Aqueous ethanol has a higher vapor pressure than water. As a consequence, drying time is decreased when ethanol is used [15, 16, 29] obtained 49.5% time reduction with the use of ethanol on the surface of pumpkin slices. Furthermore, immersion of potatoes in ethanol affected their cell wall, what could improve the drying rates [20]. It was also possible to verify that the temperature increase had a significant effect ($p < 0.05$) on the drying time reduction in all the experiments. In the non-pretreated samples, a reduction of 77.70% was obtained, while in the pretreated samples, the reduction was 74.58%. The internal resistance to moisture transport decreases as the drying temperature increases due to higher water mobility inside the food, while the external resistance decreases due to an increase in the water pressure gradient between the phases. A high drying temperature provides enough energy to overcome the latent heat of phase change that takes place during moisture evaporation [29]. A similar effect was found in a previous study during drying of passion fruit peel [30]. The effects of temperature and the use of pretreatment found in this study corroborate with [18]. The study proved the effect of increasing the temperature in reducing the processing time of untreated samples as well as treated samples. These results have lead to the drying process due to energy consumption savings that can be obtained in these conditions. In addition, temperature and the mixture water-ethanol volatilization are the two driving force of the drying experiments. Between both driving forces, temperature is the sharper one. Consequently, the influence of the temperature in a non-treated sample is great with shortened drying time. In the same matter, the volatilization of the mixture is important in lower temperature and not important at high temperatures.

After drying, the a_w values were reduced by up to 63.00% compared to the fresh sample (Fresh sample: 0.97 ± 0.02^a; N50: 0.37 ± 0.03^b; P50: 0.36 ± 0.05^b; N70: 0.36 ± 0.02^b; P70: 0.38 ± 0.05^b – $p < 0.05$). High a_w is among the main factors for loss in food quality; drying assists in reducing a_w [31]. After drying, in all treatments, the a_w levels of dekopon slices were very low, rendering the product stable. Similar results were found by [7] during the drying of pequi.

3.2. Color

Table 1 shows the analysis of the color parameters of fresh and dried dekopon.

Table 1 . Color parameters analyzed in dekopon slices.

Experiment Code	L^*	a^*	b^*	ΔE
Fresh	53.35 ± 0.95^a	10.77 ± 1.27^a	35.67 ± 1.15^a	-
N50	63.56 ± 3.25^{bc}	4.85 ± 0.67^b	50.11 ± 4.56^b	18.72 ± 1.82^a
P50	59.59 ± 1.22^b	9.66 ± 1.07^a	43.32 ± 1.03^c	10.02 ± 1.05^b
N70	64.93 ± 2.57^c	4.51 ± 1.3^b	51.16 ± 4.96^b	20.45 ± 0.91^a
P70	60.79 ± 2.49^{bc}	6.52 ± 0.38^b	42.43 ± 1.3^c	11.01 ± 4.55^b

N (non-pretreated samples), P (pretreated samples), 50 and 70 (air drying temperature expressed in Celsius degree). Different letters mean significant differences ($p<0.05$).

The parameter L^* was significantly different in all the treatments when compared to the fresh samples ($p < 0.05$). Moreover, a small variation of this parameter was observed in the P50 sample. With parameter a^*, the sample P50 presented a difference when compared to all the dehydrated samples. However, this value was statistically similar to the fresh samples ($p < 0.05$), reaffirming that minor alterations occurred with pretreatment at a low temperature. The parameter b^* showed a significant difference ($p < 0.05$) in all the treatments when compared to the fresh samples. Finally, in the total color difference (ΔE) experiment, the lowest variations were established in the pretreated samples, and a significant difference was observed when compared to the non-pretreated samples ($p < 0.05$). Treatment with ethanol provides less variation in color. This is, possibly, due to the inert environment formed after ethanol volatilization that helps the material to isolate oxygen, reduces the chance of an oxidation reaction and helps the maintenance of the color of the material [18]. Before [16] studied the ethanol application on the surface of bananas at different stages of maturation as well as the use of an ethanol modified atmosphere. They reported only minor color change in the samples, which resembles the current study. The influence of application of ethanol as a pretreatment to the drying process was observed by [18], where they confirmed the efficacy of alcohol in the reduction of color change in eggplant slices. The reduction in the change of color parameters by ethanol may be related to decreased processing time, and minimized effects of browning reactions, as reported by [16]. The temperature effect was not statistically significant with respect to ΔE, although N50 was less varied than N70. This fact is explained by the evidence that the exposure of fruits to high temperatures can generate increase rate of compounds due to the increase in the speed of the Maillard reaction [32].

3.3.Total phenolic compounds

Table 2 shows the results of total phenolic composition in dekopon slices in fresh and dried samples.

Table 2 . Total phenolics compounds of dekopon slices.

Experiment Code	Total phenolics compounds [$mg.100\ g^{-1}$]*
Fresh	1136.49 ± 11.93^{a}
N50	642.89 ± 6.14^{b}
P50	766.67 ± 10.25^{c}
N70	609.75 ± 4.77^{d}
P70	622.16 ± 6.06^{db}

N (non-pretreated samples), P (pretreated samples), 50 and 70 (air drying temperature expressed in Celsius degree). Different letters mean significant differences ($p<0.05$).
*expressed as gallic acid in the dry matter.

A reduction in the content of phenolic compounds was observed in all the treated samples when compared to the fresh fruit (N50: 43.43%; P50: 32.54%; N70: 46.35% and P70: 45.26%). The use of ethanol caused lower degradation of the compounds in the tested temperatures, even at 50 °C ($p < 0.05$). Previously [10] reported that the heating of products can reduce the content of bioactive compounds due to long exposure to heat. Our results can be explained by intense evaporation of water caused by ethanol, which reduces exposure time, thus minimizing the effects of temperature and preserving the quality parameters [16].

Higher drying air temperature promoted higher reductions in the total phenolic content in the pretreated and non-pretreated samples ($p < 0.05$). Drying presents it as a disadvantage because it reduces the content of bioactive compounds in foods and degrades phenolic compounds due to the possible binding of polyphenols with other compounds or change in the chemical structure [33].

The temperature influence on phenolic content reduction was similarly found by [33] during the drying of strawberries. They also reported that the exposure time can affect the degradation of phenolic compounds. Previously study [34, 35] also observed the same effect of temperature on the degradation of phenolic compounds during the drying of mango and grape pomace.

3.4. Ascorbic acid

Table 3 shows the results of the ascorbic acid analysis of dekopon slices in fresh and dried samples.

Table 3. Ascorbic acid content of dekopon slices.

Experiment Code	Ascorbic acid [mg.100 g^{-1}]*
Fresh	2495.68±93.71^{a}
N50	1243.36±271.74^{b}
P50	2026.21±71.55^{c}
N70	1281.91±52.55^{b}
P70	1367.25±61.63^{b}

N (non-pretreated samples), P (pretreated samples), 50 and 70 (air drying temperature expressed in Celsius degree). Different letters mean significant differences ($p<0.05$).
*expressed in the dry matter.

A significant reduction of vitamin C degradation was observed when ethanol was used in the pretreatment at 50° C compared to the fresh sample ($p < 0.05$). A smaller percentage of reduction of ascorbic acid content was achieved in the sample P50, when compared to the fresh sample (N50: 50.18%; P50: 18.81%; N70: 48.63% and P70: 45.21%). The effects of ethanol on drying air temperature were evaluated by [36], who verified that the highest percentage of retention of ascorbic acid was found in the experiments using ethanol and lower drying temperature. Results from the present study confirm the influence of increased drying temperature ($p < 0.05$) in the reduction of ascorbic acid content in the pretreated samples.

Ascorbic acid has a physiological activity as vitamin C and can be easily degraded by many factors, such as, temperature [3] The use of ethanol for promoting a higher drying rate through the creation of channels in the product structure facilitating the migration of internal water to the surface exposes the product for a shorter time to the drying process which minimizes the degradation rates of ascorbic acid [36 - 38] found a similar result during drying of jujube fruits, showing that lower temperatures preserve vitamin C.

3.5. Antioxidant activity

Table 4 presents the values for the antioxidant activity of the dekopon slices under all the treatments studied.

Table 4. Antioxidant activity of dekopon slices.

Experiment Code	IC_{50} [$mg.ml^{-1}$]*
Fresh	1.98±0.19 ^{a}
N50	3.72±0.28^{bd}
P50	2.71±0.03^{c}
N70	4.03±0.08^{b}
P70	3.40±0.05^{d}

N (non-pretreated samples), P (pretreated samples), 50 and 70 (air drying temperature expressed in Celsius degree). Different letters mean significant differences ($p<0.05$).
*expressed in the dry matter.

All the treatments studied showed a significant increase in mean IC_{50} value when compared to that for fresh sample ($p < 0.05$) with a percentage increase of 87.88% (N50), 36.87% (P50), 103.54% (N70), and 71.71% (P70). Lower the IC_{50} values of a sample, greater is their antioxidant capacity; this relationship explains the fact that the fresh samples showed the lowest values [38].

The effect of the use of ethanol can be evidenced by the significant increase in the average value of IC_{50} in the pretreated samples at the two temperatures studied ($p < 0.05$). The use of ethanol provides better antioxidant activity as the pretreatment increases the drying rate, reducing the exposure time in the drying process. This decreases degradation of the bioactive compounds, such as vitamin C and phenolic compounds. In addition, the influence of the air-drying temperature was observed among the treatments, being statistically significant in the pretreated samples ($p < 0.05$). The negative effect of temperature can be explained by the fact that the exposure of products to temperatures between 60 and 70 ° C can lead to the degradation of phenolic compounds and ascorbic acid, reducing antioxidant activity [39]. Therefore, we can prove the importance of preservation of the bioactive compounds in the improvement of the antioxidant activity in the dehydrated products, as verified by [40] and [41]. During the drying of red pepper, [42] reported a reduction in the antioxidant activity after drying experiments, compared to the fresh fruit, which is similar to the one found in the present study. However, [40] reported the same effect, mentioning that fresh samples had lower IC_{50} values when compared to dehydrated samples.

4. Conclusions

The use of ethanol as a pretreatment to dekopon slices drying promoted a significant reduction on the process time, especially at 50 ºC. The drying rate was also increased with temperature. Regarding changes in quality parameters, the influence of ethanol pretreatment and temperature are, as listed: Total color difference was diminished with the pretreatment and increased with temperature. Drying operation carries out to phenolic compounds and ascorbic acid reduction anyway. However, it was observed higher retention capacity of phenolic compounds and ascorbic acid with the ethanol pretreatment. The temperature led to a significant reduction on the concentration of phenolic compounds, but did not present a significant alteration on ascorbic acid retention. Among the drying conditions, the pretreatment with ethanol followed by drying at 50 ºC resulted in the best antioxidant capacity (IC_{50} 2.71±0.03 $mg.ml^{-1}$), proving the effectiveness of the pretreatment. Furthermore, the increase in the process temperature did not result in a statistically significant reduction in the value of antioxidant activity. Therefore, immersion in ethanol as a pretreatment for dekopon drying, mainly at low temperatures, is recommended to obtain a nutritional and quality product.

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6. Declaration

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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ARTICLE 2 – Article published in the Journal Drying Technology

ULTRASOUND-ASSISTED DRYING OF ORANGE PEEL IN ATMOSPHERIC FREEZE-DRYER AND CONVECTIVE DRYER OPERATED AT MODERATE TEMPERATURE

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Abstract

Atmospheric freeze-drying (AFD) at -10 °C and moderate temperature convective drying (MTD) at 50 °C without and with ultrasound application (20.5 kW/m^3) were carried out. Alcohol insoluble residue (AIR) and its swelling capacity (SC), water retention capacity (WRC) and fat retention capacity (FRC) were measured in the dried product. Ultrasound significantly shortened the drying time in both processes, the intensification effect being more significant in atmospheric freeze-drying (57% and 27% reduction in atmospheric freeze-drying and convective drying, respectively). As regards AIR and WRC, no effect was observed of either the drying temperature or ultrasound application. On the contrary, SC was significantly lower in AFD samples. The FRC of MTD samples was similar to that of the fresh ones and higher than the values obtained for atmospheric freeze-dried samples. Therefore, convective drying at moderate temperature preserved the AIR properties better than atmospheric freeze-drying.

Keywords: By-product; process intensification; fiber; alcohol insoluble residue

1. Introduction

Citrus fruits are among the most-heavily harvested fruits in the world. Most of the production is destined for to the juice industry, where approximately 50% of the total fruit weight is discarded, generating a large amount of waste. These residues, mainly peels, can be used as a source of valuable bioactive compounds [1] with commercial and technological applications, such as dietary fiber [2,3] used to fortify food products. In this sense, citrus peels have a high moisture content which made them very susceptible to the degradation reactions. Drying processes represent an optional means of producing a stable and high quality by-product, which becomes raw matter for later processing with convective drying, at high (HTD) or moderate temperatures (MTD), being the most commonly used conventional technique. However, this operation may induce undesirable structural damage, color alterations and content reduction of nutritional compounds.[4,5] As a result, there is growing interest in applying alternative techniques, which imply higher quality products, such as atmospheric freeze-drying (AFD).[5] AFD consists of water removal by sublimation at atmospheric pressure using drying air at low temperature and relative humidity, keeping the product frozen while being dried.[5,6] This process is dependent on the air drying characteristics (temperature, velocity and relative humidity) and the food properties (dimensions, porosity, initial moisture con- tent, etc).[7] AFD can be used to dry different foods, obtaining high quality dried products.[6,8] Both elevated air temperatures (HTD and MTD) and long processing times (AFD) can cause quality loss in foods, affecting, for example, the properties of the fiber. In order to reduce these impacts caused by convective drying processes, combined techniques, such as the application of power ultrasound (US), may be considered. US can induce a reduction in the external and internal mass transfer resistance with only a mild thermal effect.[5] In a solid porous product, US causes a series of rapid compressions and expansions (sponge effect) facilitating the exit of water through the microchannels created by the propagation of the waves.[6,8] The influence of US application has been addressed in order to shorten the processing time of fruits and vegetables.[9–11] Therefore, the main objective of this study was to address the influence of process characteristics, atmospheric freeze-drying (AFD) and convective drying at moderate temperature (MTD), and power ultrasound application on the drying kinetics and functional properties of orange peel.

2. Material and methods

2.1. Raw material

Valencia Late var. oranges (*Citrus sinensis*) were purchased in a local market (Valencia, Spain). Homogeneity of size and color was the criterion considered when choosing the fruits. The oranges were washed and superficially dried. Rectangular shell samples (containing only flavedo and albedo tissue) of 48 ± 1 x 26 ± 1 x 3.18 ± 0.04mm were obtained using sharp knives. The initial moisture content was measured by placing the samples in a vacuum oven at 70 °C and 200mmHg until constant weight.[12]

2.2. Drying experiments

Two convective drying techniques were exanimate, AFD (water removal by sublimation) and MTD (water removal by evaporation), and the influence of ultra- sound application was addressed in both cases. Every kind of drying condition considered was tested in triplicate.

2.2.1. Atmospheric freeze-drying experiments

Before the AFD process, 18 orange peel samples were placed in a tree-shaped sample holder, previously described,[5,6] that ensured free-flowing air around them and a homogenous ultrasonic treatment. The set was covered with a plastic waterproof film and placed in a blast freezer (HIBER, model ABBBF051, Italy) at -35 ± 1 °C for 1 h. This was long enough to reach a temperature of -18 °C in the center of the samples. Immediately after this, the samples were unwrapped and transferred to an ultrasound-assisted convective dryer with air recirculation adapted to work at low temperatures.[6] The drying chamber is a cylinder (internal diameter 100 mm, height 310 mm, thickness 10mm) attached to a piezoelectric transducer (21.9 kHz) that produces an internal high intensity ultrasonic field. The drying air is recirculated in the system, controlling both the air velocity and temperature by means of two PID control algorithms. The drying experiments were performed at 1 m/s, without (AFD) and with (AFD-US; drying experiments were performed at -10 ± 1 °C 20.5 kW/m^3) ultrasound application. In order to keep the relative humidity low (maximum value of 15%, measured with a KDK sensor, Galltec Mela, Germany), the air is forced to flow through a tray containing desiccant material (Activated Alumina AC14, Alfphachem, Spain) which is periodically regenerated. The drying kinetics were determined from the initial moisture content of orange peel samples and the variation in sample weight during the process. The experiments were performed until the samples lost 60% of their initial weight.

2.2.2. Convective drying experiments at moderate temperature

Fresh orange peel samples (18 pieces) were placed in a similar sample holder to that used in AFD experiments. MTD experiments were performed at a temperature of 50 °C and an air velocity of 1 m/s, without (MTD) and with (MTD-US; 20.5 kW/m^3) ultrasound application until the samples lost 60% of their initial weight. The ultrasonically-assisted dryer used for this purpose has been described previously.[13] The characteristics of the drying chamber and the ultrasonic field applied were similar to those tested for AFD experiments.

2.3. Modeling of drying kinetics

The modeling of the experimental data permits the comparison and quantification of the influence of the process variables on the kinetics; the theoretical models, like the diffusion-based models, are the most adequate for this purpose because they permit insight to be gained from the phenomena involved in the drying. However, the different mechanisms of moisture removal involved in the experiments considered, evaporation in MTD experiments and sublimation in AFD ones, makes the application of this kind of model difficult. Moreover, while the moisture movement inside the MTD samples can be assumed to be due to diffusion in the overall volume, in the AFD samples it only takes place in the external dried layer whose thickness increases at the expense of the internal frozen core. Since the main aim of this study was not the development of a model but rather the quantification of the influence of process variables on drying kinetics, the empirical Weibull model, a model widely used in drying,[14] was considered (Equation 1).

$$\Psi = \frac{X_{eq} - X_t}{X_{eq} - X_0} = e^{(-\frac{t}{\beta})^{\alpha}} \qquad (1)$$

Where Ψ is the dimensionless moisture content; X_t is the moisture content (kg water/kg dm) at a drying time t (s); X_0 is the initial moisture content of samples (kg water/kg dm); X_{eq} is the moisture content at equilibrium, which was determined from the relative humidity of the drying air and the orange peel isotherm reported by Garau et al.[15] and α and β are the parameters of the Weibull model. The parameter α is the shape factor and represents a behavior index of the product: the higher its value, the lower the initial velocity of the process. Values of more than 1 predict downtimes in the process and when the value is 1, the Weibull model becomes a first order kinetic model. β, on the other hand, is related with the kinetics of the process, showing a reverse relationship with the drying rate. This parameter includes the effects on the kinetics of variables, such as the temperature, air velocity or, in this case, ultrasound application.

The Weibull parameters were identified by minimizing the sum of squared difference between the experimental and calculated moisture contents of the samples. For this purpose, the SOLVER tool of Microsoft Excel (Excel from Microsoft Office Professional Plus 2016TM) was used to apply the optimizing method of the Generalized Reduced Gradient. The percentage of explained variance (% VAR) was used to evaluate the fit of the model, following Equation (2).

$$\%VAR = \left[1 - \frac{S_{calc}^2}{S_{ex}^2}\right].100 \tag{2}$$

Where S^2 calc and S^2_{ex} are the calculated and experimental variances, respectively.[5]

2.4. Alcohol insoluble residue (AIR)

In order to evaluate the product’s functional properties, the alcohol insoluble residues (AIR) were obtained according to Garau et al. [16] with some adaptations. For this purpose, 1.5 g of the ground dried sample (5 g in the case of the fresh sample) were placed in an ethanol-water solution (85% v/v) and homogenized with an ultraturrax (mod. T25, dispersion tool S25N-18 G; IKA Labortechnik). After a boiling-cooling cycle, the sample was filtered. These steps were repeated twice with 85 and 96% v/v ethanol-water solutions. The residue contained in the filter was washed with acetone (99% v/v) and kept in a vacuum oven at 60 °C for moisture removal. The AIR was expressed as g AIR/100 g dm.

2.5. Functional properties of AIR

The swelling capacity (SC), water retention capacity (WRC) and fat retention capacity (FRC) were determined for the purposes of addressing the influence of the kind of water removal mechanism (evaporation or sublimation) and ultrasound application during drying on the quality of the dried orange peel. All of the determinations were carried out in triplicate, at least.

2.5.1. Swelling capacity (SC)

The SC was measured according to Daou and Zhang,[17] but adapted to the product. To this end, 0.2 g of AIR were placed in a graduated test tube, 10mL of distilled water were added and the tubes were left to stand for 24 h at room temperature (25 ± 1 °C). The SC was calculated from the difference between the final and initial volumes of the sample and expressed as mL/g of AIR dm.

2.5.2. Water retention capacity (WRC)

The WRC was measured according to Garau et al.[16] For this purpose, the AIR samples (0.2 g) were hydrated in 10 mL of distilled water for 24 h in centrifuge tubes. Afterwards, the samples were centrifuged (Medifriger BL-S, Selecta, Spain) at 10,000 r.p.m. for 15 min at 25 °C. The excess supernatant was decanted and the WRC expressed as g water/g of AIR dm.

2.5.3. Fat retention capacity (FRC)

The AIR samples (0.2 g) were immersed in 10 mL of sunflower oil for 24 h at room temperature (25 ± 1 °C) and then centrifuged (Medifriger BL-S, Selecta, Spain) at 6,000 r.p.m. for 15 min at 25 °C, according to Garau et al.[16] The FRC was expressed as g oil/g of AIR dm.

2.6. Statistical analysis

For the statistical analysis, α, β, AIR, SC, WRC, and FRC were considered as dependent variables and the drying process (AFD or MTD) and the application of ultrasound as factors. The analysis of variance (one way ANOVA) was calculated using Statgraphics Centurion XVI (StatPoint Technologies, Inc), to check the significance ($p<0.05$) of the differences between the values of each dependent variable. The Least Significant Difference (LSD) intervals were also estimated to determine the significance of the differences between treatments. Moreover, the values from the replicates of the different kinds of experiments carried out were averaged and represented as mean and standard deviation.

3. Results and discussion

3.1. Experimental drying kinetics

The initial moisture content of the orange peel was 2.47 ± 0.08 (kg water/kg dm), similar to that found by Tasirin et al.[2] The air drying temperature and ultrasound application influenced the length of the drying process (Figure 1).

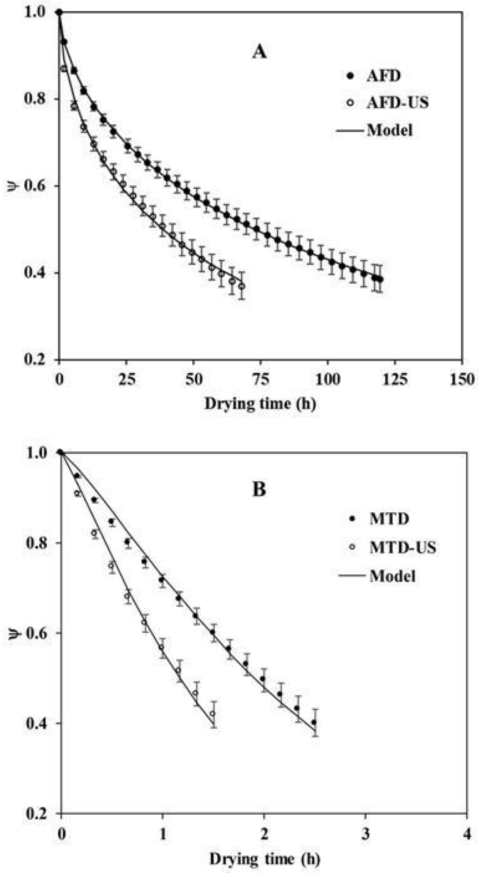

Figure 1. Experimental and calculated evolution of dimensionless moisture during drying of orange peel at: (A) – 10 °C without (AFD) and with ultrasound application (AFD-US); (B) 50 °C without (MTD) and with ultrasound application (MTD-US).

The average time required to reach a moisture content of 0.5 kg of water/kg of dm in the MTD experiment (3.8 ± 0.3 h) was 95% shorter than that needed in the AFD experiment (93 ± 18 h). The increase in the process temperature and the liquid state of water promote a higher heat transfer rate between the heat source, which is the drying air, and the product, leading to faster moisture removal.[18]

During low temperature drying, there is less energy available to promote moisture loss through the sublimation process and transport the moisture from the product to the surface. However, losses in nutritional and technological properties can occur as the drying temperature rises.[10,19] Ultrasound application led to an intensification of the drying process, promoting a significantly shorter drying time in every condition analyzed ($p<0.05$) (Figure 1). Thus, in the AFD-US experiment, the processing time required to reach 0.5 kg of water/kg dm (40 ± 6 h) was 57% shorter than in the AFD (93 ± 18 h). In the case of the MTD experiments, the application of ultrasound meant that by 23% shorter drying time was required to attain the same moisture content (3.0 ± 0.4 h for MTD-US vs. 3.8 ± 0.3 h for MTD). The most significant effect of US application occurred at low temperatures. This can be explained by the fact that the mechanical energy generated by US is constant in every case, and the lower the drying temperature, the higher the proportion that it represents in relation to the total energy available in the drying system. [10,20,21]

The influence of temperature and ultrasound application was also found in the evolution of the drying rate. Thus, as can be observed in Figure 2, the drying kinetics occurred in the falling rate period for every condition considered. As the drying progressed, however, the drying rate fell more quickly in the MTD experiments than in the AFD and in the ultrasonically assisted samples than in the conventional ones (MTD-US and AFD-US compared to MTD and AFD, respectively).

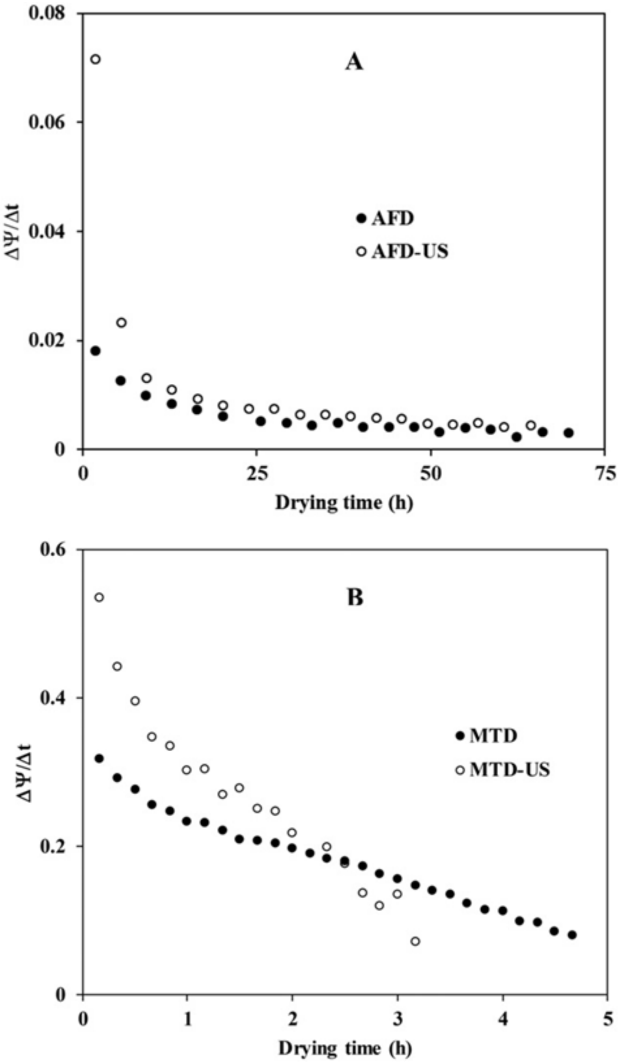

Figure 2. Evolution of drying rate during drying of orange peel at: (A) –10 °C without (AFD) and with ultrasound application (AFD-US); (B) 50 °C without (MTD) and with ultrasound application (MTD-US).

3.2. Modeling

The Weibull model fitted the experimental evolution of the moisture content during drying adequately, as shown by the similar trend of the calculated and experimental drying kinetics (Figure 1) and the values of the percentage of explained variance achieved, over 99% in every case (Table 1).

Table 1. Weibull model parameters (*a* and *b*) identified for the drying of orange peel (Valencia Late var.) at different temperatures, without and with ultrasound (20.50 kW/m^3; 21.9 kHz) application.

Treatment	α	β (s^{-1})	VAR
AFD	0.63 ± 0.02^a	395569 ± 73199^a	99.73
AFD-US	0.60 ± 0.06^a	244711 ± 43912^b	99.64
MTD	1.14 ± 0.08^b	9290 ± 183^c	99.40
MTD-US	1.3 ± 0.2^b	6398 ± 531^d	99.16

AFD (atmospheric freeze-drying; 10 °C); AFD-US (ultrasound assisted atmospheric freeze-drying; 10; 20.5 kW/m^3); MTD (convective drying at moderate temperature; 50 °C); and MTD-US (ultrasound assisted convective drying at moderate temperature; 50 °C; 20.5 kW/m^3). Letters in the same column show homogeneous groups determined by Least Significant Difference ($p < 0.05$) intervals.

The figures identified for the shape factor, a, demonstrated the differences between the MTD and AFD experiments. Thus, in the case of the AFD experiments, α was lower than 1.0, indicating the process was mainly controlled by the internal resistance to mass transfer. At this temperature -10 °C, the moisture movement inside the material is very slow, and the influence of external resistance becomes negligible. On the contrary, the values of α identified in the MTD experiments were over 1.0, indicating the existence of downtimes during the process. Thus, the low air velocity used, 1 m/s, did not reduce the boundary layer thickness enough to compensate for the faster internal moisture transport that took place at 50 °C (MTD experiments) compared to -10 EC (AFD experiments). Therefore, in the MTD conditions tested, both internal and external resistances influenced the moisture removal. The application of ultra- sound did not significantly affect the shape factor, meaning that ultrasound was not observed to exert any significant influence on the relative importance of internal and external resistances. The identified values of the b parameter also demonstrated the big difference between the two drying temperatures tested, being two orders of magnitude larger in the AFD experiments than the MTD ones (Table 1). The reverse relationship between this parameter and the kinetics must be highlighted. These results show that there is big resistance to mass transport in the low temperature process, leading to a long processing time. During AFD, the removal of the moisture in the orange peel took place by sublimation, whereas in MTD this process was by evaporation. This, and the differences in the amount of energy available in the system due to the different drying-air temperatures, may explain the differences in the magnitude.

Ultrasound application also significantly affected the drying velocity in both kinds of drying experiments. Thus, the β parameter identified in ultrasonically-assisted AFD experiments was 38% lower than the one identified in the non-assisted ones. In the case of the

MTD experiments, the reduction was 31%. These results showed that the increase in drying kinetics produced by ultrasound was greater at the lowest drying temperature tested. This coincides with what has been reported by other authors [21,22] and can be explained, as pointed before, by the fact that the mechanical energy supplied by US is constant in every experiment. So, at low temperatures, the proportion of ultrasonic energy in relation to the total energy available is greater than at higher temperatures.[21] Ultrasound can affect external mass transport, by inducing microstirring at interfaces, and internal mass transport, due to the mechanical stress provoked by the compression and expansion acoustic forces. In the latter, it must be taken into account that while ultrasound influences the whole sample in the case of MTD experiments, it only affects the external dried layer in the AFD because no movement of molecules can take place in the frozen core. In any case, the Weibull model does not permit a clear distinction between the ultrasound effects on internal and external resistances.

3.3. Alcohol insoluble residue (AIR)

The average AIR value of the fresh sample (52.89 ± 3.08 g AIR/100 g dm) was similar to that reported by Garau et al.[16] (48.30 g AIR/100 g dm). The small difference observed can be attributed to the different variety of orange (Canoneta vs. Valencia Late variety) and the natural variability of the raw matter. The drying processes considered did not produce changes in the AIR content of the samples. Thus, the AIR values measured in the samples dried under the different conditions were not significantly ($p<0.05$) different from those measured in the fresh samples. In this sense, Garau et al.[16] reported no influence of drying temperature on the AIR of orange peel.

3.4. Functional properties

The functional properties can be correlated with the quality of dietary fiber and the processing, such as drying, can affect both the physical properties of the fiber’s matrix and also the hydration capacity.[23] For that reason, and for the purposes of evaluating the effects caused by the processing on the structure of the cell wall-forming polysaccharides of orange peel samples, the swelling capacity (SC), water retention capacity (WRC) and fat retention capacity (FRC) were measured. Drying produced a marked reduction in the SC of the AIR from orange peel (Figure 3).

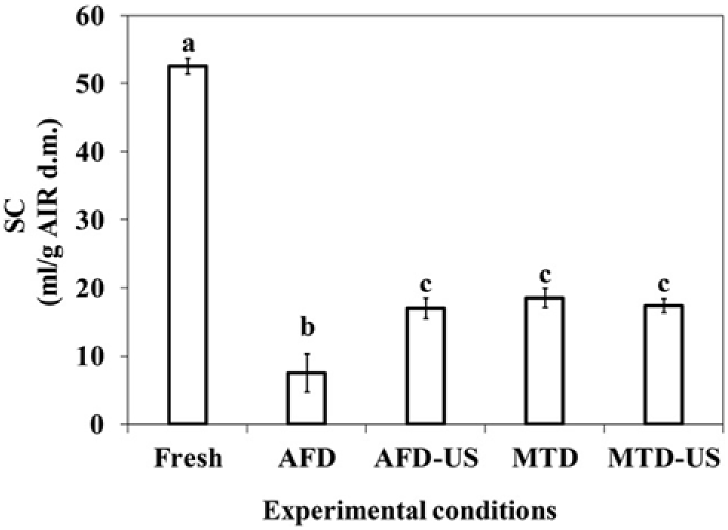

Figure 3. SC – Swelling capacity of AIRs from fresh and dried orange peel. Same letter shows homogeneous groups deter- mined by Least Significant Difference ($p < 0.05$) intervals.

Thus, the SC was by 65% lower in the AIR from the MTD experiments (18.52 ± 1.45 mL/g AIR dm) than in the AIR from the fresh samples (52.53 ± 1.13 mL/g AIR dm). The application of US in these conditions (MTD-US) did not significantly affect the observed SC (17.34 ± 1.01 mL/g AIR dm). The swelling capacity is an important property of fibers and is related with a satiating effect. Therefore, maintaining this characteristic may not only be beneficial for human health but may also lead to improvements in the food industry applications.[24] As for the AIR from the AFD experiments (10.51 ± 5.61 mL/g AIR dm), the SC reduction was significantly greater than that observed in the AIR from the MTD and MTD-US experiments ($p<0.05$). Garcia-Amezquita et al.[25] reported a higher SC in the powder of orange peel obtained by convective drying at 55 °C than in the powder of orange peel obtained by vacuum freeze-drying. The lower values of the SC during the AFD experiments can be attributed to the structural changes caused by the formation of the ice crystals in the food matrix, which leads to a gradual collapse in the tissue organization and cellular destructuration during the long process time needed by this kind of drying. Besides, the effect of ultrasound application in these conditions (AFD-US) produced an AIR with a SC (16.98 ± 1.50 mL/g AIR dm) similar to that observed in the MTD and MTD-US experiments. This can be explained by the fact that the ultrasonic effects are more pronounced in a more rigid and porous matrix, such as that provided by the freezing and sublimation of the orange peel during the atmospheric freeze-drying process. These effects significantly shorten the drying time and this may contribute to the lower degree of degradation of the SC in the AFD-US than in the AFD experiments.

The water retention capacity (WRC) was also analyzed in the AIRs of both fresh and dried orange peel. Thus, the average measured WRC (g of water/g AIR dm) values were 18.12 ± 1.71 for the fresh sample, 18.43 ± 3.70 for the AFD; 16.86 ± 3.01 for the AFD-US, 19.23 ± 1.19 for the MTD and 19.18 ± 1.01 for the MTD-US. The determination of Least Significance Intervals ($p<0.05$) demonstrated that the small differences between treatments were non-significant ($p<0.05$). Abou-Arab et al.[26] reported small differences in the WRC of orange peel powder obtained from solar, convective and microwave drying (no temperature data is provided). Garcia-Amezquita et al.[25] also found small differences in the WCR between hot air dried (55 °C) and vacuum freeze-dried orange peel. These results could indicate that the different drying conditions tested do not significantly affect the WRC, which is of interest, as the processed product is similar to the fresh one. The WRC is an important factor because, according to Nesrine et al.[27] it allows these by-products to be used as functional ingredients by reducing the amount of calories ingested, preventing syneresis in dairy products and modifying the viscosity and texture of others.

The FRC values were affected by the processing (Figure 4), as it has been previously reported by Garau et al.[16].

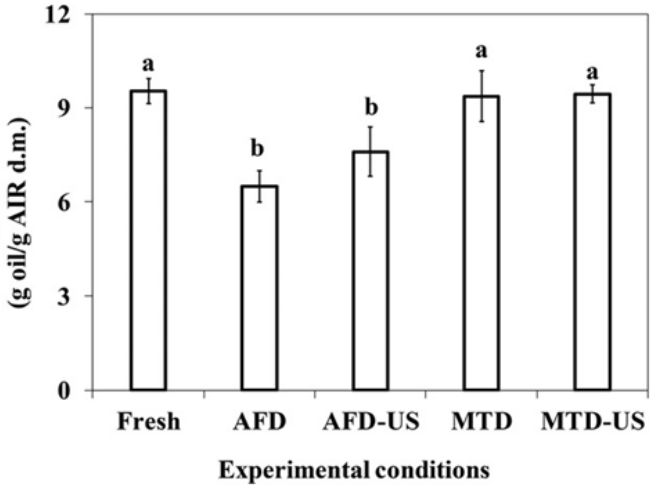

Figure 4. FRC – Fat retention capacity of AIRs from fresh and dried orange peel. Same letter shows homogeneous groups determined by Least Significant Difference ($p<0.05$) intervals.

After drying, the AFD experiments showed a significant 31% reduction in the FRC (6.5 ± 0.5 g of oil/ g AIR dm) compared to the fresh sample (9.5 ± 0.4 g of oil/g AIR dm), while the reduction in the MTD experiments (9.4 ± 0.8 g of oil/g AIR dm) was negligible. The differences between the AFD and MTD experiments were significant ($p<0.05$), indicating a trend toward a better fat retention capacity in the samples processed at higher temperatures. Similar behavior has been found by Garcia-Amezquita et al.[25] after the freeze-drying and convective drying (55 °C) of orange peel. In the same sense, Garau et al.[16] also observed a higher FRC in the orange peel samples dried at 50 °C than in others dried at lower temperatures. The application of power ultrasound promoted an increase by 17% in the FRC value of the AIR from the AFD-US experiments (7.6 ± 0.8 g of oil/g AIR dm) compared to the AFD ones, these differences not being significant ($p<0.05$) probably due to the great variability. The shortening of the atmospheric freeze-drying process produced by ultrasound could limit FRC degradation. On the contrary, the FRC observed in the AIR from the MTD and MTD-US experiments was the same (9.4 ± 0.8 g vs. 9.4 ± 0.3 of oil/g AIR dm, respectively). The results show that convective drying at moderate temperature was more effective than atmospheric freeze-drying as a means of preserving the FRC of the AIR obtained from orange peel. In atmospheric freeze-drying conditions, ultrasound application could contribute to this preservation. This preservation is important for industrial applications because it can promote flavor retention, increase the yield of food products and impart greater stability to the products and emulsions.[27]

4. Conclusions

The process characteristics linked to temperature and ultrasound application significantly influenced both the orange peel drying kinetics and the quality of the alcohol insoluble residue obtained from dried products. The processing time was highly dependent on the mode of moisture removal (sublimation or evaporation) and ultrasound application. Even with the intensification of the process resulting from the application of ultrasound, atmospheric freeze-drying required a very long time to reach the expected final moisture content. The drying conditions tested were found to exert no significant influence on either the alcohol-insoluble residue obtained from dried product or their WRC. On the contrary, atmospheric freeze-drying generated samples with slightly reduced SC and FRC when compared to those obtained with convective drying at 50 °C. Ultrasound application did not significantly affect the fiber quality. Therefore, in the case of orange peel, the AFD did not represent a viable alternative to convective drying at moderate temperatures, neither in terms of drying time nor fiber quality. Moreover, ultrasound application enhanced the drying rate without reducing the functional properties of the fiber. This could be linked to energy saving and consequently to a reduction in process costs. However, this requires further research.

Nomenclature

Acronyms

AFD	Atmospheric freeze-drying
AIR	Alcohol insoluble residues, g AIR/100 g dm
FRC	Fat retention capacity, g oil/g of AIR dm
HTD	High temperature drying
MTD	Convective drying at moderate temperature
PID	Proportional-Integral-Derivative
SC	Swelling capacity, mL water/g of AIR dm
US	Ultrasound
WRC	Water retention capacity, g water/g of AIR dm

Variables

dm	Dry matter
S^2_{calc}	Calculated variance
S^2_{ex}	Experimental variance
t	Time, s
X_{eq}	Moisture content at equilibrium, kg water/kg dm
X_t	Moisture content at time t, kg water/kg dm
X_0	Initial moisture content, kg water/kg dm

Greek Letters

α	Shape factor of Weibull model
β	Kinetics factor of Weibull model, s^{-1}
Ψ	Dimensionless moisture content

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ARTICLE 3 – Article submitted to the Journal Innovative Food Science and Emerging Technologies

PEF AS PRETREATMENT TO ULTRASOUND ASSISTED CONVECTIVE DRYING: INFLUENCE ON QUALITY PARAMETERS OF ORANGE PEEL

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Abstract

The influence of the combined application of pulsed electric fields (PEF) pretreatments and ultrasound (US) during drying in color, total phenolics content, ascorbic acid and antioxidant activity of orange peel was studied. For this fact, a series of drying experiments (50 °C) were performed without and with ultrasound application (20.5kW/m^3) and with and without PEF pretreatments (1.20 kV/cm) at two different times (200 µs and 600 µs). Thus, while ultrasound significantly shortened drying time, PEF pretreatments slightly extended the process. The color of dried samples was not affected by the shorter PEF pretreatment tested, while the longer one reduced the b*and chroma values. PEF and US application significantly increased the percentage of retention of phenolic compounds. In addition, all treatments with PEF showed similar percentage of ascorbic acid retention, and only the longer pretreatment tested (600 µs) produced a reduction of the antioxidant activity retention. Ultrasound did not significant affect ascorbic acid content or antioxidant activity. Therefore, the combined use of PEF pretreatment and ultrasound application during drying of orange peel can result an interesting way for both shortening of drying and preserving important compounds.

Keywords: By-products; process intensification; color; antioxidant properties.

1. Introduction

The need for healthy, easy preparation and practical consumption foodstuffs appears as one of the current priorities of the world's population. In this sense, the health benefits of fruit and vegetable consumption have been well established. Orange is a fruit produced and consumed worldwide for having appreciated flavor and a variety of nutrient. The main industrial processing of orange involves the juice production. This activity generates a massive amount of residues being orange peel one of the mayor components. This by-product is a rich source of vitamin C, phenolic compounds and dietary fiber (Slama & Combarnous, 2011; Luengo, Álvarez, & Raso, 2013; Adiamo, Ghafoor, Al-Juhaimi, Babiker, & Mohamed Ahmed, 2018; Garcia-Amezquita, Tejada-Ortigoza, Campanella, & Welti-Chanes, 2018). However, as many biological products, orange peel has a high moisture content, making it adequate for the microbial and enzymatic degradation reactions. Therefore, there is a need for the application of conservation techniques which provide the stability of the product (Bejar, Kechaou, & Mihoubi, 2011; Onwude, Hashim, Abdan, Chen, & Oladejo, 2017) allowing a later valorization processing.

One of the most applied conservation techniques is hot-air convective drying (HAD), mainly due to its user-friendliness (Valadez-Carmona et al., 2017). This technique promotes the removal of the moisture by creating a vapour pressure gradient between the product and the drying air. The energy needed by the process is provided by the high temperature of air. Thus, a stable product with reduced weight and volume is obtained (Pérez-Won et al., 2016). However, hot air drying (HAD) can promote changes in the material structure, color alterations, oxidation reactions, shrinkage or nutritional and functional quality degradation linked to the long exposition time to high temperatures, which involves also a high energy consumption (Santacatalina et al., 2014; Pérez-Won et al., 2016; Corrêa, Rasia, Mulet, & Cárcel, 2017; Vallespir, Rodríguez, Cárcel, & Simal, 2019). Therefore, there is a great interest in the development and application of techniques that can help to minimize the decresase of quality and the energy costs. Some of the thechniques tested includes the application of microwave, osmotic dehydration, power ultrasound or pulsed electric fields (Rojas & Augusto, 2018; Ambros, Mayer, Schumann, & Kulozik, 2018; Martins, Cortés, Eim, Mulet, & Carcel, 2018; Mello Jr, Corrêa, Lopes, de Souza, & da Silva, 2019).

Pulsed electric field (PEF) is a non-thermal technique that involves the application of short and repeated high voltage pulses to biological product. This can promote changes in the electrical conformation of the cell membrane, inducing the generation of pores, phenomenon known as electroporation. These pores can make easy the mass transfer and the exit of inner components of cell which can enhance operations such as extraction or drying (Traffano-Schiffo et al., 2017; Risvi, Lyng, Frontuto, Marra, & Cinquanta, 2018). Thus, the use of PEF as pretreatment has been previously tested in the drying of blueberries, parsnip or carrot and the results showed that PEF application can contribute to the shortening of drying time (Yu, Jin, & Xiao, 2017; Risvy, Lying, Frontuto, Marra, & Cinquanta, 2018). However, the effect of PEF application depends of the conditions considered. Thus, Toepfl, Siemer, Saldana-Navarro, & Heinz (2014) found a reduction in the drying rate of radish when increasing the number of pulses applied. Regarding the quality of products, some authors have found a reduction of nutritional quality (Toepfl, Siemer, Saldana-Navarro, & Heinz, 2014; Yu, Jin, & Xiao, 2017) and other (Soliva-Fortuny, Balasa, Knorr, & Martín-Belloso, 2009) reported the reduction of product damage of when comparing with other techniques.

The use of high intensity ultrasound (US) has been widely studied in order to intensify the drying process and preserve the characteristics of dried products (Santacatalina et al., 2014; Clemente, Sanjuán, Cárcel, & Mulet, 2014; Santacatalina, Contreras, Simal, & Cárcel, 2016; Corrêa, Rasia, Mulet, & Cárcel, 2017; Cárcel, Castillo, Simal, & Mulet, 2018). The effects induced by US application can contribute to the decreasing of internal (sponge effect) and external (microstreaming at interfaces) resistance to mass transport (Cárcel, Castillo, Simal, & Mulet, 2018; Martins, Cortés, Eim, Mulet, & Cárcel, 2018). However, US can also affect the quality of dried food (Rodríguez et al., 2018) depending this influence of the drying conditions used as reported, namely during drying of passion fruit peel (Nascimento, Mulet, Ascheri, Wanderlei, & Cárcel, 2016) or green pepper (Szadzinska, Łechtanska, Kowalski, & Stasiak, 2017).

The aim of this study was to assess the influence of the combined use of PEF as pretreatment and the application of ultrasound during drying in some quality parameters of orange peel.

2. Material and methods

2.1. Raw material

Valencia Late var. orange fruits (*Citrus sinensis, Valencia Late var.*) used in this study were purchased in a local market (Valencia, Spain). The fruits were selected to be homogenous according to their size and color. Oranges were washed and superficially dried with the aid of absorbent paper. Then, rectangular shaped samples (48 ± 1 x 26 ± 1 x 3.18 ± 0.04 mm) of orange peel were extracted with the assistance of sharp knives. The moisture content was measured in triplicate by measuring the weight difference after maintain peel samples at 60 ºC in a vacuum oven until constant weight (AOAC, 1997).

2.2. Pulsed electric field (PEF) treatment

The PEF pretreatments were carried out in a laboratory scale system, with a maximum positive pulse voltage range up to 10 kV (EPULSUS-PM1-10, Energy Pulse System, Lisbon, Portugal). The generated pulses were applied to the samples in a chamber containing electrodes (distance between electrodes of 8.2 cm). For each experiment, the sample holder containing the peel samples was filled with tap water (sample/water ratio of 1:4.7 g/mL) as electricity driven medium. In this study, two PEF treatments were considered regarding the number of pulses, 8 and 24 pulses, of 25 µs each, which means a total treatment time of 200 and 600 µs (PEF 200 µs and PEF 600 µs), respectively. A frequency of 10 Hz and an electrical field strength (E) of 1.20 kV/cm (Eq. 1), calculated according to Won, Min & Lee (2015) complete the electrical parameters fixed for these treatments.

$$E = \frac{U}{d} \tag{1}$$

where E is the electrical field strength (kV/cm), U is the output voltage (V) and d is the distance between electrodes (cm). After each treatment, the samples were removed from the treatment chamber and superficially dried with absorbent paper before drying experiments.

2.3. Hot air drying (HAD) experiments

HAD experiments were performed in an ultrasonically assisted convective dryer (Garcia-Perez, Ortuño, Puig, Carcel & Perez-Munuera (2012); Santacatalina et al., 2015). In this system, the drying chamber is constituted by an air bone ultrasonic device, specifically, an aluminum-vibrating cylinder (internal diameter 100 mm, height 310 mm, thickness 10 mm) attached to a piezoelectric transducer (21.9 kHz) which is able to generate an internal high intensity ultrasonic field. Drying is conducted automatically with the control of temperature and air velocity, and a scale coupled which permit the weighing of the samples at preset time. Every drying experiments were performed at 50±1 °C and 1 m/s and they were extended until the samples lost 60±1% of the initial weight. Different conditions were tested by combining PEF pretreatment (200 µs and 600 µs) with the drying without and with (20.5 kW/m) US application. Moreover, conventional hot air drying experiments (HAD) were carried out as reference (Table 1) Each experimental combination was performed at least in triplicate.

Table 1. Conditions tested in drying experiments

Experiment code	PEF pretreatment time (µs)	US application during drying (20.5 kW/m^3)
HAD	0	No
HAD-US	0	Yes
HAD-200 µs	200	No
HAD-US-200 µs	200	Yes
HAD-600 µs	600	No
HAD-US-600 µs	600	Yes

2.4. Quality parameters

2.4.1. Color

The color of dried orange peel samples was determined by measuring the CIELAB spectrum color parameters L^* (lightness/darkness), a^* (redness/greenness) and b^* (yellowness/blueness) using a colorimeter (CM-2500d model, Konica Minolta, Japan) provided with a D65 illuminant reference system and a 10° opening angle. It was considered the excluded specular component (SCE). The chroma value (C^*), as measurement of color saturation, was obtained from Eq. (2) (Wiktor et al., (2016).

$$C^* = \sqrt{(a^{*2} + b^{*2})} \tag{2}$$

2.4.2. Antioxidant properties

The measurements of the antioxidant properties (TPC, AA, and AC) of fresh and dried orange peel were carried out in an ethanolic extract. For that purpose 1g of crushed in a domestic grinder orange peel powder (particle size smaller than 200 µm) was introduced into 20 mL of ethanol (96% v/v) and homogenized with an ultraturrax for 1 min at 13000 r.p.m. Then, the mix was filtered and stored at 4 ± 0.5 ºC, protected from light, until analysis.

2.4.2.1 Total phenolics content (TPC)

The TPC was determined through the Folin-Ciocalteu method (Singleton, Orthofer, & Lamuela-Raventós, 1999). For this, 100 µL of the ethanolic extract of samples were mixed with 200 mL of Folin-Ciocalteu’s phenol reagent (Sigma-Aldrich, Madrid, Spain) and 2 mL of distilled water. After 3 min at 25 °C, 1 mL of Na_2CO_3 (Panreac, Barcelona, Spain) solution (Na_2CO_3-water 20:80, w/v) was added and the mixture was kept in the dark at room temperature for 1 h. Finally, the absorbance was read at 765 nm using a spectrophotometer (Helios Gamma, Thermo Spectronic, Combridge, UK). A standard curve was previously prepared using solutions of a known concentration of gallic acid hydrate (Sigma-Aldrich, Madrid, Spain) in distilled water. Results were expressed as mg of gallic acid (GAE) per g of dry matter of orange peel samples. The measurements were performed in triplicate for each condition tested.

2.4.2.2 Ascorbic acid content (AA)

The AA was measured according to Jagota & Dani (1982). For this, it was mixed 0.5 mL of the ethanolic extract of sample with 0.5 mL of a trichloroacetic acid solution (7.5%). After 5 min at 4 °C, the mix was filtered. Subsequently, 0.2 mL of extract, 2 mL of distilled water and 0.2 mL of diluted solution (1:10 v/v) were blended and maintained for 10 min at room temperature. After that, absorbance was measured at 760 nm in a spectrophotometer (Helios Gamma, Thermo Spectronic, Combridge, UK). The procedure also was performed in triplicate for each condition considered. The concentration of vitamin C was obtained from a calibration curve made up of solutions of known ascorbic acid concentration.

2.4.2.3 Antioxidant capacity (AC)

The AC was determined by using the Ferric-Reducing Ability Power (FRAP) method, which was described by Benzie & Strain (1996). In a spectrophotometer cuvette, 30 µL of distilled water, 30 µL of ethanolic extract of sample and 900 µL of FRAP was mixed in this order. The FRAP reagent was prepared by adding 2.5 mL of 10 mM TPTZ (Fluka, Steinheim, Germany) in a 40 mM HCl (Panreac, Barcelona, Spain) solution plus 2.5 mL of 20 mM $FeCl_3.6H_2O$ (Panreac, Barcelona, Spain) and 2.5 mL of 0.3 M acetate buffer (Panreac, Barcelona, Spain), pH 3.6. For the AC determination, it was used 30 mL of each sample completed with 30 mL of distilled water and 900 mL of FRAP reagent and kept at 37 °C for 30 min. Using a spectrophotometer (Helios Gamma, Thermo Spectronic, Cambridge, UK) the absorbance was read at 595 nm. A calibration curve was previously obtained using ethanol solutions of known Trolox (SigmaeAldrich, Madrid, Spain). The procedure was performed in triplicate and concentrations were described as millimole Trolox equivalent per gram of dry mass of orange peel.

2.5. Statistical analysis

For the statistical analysis, color parameters, TPC, AA and AC were considered as process dependent variables, and PEF pretreatments and US application as factors. The analysis of variance was calculated using Statgraphics Centurion XVI (StatPoint Technologies, Inc) to check the significance ($p<0.05$) of the differences between the values of each dependent variable. The Least Significant Difference (LSD) intervals were also estimated to determine the significance of the differences between treatments. Additionally, the values from the replicates of the different kinds of experiments carried out were averaged and represented as mean and standard deviation.

3. Results and discussion

3.1. Drying experiments

The initial moisture content of orange peel was 2.70 ± 0.31 kg water/kg dry matter being this value similar to that reported in the literature (Angoy et al., 2020). The application of PEF as a pretreatment not only did not shorten drying process but extend it (Table 2).

Table 2. Time needed to achieve moisture content of 0.6 kg water/kg dry matter when orange peel dried at different conditions; average values and standard deviation are shown for drying time.

Treatment	Drying time (h)
HAD	3.50 ± 0.29^{a}
HAD-US	2.61 ± 0.48^{b}
HAD-200 µs	4.36 ± 0.17^{c}
HAD-US-200 µs	2.36 ± 0.34^{b}
HAD-600 µs	4.25 ± 0.12^{c}
HAD-US-600 µs	3.22 ± 0.19^{ab}

HAD (hot air drying; 50 °C); HAD-US (ultrasound assisted at hot air dying; 50 °C, 20.5 kW/m^3); HAD-200 µs (hot air drying; 50 °C, PEF pretreatment time); HAD-US-200 µs (ultrasound assisted at hot air dying; 50 °C, 20.5 kW/m^3, PEF pretreatment time); HAD-600 µs (hot air drying; 50 °C, PEF pretreatment time); HAD-US-600 µs (ultrasound assisted at hot air dying; 50 °C, 20.5 kW/m^3, PEF pretreatment time). Letters in the same column show homogeneous groups determined by Least Significant Difference ($p<0.05$) intervals

Thus, the time needed to reach a moisture content of 0.6 kg water/kg dry matter in HAD experiments was 19 and 17% shorter than in HAD-200 µs and HAD-600 µs, respectively. Orange peel presents a porous structure where the moisture movement is easier than in other more compact materials. The longer drying process in PEF pretreated samples could be related with a possible collapse generated by a likely excessively intense electric treatment, which can make difficult the inner moisture transport. A similar effect was observed by Liu et al. (2016) during drying of radish. However, the opposite results can be found in the literature, namely a shortening of drying time when PEF was applied as pretreatment to the drying processes of apple (Wiktor et al., 2013) or red pepper (Won, Min, & Lee, 2015). These different results among studies can be related not only with the characteristics of each product studied but also with the operational conditions of the PEF treatment.

The application of ultrasound in the drying process of orange peel samples accelerated the drying process in all conditions tested (Table 2). The time required to reach a moisture content of 0.6 kg water/kg dry matter was 25% lower in HAD-US experiments compared to HAD ones. Similar behavior has been previously reported in the literature for the ultrasonically assisted drying of various fruits and vegetables. Thus, Nascimento et al. (2016) found 49% drying time reduction for passion fruit drying (50 °C, 1 m/s) when ultrasound was applied (30.8 kW/m^3). Rojas, Augusto, & Cárcel (2020) reported 41% reduction in the case of apple drying (50 °C, 1 m/s and 20.5 kW/m^3) and Ortuño et al. (2010) observed a 45 % decrease of drying time for orange peel (40 °C, 1 m/s and 37 kW/m^3) of Navel variety.

The effects on drying time of the combined application of PEF pretreatment and ultrasonically assisted drying depended of the PEF pretreatment applied. Thus, compared with the HAD experiments, HAD-US-600 µs meant only a 8% drying time shortening while in the case of HAD-US-200 µs this reduction reach to 33% (Table 2). The effectiveness of ultrasound on drying rate is related with product structure properties such as porosity (Ozuna, Álvarez-Arenas, Riera, Cárcel, & Garcia-Perez, 2014). As PEF pretreatment can affect internal structure, it could influence on the magnitude of ultrasound effects. In this sense, the lesser intense PEF treatment of HAD-US-200 µs experiments (only 8 pulses of 1.2 kV/cm) could enhance the ultrasound effects. On the contrary, the more intense PEF treatment applied in HAD-US-600 µs (24 pulses) could partially degrade the inner structure making difficult not only the effects of ultrasound but even the drying itself.

3.2. Quality parameters

3.2.1. Color

Color is a very important parameter in the sensory evaluation of dried fruits and vegetables. Therefore, the understanding of the influence of drying processes and the pretreatments on possible changes in the color of products is essential. Thus, the final color parameters of the orange peel samples were measured to determine the influence of process variables studied, PEF pretreatments and US application during drying. The results obtained showed the use of PEF pretreatments had no significant influence on the values of L^* and a^* (Table 3).

Table 3. CIELAB color parameters (L^*, a^* and b^*) and chroma (C^*) of orange peel dried at 50 °C without (HAD) or with (20.5 kW/m^3) ultrasound (US) application and PEF (200 µs and 600 µs) pretreatment

Treatment	L^*	a^*	b^*	C^*
HAD	62.32 ± 0.63^a	27.30 ± 0.97^a	33.53 ± 0.68^a	43.24 ± 0.82^a
HAD-US	45.61 ± 2.34^b	11.88 ± 4.60^b	9.20 ± 3.87^b	34.90 ± 1.33^b
HAD-200 µs	62.28 ± 1.43^a	27.61 ± 1.05^a	33.96 ± 2.05^a	43.78 ± 2.00^a
HAD-US-200 µs	61.98 ± 1.45^a	27.50 ± 0.90^a	31.45 ± 1.66^a	41.80 ± 1.35^{ac}
HAD-600 µs	60.61 ± 1.50^a	27.28 ± 1.29^a	28.17 ± 2.07^c	39.22 ± 2.26^c
HAD-US-600 µs	60.98 ± 2.18^a	26.39 ± 0.80^a	30.21 ± 1.44^c	40.12 ± 1.16^c

Same letters in each column show homogeneous groups determined by least significant difference intervals ($p<0.05$).

Similarly, Wiktor et al. (2016) did not found changes on lightness of PEF treated carrot samples. On the contrary, they observed changes in a^* parameter, probably linked with electroporation. Furthermore, Rizvi et al., (2018) observed that the effect of the pre-treatment promoted reductions in the value of L^* in carrots and the increase of the a^* figure in parsnips. Regarding b^* and chroma (C^*), only in the more intense PEF treatment tested, HAD-US-600 µs, it was observed a decrease compared to the values obtained for HAD samples. Wiktor et al. (2016) also reported that the increase in the intensity of PEF treatments promoted decreases in the b^* and C^*. Rahaman et al. (2019), during the study of the influence of PEF on pumpkin samples, also observed that the PEF pretreatment developed changes in b^* and C^* parameters . This variability of results obtained in several studies on the application of PEF can be a consequence of several reasons, including differences in equipment, process conditions, application of different pretreatments and even the intrinsic characteristics of each product (Raso et al., 2016).

The ultrasound application during drying induced changes in all the analyzed color parameters ($p<0.05$). Thus, the L^*, a^*, b^* and C^* figures obtained in HAD-US experiments were significant lower than those of HAD ones (Table 3). Martins et al. (2018), studying the drying of apple peel in similar conditions of temperature and ultrasound power applied, does not observed differences in L^* and b^* figures of ultrasonically and non-ultrasonically assisted dried samples but a significant increase of a^* and C^* with the application of ultrasound. Nowacka & Wedzik (2016) identified several effects with the application of ultrasound during the drying process of carrot slices, and in all cases studied they reported a reduction in L^* and an increase in b^* by ultrasound applications.

Regarding the color parameters of experiments carried out with the combination of PEF and US application, the values obtained were similar ($p<0.05$) than those obtained in HAD experiments. Only, a small, but significant ($p<0.05$), decrease of b^* and C^* where found in the HAD-US-600 μs, which was similar than the observed in HAD-600 μs samples. Therefore, the PEF pretreatment seemed to reduce the effect of ultrasound application on color parameters.

3.2.2. Antioxidant properties

3.2.2.1. Total phenolic content (TPC)

The TPC of fresh orange peel was 0.30±0.03 mg GAE/g dry matter. This content was similar to that reported by Teixeira et al. (2020), 0.31±0.06 mg GAE/g dry matter, and higher than those found by Montero-Calderon, Cortex, Zulueta, Frigola, & Esteve (2019), 0.16±0.06 mg GAE/g dry matter. In addition, Park, Lee & Park (2014) reported a range of TPC for orange peel from 1.39 to 1.85 mg GAE/g dry matter. Drying affected TPC reducing its value in every condition tested. The lower capacity of TPC retention, 27%, was observed in the HAD experiments, as shown in Figure 1. As Wiktor et al. (2019) reported, this result can be attributed to the longer drying time of these experiments which means also a longer thermal treatment.

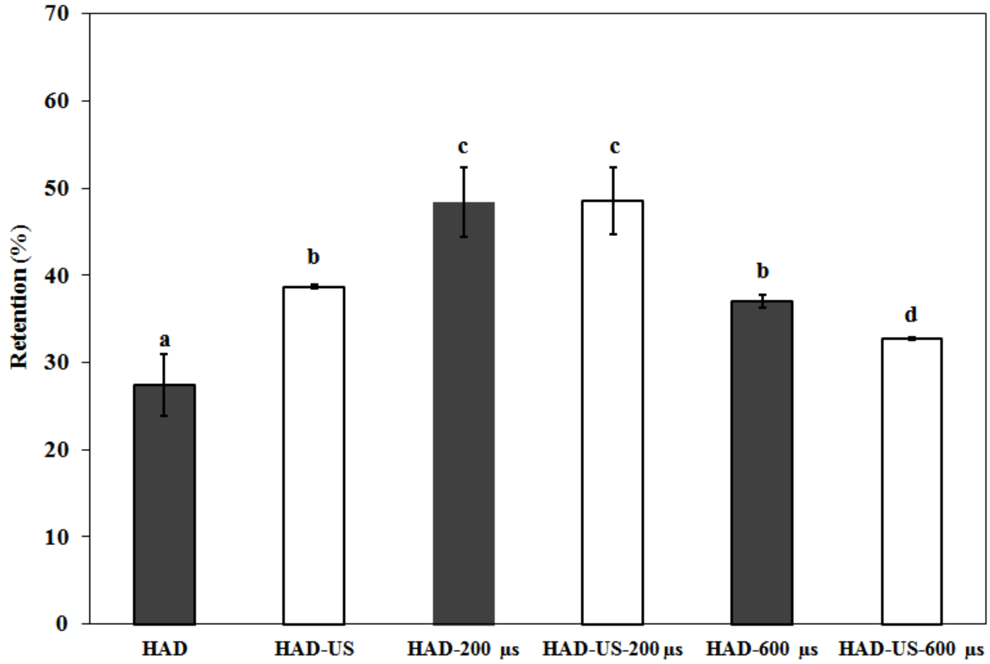

Figure 1. Retention of the total phenolic content (TPC) of orange peel after drying at 50 °C without and with (US) ultrasound (20.5 kW/m^3) application and PEF pretreatment (200 and 600 µs). Mean values and standard deviation are shown. Different letter indicates different least significant difference intervals ($p<0.05$).

The effect of PEF pretreatment on the percentage of TPC retention was positive, obtaining significantly ($p<0.05$) greater retention than HAD experiments, specifically 48 and 37% in the HAD-200 µs and HAD-600 µs experiments. As can be observed in Figure 1, the more intense PEF pretreatment applied in HAD-600 µs experiments provided a significant smaller TPC than those found in HAD-200 µs. This fact can indicate the existence of an optimum PEF pretreatment, which could provide the maximum TPC retention. An increase or decrease in this optimum intensity could reduce the TPC obtained. In addition, the optimum intensity that provide the higher retention of phenolic compounds may be specific for each type of food matrix, as noted by Kim, Kwon, & Lee (2019), in which work with panax ginseng, reported that higher intensities of PEF tested promoted greater retention of phenolic compounds.

The application of ultrasound during drying (HAD-US) significantly ($p<0.05$) increased the TPC retention compared with HAD experiments (38% vs 27%, respectively). Similar positive effect of ultrasound application on TPC was reported by Nascimento et al. (2016) during the ultrasonically assisted drying (30.8 kW/m^3) of passion fruit peel at moderate temperature (50 °C).

The TPC retention obtained when combining PEF and US was similar than the same experiments carried out without US application. Thus, the HAD-US-200 µs experiments promoted 48% retention of phenolic compounds (vs 48% of HAD-200 µs) and 33% in the case of HAD-US-600 µs (vs 37% of AD-600 µs), being both values significantly different from the HAD experiment ($p <0.05$) (Figure 1). This fact indicates that, in the case of TPC, the effects both techniques can be complementary. PEF pretreatment contribute to a better TPC preservation and US contribute to a significantly increase of drying rate.

3.2.2.2. Ascorbic acid (AA)

Ascorbic acid is a compound of high nutritional relevance, which is highly sensitive to thermal processes. This is the main reason because it is used as indicator of thermal treatment damage. The ascorbic acid content of fresh orange peel samples was 0.25 ± 0.01 mg ascorbic acid/g dry matter being this value in the range of those found in the literature. Thus, Tasirin et al. (2014) reported a content of 0.50 ± 0.02 mg ascorbic acid/g dry matter and Hernández-Carranza et al. (2016) observed values between 0.18 to 1.02 mg ascorbic acid/g dry matter according to the extraction parameters used. Regarding the application of PEF pretreatments, HAD-200 µs and HAD-600 µs experiments showed 47 and 48% retention, being this figures, although significantly lower ($p <0.05$), quite similar than the measured in HAD experiment (51% retention) (Figure 2). These results are similar than those reported by Wiktor et al. (2019) during PEF pretreated (5.5 kV/cm and 10 exponential decay pulses) cranberries dehydration but greater than that reported by Yu, Jin, & Xiao (2017) in blueberries processing (2kV/cm and 200 pulses/second). Wiktor et al. (2019) suggests that PEF can result in activation or inactivation of enzymes and other bioactive compounds, depending on the food matrix, and the pretreatment parameters.

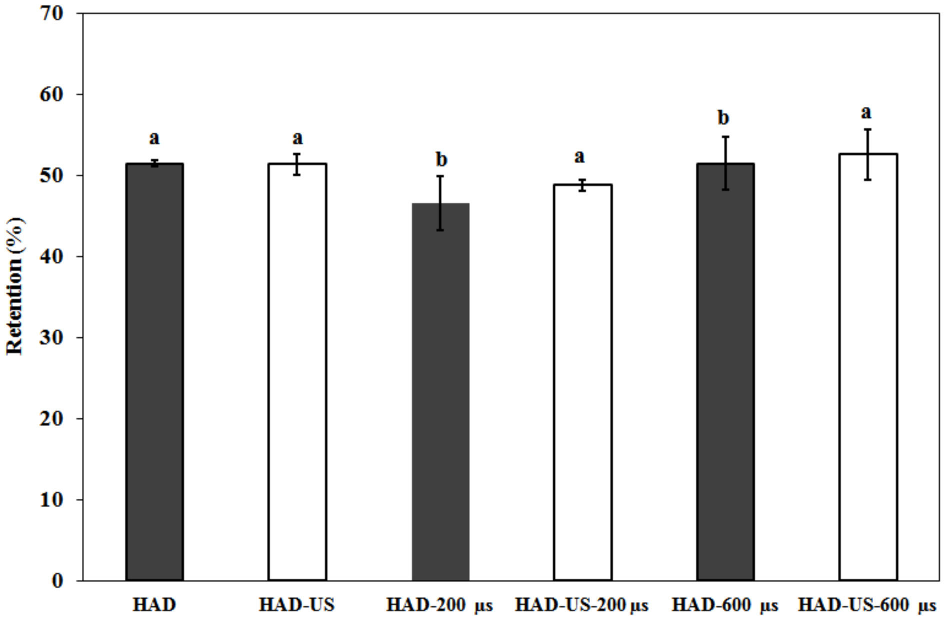

Figure 2. Retention of the total ascorbic acid (AA) of orange peel after drying at 50 °C without and with (US) ultrasound (20.5 kW/m^3) application and PEF pretreatment (200 and 600 µs). Mean values and standard deviation are shown. Different letter indicates different least significant difference intervals ($p<0.05$).

The application of ultrasound during drying process did not directly affect AA retention percentage in the samples under study being this (51% in HAD-US) not significantly different ($p<0.05$) than those obtained in HAD experiments. Martins et al. (2018) reported that the application of ultrasound during the drying of apple peel did not affect the retention of ascorbic acid during drying at low and moderate temperatures (-10, 30 and 50 °C). The combined application of US and PEF not significantly affected the AA retention.

3.2.2.3. Antioxidant capacity (AC)

The antioxidant capacity of the samples under study was 7.40 ± 0.15 mg Trolox/g dry matter. This result was slightly greater than that reported by Hernández-Carranza et al. (2016) who found AC orange peel in the range of 5.01 - 6.03 mg Trolox/g dry matter. The PEF application did not influence the retention percentage of AC in HAD-200 µs experiments compared to HAD ones (Figure 3).

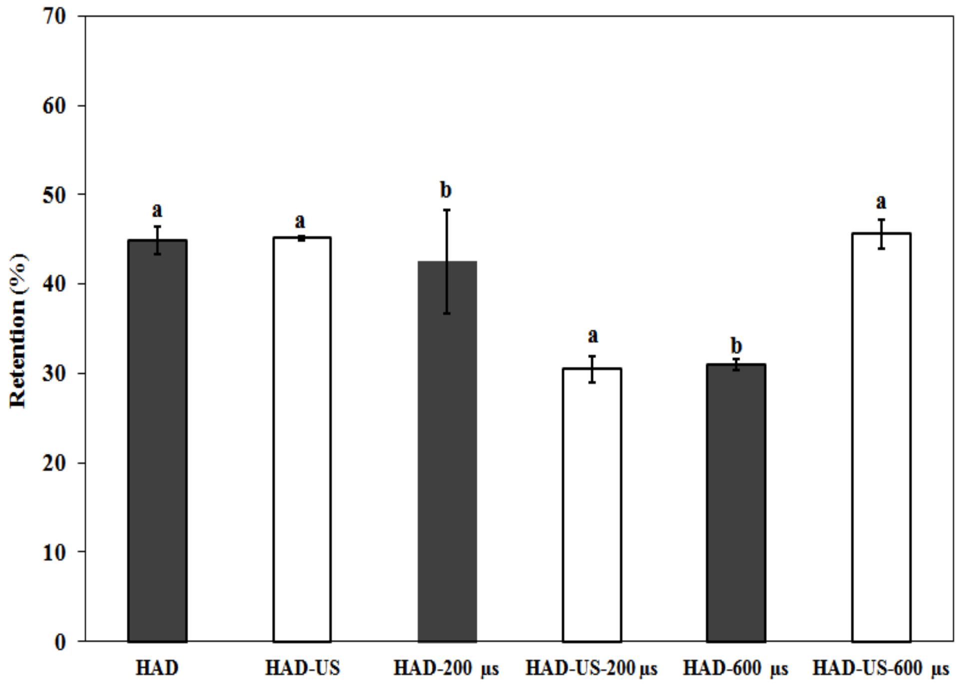

Figure 3. Retention of the antioxidant capacity (AC) of orange peel after drying at 50 °C without and with (US) ultrasound (20.5 kW/m^3) application and PEF pretreatment (200 and 600 µs). Mean values and standard deviation are shown. Different letter indicates different least significant difference intervals ($p<0.05$).

However, the experiments carried out with the more intense pretreatment, HAD-600 µs, showed lower ($p <0.05$) AC retention (31%) than of HAD experiments (45%) (Figure 3). Yu, Jin, & Xiao (2017) studying the blueberries drying at 45 and 60 °C, found that the PEF (2kV/cm and 96 ms of total time process) pretreatment reduced the values of AC compared to the un-pretreated samples. Similarly, Wiktor et al. (2015) found that, in general, the application of PEF reduced the antioxidant capacity of apples. The decrease in antioxidant activity may be related to cell leakage that occurs during pretreatment, which promotes greater exposure of the bioactive compounds to the drying process, thus leading to greater degradation (Lammerskitten et al., 2019)

No influence of ultrasound application during drying was observed in the antioxidant capacity of the orange peels. Thus, both HAD and HAD-US experiments showed the same AC retention figure, 45% (Figure 3). Martins et al. (2018) also found no significant difference of ultrasound application (20.5 kW/m^3) during the drying of apple peel at -10, 30, 50 and 70 ° C and under similar conditions of ultrasonic power. The combination of PEF and US showed lower AC retentions compared to experiments without US (45% in HAD-200µs vs 37% in HAD-US-200µs; 31% in HAD-600µs vs 25% in HAD-US-600µs), being both values of HAD-US-200µs and HAD-600µs significantly different from the HAD experiment ($p<0.05$).

Therefore, in relation to the AC, these data indicate that the PEF contributes to better preservation and the US plays an important role in reducing the drying time, being complementary techniques for the dehydration process of orange peels.

4. Conclusions

Ultrasound application shortened the convective drying of orange peel. The PEF pretreatment did not reduce drying time but increased. PEF pretreatment did not significantly affected the color of samples and only a slightly reduction in *b** and *C** values were found in the more intense PEF treatment tested (PEF 600 µs). On the contrary, all color parameters values were reduced by ultrasound application. The application of PEF and US promoted higher retention of total phenolic compounds while no important effect was found in the ascorbic acid content compared to a conventional drying process. As for the antioxidant activity retention, no significant influence was found at the lesser intense PEF treatment tested (HAD-200 µs), but a reduction in the higher one (HAD-600 µs). This result seems to indicate the existence of an optimum PEF intensity pretreatment, which can enhance not only ultrasonic drying but also the quality of dried product. Therefore, the combined use of both technologies to the conventional food drying process is feasible in obtaining dried products with lesser impact on quality.

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ARTICLE 4 – Article to be submitted in the Journal Food Engineering

Effect of Pulsed Electric Field and Ultrasonically Assisted Convective Drying on Kinetics of Orange Peel

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Abstract

The effective diffusivity can be increased in air drying of vegetables and fruits by applying an pretreatments such as ultrasound an pulsed electric field during air-drying. This work has examined the influence of the combination of both techniques on the dehydration of orange peel (*Citrus sinensis*). Tests were carried out drying orange peel using conventional air – drying (50 °C and 1 m/s), ultrasound-assisted (20.5 kW/m^3; 21.7 kHz) and pulsed electric field as pretreatment (PEF-200 µs and PEF-600 µs). The drying kinetics was modeled considering that the samples assumed an infinite slab behavior, with unidirectional moisture flow. The results showed that the effects of ultrasonic promoted reduce air drying time (36% compared to control experiments). The same result was not observed with the application of PEF. However, the combined effect of PEF and US promoted significant reductions in the process time compared to the control experiment (20% - PEF-US-600 µs and 28% - PEF-US-200 µs). The application of US promoted a 2.0, PEF-US-200, 1.7 and PEF-US-600, 1.4 times bigger in the D_e compared to control.

Keywords: By-products; Drying; Pretreatments; Ultrasound; Process intensification.

1. Introduction

Orange is one of the mainly cultivated fruits in the world and the most of the fruits are used in the juice industry, generating a large amount of waste that can be used by-product, as for example the peel orange (Razzaghi et al., 2019). The consumption of these by-products brings advantages to the human diet, as they are a nutrients source such as fibers, vitamins and phenolic compounds (Rafiq et al., 2018; Razzaghi et al., 2019). However, the vegetables have a high moisture content which makes them susceptible to deterioration reaction, causing post-harvest losses.

For many decades the hot air drying technique has been recognized as the conventional method of dehydration food as it increase the shelf life of products, reduces costs packaging, store and transport. However, despite being widely used, convective drying is an industrial operation involving high energy consumption (Gamboa-Santos et al., 2014). During the drying process the heat and mass transfer occurs, with diffusion as the dominant factor that controls the transfer of moisture from the interior of the product to the external surface, this water being transferred to the environment through the air flow (Beigi, 2016).

In order to predict the behavior of solids drying and to optimize process parameters, mathematical model are applied. The main models that describe the drying behavior of organic materials are theoretical, semi-theoretical and empirical. The semi-theoretical models are based on theoretical principles and are easily of application for describes the drying food process. Theses mathematical models are generally derived from Fick’s second law with some adaptations (Torki-Harchegani et al., 2016; Beigi, 2016).

The hot air drying brings some disadvantages as change in the structure and degradation of bioactive compounds present in the food can be related to high exposure time of the product to high temperatures. Therefore, to minimize such degradations and reduce the time process and energy consumption several pretreatment may be used. One of the possible techniques applied as pretreatment to drying is the pulsed electric fields (PEF), with consists of the application of an external electric field generating damages to the structure of the cell membrane, being this effect knows as electro-permeabilization that has the ability to increase mass transfer rates during the dehydration process (Barba et al., 2015; Ostermeier et al., 2018). Many studies are being carried out in this context (Ade-Omowaye et al., 2002; Liu et al., 2016; Yu et al., 2017; Ostermeier et al., 2018).

Also, in order to optimize the drying processes, high intensity ultrasound can be applied simultaneously to the drying techniques. The application of ultrasound (US) can promoted on reduction on the time drying until 50% (Magalhães et al., 2017) because it causes mechanical stress in the tissues and produces micro stirring at the solid-gas interfaces affecting the transport of moisture (Nascimento et al., 2016). However, the effects of ultrasound depend on the structural characteristics of each product, as well as on the variables of the drying process (air velocity and temperature) (Clemente et al., 2014; Nascimento et al., 2015). Therefore, in this context several authors are studying the effect of ultrasound in different foods (Gamboa-Santos et al., 2014; Santacatalina et al., 2015; Corrêa et al., 2017; Magalhães et al., 2017).

The aim of this study was to evaluate the effect of the PEF as pretreatment and ultrasound application on the drying kinetics and effect in the structure of orange peel.

2. Materials and methods

2.1. Raw matter

Experiments were performed with orange peel samples (*Citrus sinensis*) purchased in a local market of Valencia, Spain. The fruits were selected according to size, shape and degree of maturation aiming at greater uniformity between the samples. Rectangular orange peel samples, containing only flavedo and albedo tissues (48 ± 0.1 x 26 ± 1 x 3.18 ± 0.04 mm), were obtained with the help of sharped knives. The initial moisture content was measured by placing the samples in an oven at 70 °C until reaching constant weight, according to standard method n° 934.06 (AOAC, 1997).

2.2. Pulsed electric fields (PEF) treatments

The EPULSUS-PM1-10 (Lisbon, Portugal) system was used for PEF treatments. The generated pulses were applied to the samples in a chamber containing electrodes and for each experiment this sample holder was filled with tap water (ratio of sample/water of 1:4.7 g/mL). In this study was tested two PEF treatments considered regarding number of pulses, 8 and 24 pulses of 25 µs, totalizing 200 and 600 µs, respectively (PEF-200 µs and PEF-600 µs) as well as a frequency of 10 Hz. In addition, was used a electrical field strengths of 1.20 kV/cm, calculated according to the following Eq. (1) (Won et al., 2015), with a distance between electrodes of 8.2 cm.

$$E = \frac{U}{d} \tag{1}$$

Where E is the electrical field strength (kV/cm), U is the output voltage (V) and d is the distance between electrodes (cm).

2.3. Drying experiments

The ultrasonic assisted convective dryer used in this study was previously described (Garcia-Perez et al., 2012). Ultrasonic system consists of an aluminum-vibrating cylinder (internal diameter 10 cm, height 31 cm, and thickness 1 cm) controlled by a piezoelectric composite transducer (21.7 kHz). The US has the ability to produce a high-intensity acoustic field in the medium (154.3 dB). The process operates automatically, the temperature and air velocity being controlled, using a balance to weight the samples at preset times (Garcia-Perez et al., 2012).

Orange peel samples not pretreated (NP) and pretreated (PEF - 200µs and PEF – 600 µs) were convective dried at 50 °C and 1 m/s, with (US; 20.5 kW/m^3; 21.7 kHz) and without (AIR) ultrasound application. The air conditions were monitored during drying to determine the relative humidity of the drying air, which presented an average value of 26.50±0.90%. The drying process was extended until samples lost 60% of their initial weight and all conditions were tested by triplicate. Drying kinetic of samples was determined from the initial moisture content of orange peel and the weight loss during drying.

2.4. Modelling

Experimental data modeling was performed to quantify the influence of the use of PEF and the US application on drying kinetics. For this, it was considered that the samples assumed an infinite slab behavior, with unidirectional moisture flow. Therefore, the model used was based on Fick’s second law, according to Eq. (2).

$$\frac{\partial W(x,t)}{\partial t} = D_e \frac{\partial^2 W(x,t)}{\partial x^2} \tag{2}$$

Where W is the moisture content (kg water/kg dry matter, d.m.), D_e is the effective diffusivity (m^2/s), t is the time (s), and x is the direction of the water transport (m). To solve Eq. (2) it was considered that the moisture of the samples was uniform at the beginning of the drying process. After this, it was considering that in this drying process find an external resistance to water loss, Eq. (3).

$$-D_e \rho_{ss} \frac{\partial W(L,t)}{\partial x} = k(a_w(L,t) - \varphi_{air}) \tag{3}$$

Where ρ_{ss} is the density of dry solid (kg d.m./m^3), k is the mass transfer coefficient (kg water/m^{2}s), a_w is the water activity, and φ_{air} is the relative humidity of drying air. Applying this equation can explain the immigration of water from the cells to the outer surface through the diffusion, and after, how it moves by convection into the drying air. The Matlab 2015B® (The Mathworks, Inc, Natick, USA) software was used to identify kinetic parameters, effective diffusivity D_e and mass transfer coefficient (k). The SIMPLEX method available in Matlab 2015B® was applied for optimization.

The percentage of variance explained (%VAR) by the model was determined to verify the accuracy of data adjustments (Eq. 4).

$$VAR = \left[1 - \frac{S^2_{calc}}{S^2_{ex}}\right].100 \tag{4}$$

Where S^2_{calc} is the calculated variance and S^2_{ex} is the experimental variance.

2.6. Statistical Analysis

The results were evaluated by means of multifactorial ANOVA. The LSD (least significance difference) intervals ($p<0.05$) were estimated, using the software Statgraphics Centurion XVI (StatPoint Technologies, Inc).

3. Results and discussion

3.1. Drying

The initial moisture content of orange peel was 2.94 ± 0.33 kg water/kg (dry matter). The drying kinetics of orange peel samples presented the typical behavior observed for the other vegetables (Magalhães et al., 2017). The final moisture of samples was 0.63 ± 0.03 kg water/kg (dry matter).

Fig. 1 show the drying kinetics obtained in the samples pretreated with different conditions of PEF and with (US) and without (AIR) application of ultrasound during air drying at 50 ºC. As can be expected, the ultrasound application seriously affected the drying of orange peel, reducing the process time. Therefore, the average time required to reach the moisture content of 0.63 ± 0.03 kg water/kg (dry matter) (Table 1) in NP-US experiment was 36% of those carried out at NP-AIR. The application of US in food drying processes can promote an increase in dehydration kinetics, affecting internal and external resistance. The influence on diffusivity can be attributed to the “sponge effect” or the creation of microchannels that facilitates the exit of water from inside the food matrix (Cárcel et al., 2012). This effect was observed by Nascimento et al. (2016) during the drying of passion fruit peel and by Garcia-Pérez et al. (2009) in the study of the drying of lemon peel.

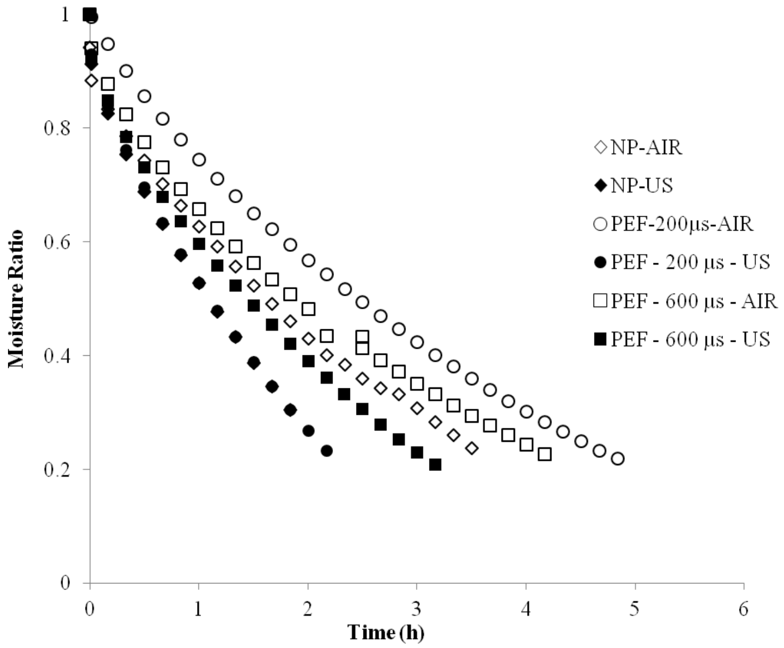

Figure 1. Experimental drying kinetics of the orange peel carried out without (AIR) and with (US) ultrasound application and different pretreatment of PEF at 1m/s and temperature at 50 °C.

On the other hand, the PEF application as a pretreatment did not presented positive effect in the drying kinetic (Fig. 1). The average time required in the NP-AIR was 20 and 28% of those carried out at PEF-600µs-US and PEF-200µs-US, respectively. The PEF application may have promoted an intense collapse in the microstructure of the orange peels, compromising the diffusive process. However, the combined effect between PEF and US promotes reductions in drying time when compared to the control experiment (NP-AIR) and this can be explained by the fact that the structural changes developed by the electrical pulses favor the propagation of the ultrasound acoustic waves, developing a positive effect in reducing drying time.

3.2. Modeling of drying kinects

In order to quantify the influence of ultrasonic waves, as well as the effect of electrical pulses on the mass transfer process during the convective drying of orange peel, it is convenient and important to consider modeling. The model used that considers the external resistance to mass transfer reached percentages of explained variance greater than 99% in all experiments (Table 1). Thus, it is understood that considering external resistance to the mass transfer process seems to be adequate and important to describe the behavior of experimental drying of orange peel.

Table 1. Drying time needed to obtain a moisture content of 0.6 kg water/kg dry matter of orange peel at 50°C, without (AIR) and with (20.5 kW/m^3; 21.7 kHz) ultrasound (US) application and different PEF treatments**.**

Treatment	Drying time (h)	D_e ($x10^{-10}$ m/s^1)	K ($x10^{-3}$ kg water/m^2s)	% Var
NP-AIR	3.5 ± 0.3^{a}	11.9 ± 1.4^{a}	0.7 ± 0.1^{a}	99.8
NP-US	2.6 ± 0.5^{b}	24.6 ± 1.6^{b}	1.2 ± 0.3^{b}	99.7
PEF-200µs-AIR	4.9 ± 0.4^{c}	7.5 ± 1.7^{c}	0.9 ± 0.2^{ab}	99.8
PEF-200µs-US	2.7 ± 0.7^{ab}	16.5 ± 4.4^{a}	1.4 ± 0.1^{b}	99.7
PEF-600µs-AIR	4.6 ± 0.5^{c}	9.6 ± 1.7^{c}	1.0 ± 0.7^{abc}	99.8
PEF-600µs-US	2.9 ± 0.2^{b}	18.7 ± 4.9^{b}	1.6 ± 0.2^{bc}	99.6

The application of ultrasound promoted a significant increase in the value of D_e. Thus, the value found for NP-US was 2.0 times bigger than those identified in the NP-AIR experiment. This increase was similar to that observed by Martins et al. (2018) during the drying of apple peel under the same conditions of temperature and ultrasound power. The successive compressions and expansions of the material, promoted by ultrasonic vibration that makes it easier for the moisture/vapor to escape from inside the sample to the outside, may be responsible for the effect found in reducing the resistance to mass transport with the application of ultrasound (García-Pérez et al., 2011). In addition, the value of the mass transfer constant (k) was 1.7 times bigger in the NP-US than the value found for NP-AIR, being statistically significant ($p<0.05$) (Table 1). Similar results was observed by Nascimento et al. (2016) during the drying of passion fruit peel.

The effects of applying PEF during the orange peel drying process were not significant ($p < 0.05$) with respect to the mass transfer coefficients obtained by the model under study (*De* and *k*), being negligible in all the experimental conditions shown in Table 1. Such factor may be related to the structural collapse generated by the effect of electroporation that promoted drastic changes in the structural matrix of the orange peel samples, compromising the diffusivity process. However, this collapse can facilitate the propagation of ultrasonic waves causing an increase in the diffusive process, and it was observed that the *De* and *k* values of the PEF-200µs-US and PEF-600µs-US experiments were higher than the control experiment (NP-AIR) (Table 1).

4. Conclusions

The application of ultrasound during the drying of orange peel increased the mass transfer rate, reducing the drying time by 54 min (NP-US versus NP-AIR). Consequently, the coefficients of the models applied were higher with the use of ultrasound compared to the control experiment with 99% VAR.

The use of PEF, isolated, was not able to promote an increase in mass transfer rates and consequently reductions in process time (PEF-200 µs and PEF-600 µs compared to NP-AIR). However, it was possible to observe an interesting combination alternative between PEF and US in the intensification of the drying process of orange peel slices, with reductions in drying times and an increase in the values of the parameters of the model under study. This result proves that the structural collapse caused by the electrical pulses somehow improves the propagation of ultrasound waves, being, therefore, a viable alternative for the process of dehydration of orange peel at moderate temperature.

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ARTICLE 5 – Article to be submitted in the Journal Food Engineering

Process intensification combining freezing pretreatment and power ultrasound-assisted air drying orange peel

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Abstract

Technologies of low drying (freezing) temperature and non-thermal (power ultrasound), is mostly suitable for the drying of fruits and vegetables. Thus, the freezing as pretreatment (slow and fast freezing) and power ultrasound-assisted air drying of orange peel has been explored in this work. Experiments were carried by two freezing types (slow freezing: -3 °C/24h; fast freezing: -35 °C/30 min) and power ultrasound (20.5 kW/m^3; 21.7 kHz) at 50 °C and 1.0 m/s. The kinetics of orange peel and modeling experimental date adjustment were determined. The studied freezing pretreatments did not promote reductions in drying time, but the applied acoustic power gave rise to a significant reduction of drying time (28%) ($p<0.05$). In addition, the combined effect of the two techniques also promoted significant reductions in process time (AIR-US-FF: 12%; AIR-US-SF: 40%) ($p<0.05$). Moreover, the application of US led to significant increases in diffusivity coefficients (D_e and K) in the mathematical model this study, no significant difference being that for other treatments.

Keywords: Orange peel. Drying time. Pretreatments. Freezing. Ultrasound

1. Introduction

Citrus fruits represent a large percentage of the fruit crop worldwide, including orange, tangerines and lemon (Bechlin et al., 2020). The Food and Agriculture Organization (FAO) reports that one third of all foods suffer loss of quality, being wasted before consumption. Such loss generates waste in the entire production process, increasing costs and demands for environmental resources (Bilbao-Sainz et al., 2018).

The orange fruits have a large part of residues, mainly the peel and can be presented as by-products of interest. Orange peels have compounds of high biological value, especially essential oils and phenolic compounds, pectin, sugars, vitamins and other compounds, and also have high moisture content. In addition, by-products may have technological properties with high industrial potential. Therefore, the orange peel becomes highly perishable and its processing can be one of the viable alternatives for its conservation, since depositing these by-products inappropriately to the environment can cause environmental damage (Keat, Ali, & Forney, 2014; Bechlin et al., 2020).

Freezing food products is a conservation technique widely used throughout the production chain and has important characteristics such as good preservation of nutritional (vitamins, minerals) and sensory (appearance, texture, taste) properties. In addition, it promotes reductions in chemical reaction rates and control of microbial activity, thus maintaining the quality of the stored product (Sadot et al., 2020). There are two traditional ways of applying the freezing technique, the process being slow and fast. The quality of the frozen product is generally better when applying the fast freezing technique compared to the slow freezing technique. This difference is explained by the fast processing promoting the formation of smaller ice crystals, which can lead to less damage to the membranes of the tissues (Delgado & Sun, 2001; Sadot et al., 2020).

In addition to the food preservation function, freezing has been applied as a pretreatment to drying processes. Convective drying is an old unit operation and is widely used in the food, chemical and pharmaceutical industry. However, drying can cause several changes in the nutritional and physicochemical properties of fruits and vegetables. In general, the changes can be perceived at the macroscopic level. However, they need to be carefully evaluated, since they can be the result of microstructure changes generated by the drying process (Onwude, Hashim, & Chen, 2016; Vallespir, Cárcel, Marra, Eim, & Simal, 2017).

Therefore, freezing with pretreatment and drying can be applied to intensify the process in fruits and vegetables, increasing the mass transfer rates. Freezing pretreatment (-20 and -80 °C) promoted reductions in the drying time of beetroot, apple and eggplant (50 °C and 1.0 m/s) (Vallespir et al., 2018). Similar results were found by Arévalo-Pinedo & Murr, (2007) at -20 ° C during the drying of carrots and pumpkin, and Ando, Maeda, Mizutani, & Wakatsuki (2016), who report 40% reductions in carrots process (-20 ° C). In addition, Junqueira, Corrêa, Oliveira, Avelar, & Pio (2017) observed increases in mass transfer rates during the processing of cape gooseberry fruits by applying rapid freezing by immersion in liquid nitrogen (-196 °C/10 s) and freezing slow (-18 °C).

Another method that has the ability to reduce convective drying time is the ultrasound application (US). The mechanical energy that the ultrasonic waves provide to the system has the ability to promote sustained compression and expansion in the tissues, being similar to what occurs when a sponge is squeezed and released consecutively, characterizing the “sponge effect” (Fuente-Blanco et al., 2006; Vallespir et al., 2017). The forces involved in the ultrasound effect can overcome the surface tension that acts by keeping the water molecules inside the capillaries of the tissues, generating microscopic channels and consequently increasing the mass transfer rates. Therefore, the effect of ultrasound acts to reduce internal and external resistances that limit the flush of water from the interior of the pores to the food surface (Vallespir et al., 2017). Several studies have been carried out in order to verify the influence of ultrasonic waves in the reduction of drying time and in order to corroborate with this theory Tao et al., (2018) observed reductions of 35 to 50% in garlic slices (50 to 70°C; 1513.5 W/m^2), Magalhães et al., (2017) found a similar effect in apple cubes, with the most pronounced effect on the lowest temperature and air velocity studied (45 °C and 1.0 m/s). In the same sense Kowalski and Pawłowski (2015) and Martins et al. (2018) proved the effectiveness of applying ultrasound to apple and apple peel, respectively. In a process involving orange peel, a positive effect of sonication was also observed by Ortuño et al. (2010) generating a reduction in the drying time over 45 % (40 °C; 1.0 m/s; 21.7 kHz) and (Garcia-Perez et al., 2012).

Therefore, the main aim of this study was to evaluate the effect of two different freezing treatments (slow and fast) before ultrasound assisted convective drying on the drying kinetic of orange peel.

2. Materials and methods

2.1.Sample preparation

Rectangular orange peel (*Citrus sinensis* var. Valencia Late) were purchased in a local market (Valencia, Spain) and used in this study. The size and color were used as sample homogenization parameters. The orange peel samples were extracted with the assistance of sharp knives (48 ± 1 x 26 ± 1 x 3.18 ± 0.04 mm). The moisture content peel fresh was measured in triplicate in a vacuum oven until constant weight at 60 °C (AOAC, 1997).

2.2.Freezing pretreatment

To apply the pretreatments, the samples were placed in a sample holder. For slow freezing (SF) the sample holder was kept at -3° C/24h in a domestic freezer and for rapid freezing (FF) kept at -35° C/30 min in a blast freezer (Hiber, model 051S). The temperature of the samples during freezing was controlled with the use of a thermocouple inserted in one of the samples.

2.3.Convective drying

Before starting the drying process, the samples were defrosting (2 °C/24h) and then taken to the process. Drying experiments were conducted in an ultrasonically assisted convective drier, which has already been described in the literature (Garcia-Perez et al., 2012) (Figure 1).

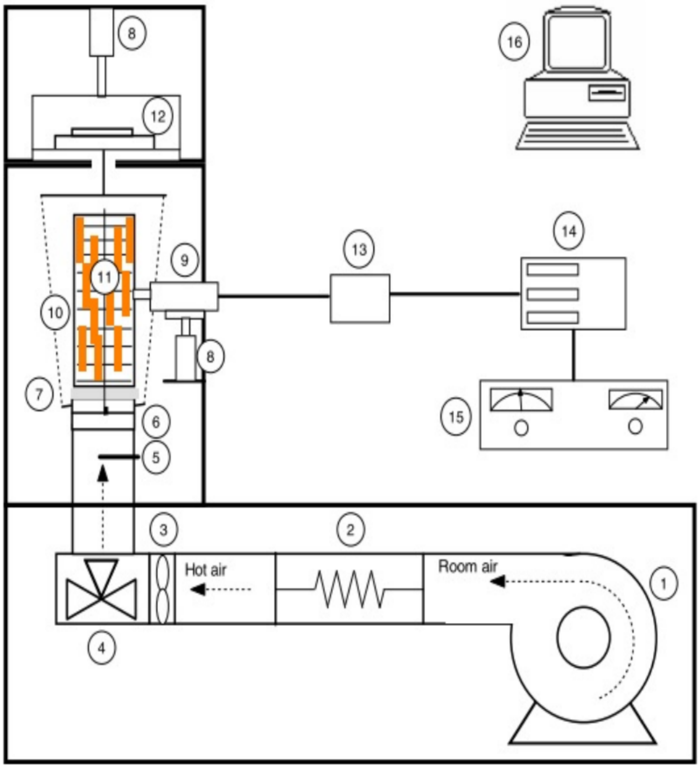

Figure 1. Layout of ultrasonically assisted convective drier: 1. Fan; 2. Heating unit; 3. Anemometer; 4. Three-way valve; 5. Thermo-couple; 6. Sample loading chamber; 7. Coupling material; 8. Pneumatic moving arms; 9. Ultrasonic transducer; 10. Vibrating cylinder; 11. Sample holder; 12. Balance; 13. Impedance matching unit; 14. Wattmeter; 15. High power ultrasonic generator; 16. PC.

An airborne US device constitutes the drying chamber, it includes an aluminum-vibrating cylinder (internal diameter 10 cm, height 31 cm, and thickness 1 cm) driven by a piezoelectric composite transducer (21.7 kHz). The US device is able to generate a high-intensity acoustic field in the medium (154.3 dB). The drying process is automated, the temperature and air flow are controlled and a scale is used to measure the variation in mass throughout the process. Drying experiments were performed at 1 m/s and 50 °C, with (US; 20.5 kW/m^3; 21.7 kHz) and without (AIR) ultrasound application. The drying was extended until samples lost 60% of their initial weight. Each condition was tested by triplicate. Drying kinetic was determined from the initial moisture content and the weight loss logged during drying. Each experimental combination of test was performed at least in triplicate and Table 1 showed all experiments conditions summarized.

Table 1. Experimental conditions in drying experiments

Experiment code	Freezing pretreatment	US application during drying (20.5 kW/m^3)
AIR	No	No
AIR-US	No	Yes
AIR-SF	Slow Freezing	No
AIR-US-SF	Slow Freezing	Yes
AIR-FF	Fast Freezing	No
AIR-US-FF	Fast Freezing	Yes

2.4.Drying process modelling

In order to model the experimental data obtained by drying kinetics, a model based on the diffusion process was used (Eq. 1). For this, it considered that the orange peel samples taken a uniform, isotropic slabs geometry. During the entire drying process it was considered that the effective diffusivity was constant.

$$\frac{\partial X(x,t)}{\partial t} = D_e \frac{\partial^2 X(x,t)}{\partial x^2} \qquad (1)$$

In the Eq. (1), X is the local moisture content of the sample (kg water/kg dry matter); t is the process time (s); x is the direction of the moisture transport (m); and D_e is the effective moisture diffusivity (m²/s).

A general boundary condition in convective drying process is that of considering the external mass transport resistance as negligible compared with the internal. Nevertheless, the low air velocity (1m/s), makes both external an internal mass transport resistances significant. Therefore, the coupled internal and external mass transport at the surface of the material was taken into account by Eq. (2) (Garcia-Perez et al., 2012).

$$-D_e \rho_{ss} \frac{\partial W(L,t)}{\partial x} = k(a_w(L,t) - \varphi_{air}) \qquad (2)$$

Where ρ_{ss} is the density of dry solid (kg dry matter/m^3), k is the mass transfer coefficient (kg water/m^{2}s), a_w is the water activity, and φ_{air} is the relative humidity of drying air. The Matlab 2015B® (The Mathworks, Inc, Natick, USA) software was used to identify kinetic parameters, effective diffusivity (D_e) and mass transfer coefficient (k). The SIMPLEX method available in Matlab 2015B® was used for optimization. For that, the sorption isotherm of orange peel published by Garau et al. (2006).

In order to determine the goodness of the fit to the experimental data were calculated the percentage of explained variance (%VAR) and the mean relative error (%MRE), represented by Eq. (3) and (4), respectively.

$$\%VAR = \left[1 - \frac{S_{calc}^2}{S_{ex}^2}\right].100 \tag{3}$$

$$\%MRE = \frac{100}{N}\left[\sum_{i=1}^{N} \frac{\left|W_{ex} - W_{calc}\right|}{W_{ex}}\right] \tag{4}$$

Where S^2_{calc} is the calculated variance and S^2_{ex} is the experimental variance, W_{ex} and W_{calc} are the experimental and calculated moisture contents (kg water/kg dry matter) and N is the number of experimental data.

A statistical procedure was performed in order to assess whether the application of freezing pretreatment (slow and fast freezing) and power ultrasound provokes a significant increase in the kinetic parameters (D_e and K), as compared to conventional drying process. Thus, analyses of variance (ANOVA) and LSD intervals ($p<0.05$) were determined by using the software package of Statgraphics® Plus 5.1 (StatPoint, Inc., Warrenton, VI, USA)

3. Results and Discussion

3.1. Experimental drying data

Orange peel fresh presented an average initial moisture content of 2.66 ± 0.14 (kg water/kg dry matter) which was considered as the critical moisture content due to the lack of a constant rate period under these experimental conditions. The value is similar to observed by Garcia-Perez et al. (2012) (2.89 ± 0.14 kg water/kg dry matter). Figure 2 shows the experimental drying kinetics of orange peel slabs carried out without (AIR) and with US application (AIR-US).

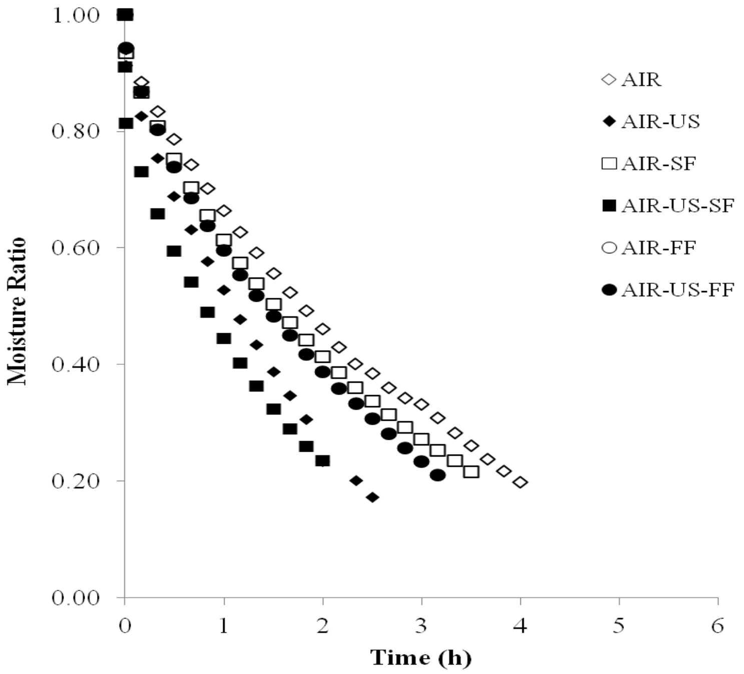

Figure 2. Experimental drying kinetics of the orange peel carried out without (AIR) and with (US) ultrasound application and different pretreatment of freezing (Slow Freezing – SF and Fast Freezing – FF) at 1m/s and temperature at 50 °C.

The evolution of moisture content versus time in all experimental conditions tested is observed in Figure 2. The drying process was interrupted when the samples reached a final moisture content of 0.50 ± 0.01 kg water/kg dry matter. The studied freezing pretreatments did not promote reductions in drying time. AIR-SF experiments showed drying time statistically similar to AIR experiments (Table 2) ($p<0.05$). In addition, the drying time need to reach final moisture content by AIR-FF experiments was 48% greater than the needed by AIR experiments. Although several articles in the literature (Junqueira, Corrêa, Oliveira, Avelar, & Pio 2017; Vallespir et al., 2017; Vallespir et al., 2019; Noshad and Ghasemi, 2020) indicate reductions in drying time with the application of the freezing process, the results of the present study can be understood by the fact that the ice crystals formed during freezing may have caused a structural collapse in the studied samples, making it difficult for the water to escape from the interior of the pores.

When ultrasound waves were applied, reduction of the drying time of 28% compared AIR-US to AIR experiments and its effect can be attributed to the successive compressions and expansions occurring in the samples, the creation of internal micro-channels or the micro-stirring at interfaces. The effect of applying ultrasound in reducing the drying time of fruits and vegetables was observed by Nascimento et al. (2016) during drying of passion fruit peel

(40 to 70 °C; 21,7kHz, 30.8 kW/m³); Vallespir et al. (2017) in the drying of beetroot (36 and 43% at 40 °C; 16.4 and 26,7 kW/m³, respectively); Ortuño et al., (2010) in the drying process of orange peel (45% at 40 °C; 90W).

In addition, analyzing the combined effect between the freezing of samples as pre-treatment and ultrasound makes it possible to verify the efficiency of the application of the two techniques with regard to reducing the drying process time linked to all the advantages that this reduction can provide to the product final. For this, in Table 2 it is possible to prove the significant reduction in process times ($p < 0.05$) comparing AIR-US-SF and AIR-US-FF whit AIR experiments. Although the freezing effect promoted changes in the microstructure of the products that did not allow a good mass transfer rate, this same change allowed a greater coupling of the product's pores with air, promoting the ultrasound transmission more easily, pronouncing its effects. The drying process time was reduced by 12 and 40% comparing AIR-US-FF and AIR-US-SF to AIR experiments. This same effects was observed by Vallespir et al., (2017) during drying of beetroot (55 and 58% at 40 °C; 16.4 and 26,7 kW/m³, respectively).

Table 2. Experimental conditions in drying experiments

Treatment	Drying time (h)
AIR	3.83 ± 0.29^{a}
AIR-US	2.75 ± 0.61^{bd}
AIR-SF	3.89 ± 0.19^{a}
AIR-US-SF	2.31 ± 0.29^{b}
AIR-FF	5.67 ± 0.17^{c}
AIR-US-FF	3.39 ± 0.10^{d}

AIR (air drying; 50 °C); AIR-US (ultrasound assisted at air dying; 50 °C, 20.5 kW/m^3); AIR-SF (air drying; 50 °C, slow freezing pretreatment); AIR-US-SF (ultrasound assisted at air dying; 50 °C, 20.5 kW/m^3, slow freezing pretreatment); AIR-FF (air drying; 50 °C, fast freezing pretreatment); AIR-US-FF (ultrasound assisted at air dying; 50 °C, 20.5 kW/m^3, fast freezing pretreatment). Letters in the same column show homogeneous groups determined by Least Significant Difference ($p<0.05$) intervals.

3.2.Modelling

Table 3 summarizes the identified D_e and k for orange peel curves at 50 °C and 1 m/s with and without pretreatment and ultrasound application. Modeling acts not only quantifying the effects of pretreatment of freezing and ultrasonic waves, but also helps to understand the external and internal resistance to mass transport that occurs in food.

Table 3. Identified values of effective moisture diffusivity and mass transfer coefficient and explained variance.

Treatment	D_e ($\times 10^{-9}$ m^2/s)	K ($\times 10^{-3}$ kg water/m^{2}s)	% VAR	%MRE
AIR	1.19 ± 0.14^a	0.76 ± 0.13^a	99.78	3.20
AIR-US	2.47 ± 0.15^b	1.16 ± 0.25^b	99.72	2.32
AIR-SF	0.90 ± 0.23^{ac}	0.82 ± 0.08^a	99.85	2.78
AIR-US-SF	1.28 ± 0.63^a	1.02 ± 0.16^a	99.86	3.61
AIR-FF	0.58 ± 0.10^c	0.72 ± 0.12^a	99.83	2.51
AIR-US-FF	1.02 ± 0.16^a	0.86 ± 0.07^a	99.74	4.02

Letters in the same column show homogeneous groups determined by Least Significant Difference ($p<0.05$) intervals.

Regardless of the drying conditions, the obtained VAR values were over 99% and the MRE were under 5%. Both statistical parameters used highlight an adjustment close to that of the drying kinetics obtained with the experimental data, thus, the assumptions considered in the development of the diffusional model seem adequate to characterize the mass transport during the orange peel drying process with respect to the experimental conditions tested. The effective moisture diffusivity for conventional drying kinetics (AIR, D_e 1.19 ± 0.14^a m²/s) was similar (Table 3) to other values reported for fruit peel in literature (Garcia-Pérez et al., 2009; lemon peel, and Nascimento et al., 2016; passion fruit peel). The D_e values found in the AIR-SF experiments, although statistically similar to the AIR ($p < 0.05$), and in the AIR-FF prove that the change in structure caused by the freezing effect was detrimental to the diffusivity process, and the drying time corroborates the explanation of such factor.

The application of power ultrasound led to a significant increase of D_e ($p < 0.05$), involving a reduction of the internal resistance to mass transfer in the drying orange peel, compared AIR whit AIR-US experiments (Table 3). As already mentioned, the “sponge effect” caused by the successive expansions and contractions of the material produced by the ultrasonic waves can be the factor responsible for this result. This fact has already been observed in the ultrasonically assisted drying of lemon peel (Garcia-Pérez et al., 2009), orange peel (Ortuño et al., 2010) and passion fruit peel (Nascimento et al., 2016).

As regards the influence of ultrasound on the external resistance to mass transport, the modeling of the drying kinetics of orange peel slabs (Table 3) showed a not significant increase of k parameter when freezing pretreatments were applied. On the other hand, the effect of ultrasound application on the k parameter was significant ($p < 0.05$) on the external resistance to mass transport. Power ultrasound has the ability to improve the mass transfer coefficient (k) due to the reduction in the thickness of the boundary layer generated by mechanical agitation of the gaseous medium that the ultrasonic waves promote at the interfaces. The ultrasound process is characterized by oscillation speeds, micro-streaming and pressure variation at the interfaces, resulting in a significant increase in turbulence causing an improvement in the transport of water from the solid surface to the air medium (Gallego-Juárez et al., 1999; Puig et al., 2012). The similar effects was observed by Garcia-Pérez et al. (2009), Ortuño et al. (2010) and Nascimento et al. (2016), in the drying of lemon peel, orange peel and passion fruit peel, respectively.

4. Conclusions

The feasibility of applying power ultrasound as a means of increasing the drying rate of the orange house has been proven. In this way, ultrasonic assisted drying has improved the mass transfer coefficient and the effective diffusivity of moisture, which allows for milder drying conditions that can promote better quality parameters for the final product. In addition, the effect combined with the freezing of samples before drying demonstrated reductions in the time of exposure of orange peel samples to the drying process and knowing that fruits and vegetables have nutritional and technological properties that can be affected for a long time exposure to heat sources the combination of treatments is feasible in view of obtaining quality dehydrated orange peel.

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GENERAL CONCLUSIONS

The application of ethanol during the drying of dekopon slices proved to be feasible in reducing the drying time. The same effect was observed by the increase in temperature, as expected and reported in several studies in the literature. In addition, the pretreatment promoted less change in color, and greater retention of phenolic compounds, ascorbic acid and antioxidant activity of dekopon dehydrated slices. Therefore, the use of ethanol presents itself as an excellent alternative for the production of dehydrated foods with reduced processing time and with high nutritional quality.

Regarding the processes involving the drying of orange peel, it is possible to state that the application of power ultrasound during the drying process is an excellent alternative with regard to reducing the drying time, both in drying at moderate temperature and in atmospheric freeze-drying. The ultrasound-assisted process presents better parameter values of the mathematical models used. In addition, the technological properties of the dehydrated orange peel were preserved more intensely with the process of dehydration at moderate temperature and the use of ultrasound.

The application of pulsed electric field does not reduce, in isolation, the drying process time of orange peel samples. However, the association with the use of power ultrasound is shown to be viable in view of the process time. In addition, the use of PEF promotes greater retention of nutritional compounds of interest, and the shorter pulse application time accompanied by ultrasound is shown to be more viable for processing.

The slow and fast freezing technique before the drying process does not show reductions in the drying time of orange peel. However, the application aligned with the use of ultrasound during the drying process has the ability to reduce the process time and, therefore, it is expected that changes in nutritional, technological, sensory properties and other quality parameters of the final product will be more preserved. Therefore, pretreatment is shown to be viable with the support of ultrasound.

Thus, it is possible to conclude that the various pretreatments have feasibility of application with regard to the preservation of compounds of high nutritional importance, technological properties and sensory characteristics. Additionally, the use of power ultrasound stands out for its great performance in various processes, especially in reducing drying time. In addition, the combination of silver plating with the use of ultrasound can be taken into consideration to obtain dehydrated products with reductions in process time and better retention of the final product quality parameters.

Therefore, according to the data found in the present study, it can be assumed that the application of ethanol presented the best responses in terms of reducing the drying process and preserving compounds that provide quality to the final product, in addition to being a low-cost treatment and easy operation compared to the others. However, we cannot emphasize the importance of the other treatments that have shown expressive and important results with regard to their application as pretreatment techniques for drying food.