IMPROVEMENT OF MASS TRANSFER BY FREEZING PRE-TREATMENT AND ULTRASOUND APPLICATION ON THE CONVECTIVE DRYING OF BEETROOT (BETA VULGARIS)

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Abstract: Effects of freezing pre-treatment and ultrasound application during drying, on the microstructure, the drying curves and the bioactive compounds of beetroot (*var. conditiva*) cubes (0.008 m edge) have been evaluated. Raw and previously frozen (at −20 °C) beetroot samples were convectively dried (40 °C and 1 m/s) without and with ultrasound application using two acoustic densities: 16.4 kW/m^3 and 26.7 kW/m^3 and a diffusional model taking into account both the external and the internal mass transfer resistances was proposed to simulate the drying curves. Freezing pre-treatment and ultrasound application promoted significant disruptions in beetroot microstructure and drying time was shortened. Thus, freezing pre-treatment and ultrasound application enhanced the mass transfer. Comparing to the figures for the drying without ultrasound, the external mass transfer coefficient increased 28-49% when ultrasounds were applied; moreover, the effective diffusion coefficient increased 60-73% and 204-211% due to the ultrasound application on drying of raw and pre-frozen samples, respectively. However, betalain content (BC), total polyphenol content (TPC) and antioxidant activity (AA) of samples decreased after drying process with ultrasound application, comparing to raw sample.

Keywords: beetroot, freezing, drying, ultrasound, diffusional model, betalain, total polyphenol, antioxidant activity

1. INTRODUCTION

Beetroot is the sixth on the rank of vegetables with the highest antioxidant content, at FRAP and TEAC assays, due to betalain and also polyphenol content (Serafini & Testa, 2009). Beetroot contains two betalain pigments: betaxanthin (yellow-orange) and betacyanin (red-violet) (Nemzer et al., 2011) which, apart from being colored, have also a high antioxidant potential (Gengatharan, Dykes, & Choo, 2015). Although the most common preparations of beetroot are boiled or juice (Wootton-Beard & Ryan, 2011), some new performances have been recently studied such as freeze and heat-dried beetroot (Figiel, 2010; Hung & Duy, 2012; Kaleta & Górnicki, 2010), dried powders processed by spray-drying, air-drying, or freeze-drying (Nemzer et al., 2011; Wruss et al., 2015) and juice microcapsules obtained by spray-drying (Janiszewska, 2014; Pitalua, Jimenez, Vernon-Carter, & Beristain, 2010). All these processes have the purpose of drying the sample to stabilize the product.

The convective drying is the most frequently used drying operation in food and chemical industry (Cárcel, García-Pérez, Riera, Rosselló, & Mulet, 2014). However, drying causes changes in the nutritional value and physical properties of fruits, vegetables and their products, therefore, these changes should be carefully evaluated. Changes in the nutritional value and physical properties could be minimized by modifying drying conditions, for instance changing temperature and air velocity, or using combined drying methods. Most of these physico-chemical changes, although observed at a macroscopic level, are caused by changes occurred at microstructural/cellular level. For example, drying has been reported to cause shrinkage of cells, plasmolysis and folding up the cell walls on pumpkin tissue during osmotic dehydration (Mayor, Pissarra, & Sereno, 2008). Therefore, microstructural changes might also be studied when fruits and vegetables are dried.

In order to intensify the drying process, many different pre-treatment methodologies have been proposed in the literature. Among them, freezing pre-treatment has been reported to enhance fruits and vegetables drying (Lewicki, 2006). Freezing treatment (at an industrial storage temperature: between −18 °C and −28 °C) prior to drying has been reported to reduce drying time and, consequently, energy consumption of green beans, carrots and potatos convective drying at 70 °C (Eshtiaghi, Stute, & Knorr, 1994); rice micro-wave vibro-fluidized bed drying at 110-185 °C (Sripinyowanich & Noomhorm, 2013); strawberries osmotic drying at 40 °C under vacuum (Taiwo, Eshtiaghi, Ade-Omowaye, & Knorr, 2003); blueberries convective drying at 60-80 °C (Zielinska, Sadowski, & Błaszczak, 2015); carrot roots convective drying at 60 °C (Ando et al., 2016). Freezing treatment might cause tissue structure disorders which would lead to physico-chemical changes of the material such as higher water absorption capacity (Lewicki, 2006), but at the same time, drying time shortening reduces thermal exposure of the material, consequently nutritional value could be better preserved.

Furthermore, it has been demonstrated that the ultrasound application in a drying system may overcome some of the limitations of the convective drying by increasing the drying rate mainly at low temperature (less than 50 °C) (García-Pérez, Rosselló, Cárcel, De la Fuente, & Mulet, 2007) and at low air velocities (less than 2 m/s) (Cárcel, García-Pérez, Riera, & Mulet, 2007; García-Pérez, Cárcel, De la Fuente-Blanco, & de Sarabia, 2006). Ultrasound application effects during hot-air drying of many products have been previously studied. Drying time reductions

(at 40 °C and 1 m/s of air velocity) due to ultrasound application (37 kW/m^3) of 32% in carrot cubes drying (García-Pérez, Cárcel, Riera, & Mulet, 2009) and of 72% in eggplant cylinders drying (García-Pérez, Ozuna, Ortuño, Cárcel, & Mulet, 2011) have been reported. The mechanical energy provided by the ultrasound application promotes alternating compressions and expansions which have a similar effect to that observed when a sponge is squeezed and released repeatedly: "sponge effect" (De la Fuente-Blanco, Riera-Franco de Sarabia, Acosta-Aparicio, Blanco-Blanco, & Gallego-Juárez, 2006). This "sponge effect" helps to release liquid from the inner part of a particle to its surface and promotes the suction of fluid from outside. The forces involved in this mechanism can be higher than the surface tension which maintains the water molecules inside the capillaries of the material, creating microscopic channels and facilitating the exchange of matter (Cárcel et al., 2014). Then both internal and external resistances to mass transfer would be enhanced.

No studies have been found in the literature about freezing pre-treatment or ultrasound assisted drying of beetroot. Therefore, the main objective of this study was to evaluate the influence of the freezing pre-treatment and the ultrasound application on the mass transfer in convective drying of beetroot cubes. For this purpose, microstructure and also the drying curves by using a diffusional model have been studied; likewise the changes in the total polyphenol content, antioxidant activity, betalain content of the food matrix due to freezing pre-treatment, drying and ultrasound application have been evaluated.

NOMENCLATURE

AD   acoustic density (kW/m^3)
D_e effective water diffusion coefficient (m^2/s)
dm   dry matter (kg)
h_m external mass transfer coefficient (kg/m^2 s)
L   half of the length (m)
n   number of experimental data
MRE   mean relative error (%)
S_x moisture content standard deviation (sample) (kg H$_2$O/kg dm)
S_{yx} moisture content standard deviation (calculated) (kg H$_2$O/kg dm)
t   time (s)
var   percentage of explained variance (%)
W   moisture content (kg H$_2$O/kg dm)
x,y,z   spatial coordinates (m)
ρ_{dm} dry matter density (kg dm/m^3)
φ relative humidity

Subscripts
0   initial
∞   drying air
cal   calculated
e   equilibrium
exp   experimental
l   local

2. MATERIALS AND METHODS

2.1. Sample processing

The beetroot (*Beta vulgaris var. conditiva*) used in this study, purchased in a local market, was selected in a range of 10.7±0.9 °Brix, washed, peeled and cut into cubes (0.008m edge) from the center regions of the beetroot tissue, not including the peel, and immediately processed. The initial average moisture content (W_0) was obtained by using the AOAC method No. 934.06 (AOAC, 2006). Two sets of experiments were carried out. In set R, samples were directly dried meanwhile in set F, samples were placed on a stainless steel load tree and frozen in a blast freezer (RDM051S, HIBER, Taiedo di Chions, Italy) at −20 °C (5.5±0.1 °C/min freezing rate) prior to drying. Frozen samples were directly placed into the preheated drier without thawing.

Drying experiments were carried out in a convective drier assisted by ultrasound, which has already been described in a previous work (Cárcel, García-Pérez, Riera, & Mulet, 2011). The equipment consisted of a pilot-scale convective drier with an aluminum cylindrical vibrating element (internal diameter 0.1 m, height 0.31 m and thickness 10 mm) working as the drying chamber where the load tree was placed. The cylinder was driven by a piezoelectric transducer (21.8 kHz); thus, the ultrasonic system was able to generate a high intensity ultrasonic field in the air medium with an average sound pressure of 154.3±0.1 dB. The drier operated completely automatic, air temperature and velocity were controlled using a PID algorithm and samples were weighted at preset times by combining two pneumatic systems and a PLC (CQM41, Omron, Tokyo, Japan). Drying experiments were carried out at constant air velocity (1 m/s) and drying air temperature (40 °C), without (R0 and F0 samples) and with ultrasound, applying two different acoustic densities 16.4 kW/m^3 (40 W) (R1 and F1 samples) and 26.7 kW/m^3 (65 W) (R2 and F2 samples). All the drying experiments were carried out, at least, in triplicate and extended until sample weight loss of 80% of the initial one was achieved.

2.2. Microstructural Analysis

Beetroot samples were prepared for light microscopy observation according to the methodology described by Eim et al. (2013) with minor modifications. Samples were fixed in formaldehyde (10%) followed by dehydration, embedded in paraffin (60 °C for 3 h), and sectioned into 4-5 μm sections by using a microtome (Finesse 325, Thermo Shandon, Cheshire, UK). The sections were stained with Periodic Acid–Schiff (PAS) and Hematoxilin Eosin (H-E) to visualize cell walls (Paciulli et al., 2015). The microstructural images were obtained using an optical microscope (BX41, Olympus, Tokyo, Japan) and a camera (DP71, Olympus, Tokyo, Japan) at 200 magnification.

2.3. Modelling

With the aim of obtaining a mathematical model representative of the moisture transport during the drying process, the Fick's second law was combined with the microscopic mass transfer balance and the process was considered to be isothermal. The governing equation for a differential element of cubic shape was formulated (Eq. 1) considering liquid diffusion being the main transport mechanism.

$$D_e \left(\frac{\partial^2 W_l}{\partial x^2} + \frac{\partial^2 W_l}{\partial y^2} + \frac{\partial^2 W_l}{\partial z^2} \right) = \frac{\partial W_l}{\partial t} \tag{1}$$

A constant and effective diffusion coefficient (D_e), representative of the global transport process, might include molecular diffusion, liquid diffusion through the solid pores, vapor diffusion and all others factors which affect drying characteristics (Rodríguez, Eim, Simal, Femenia, & Rosselló, 2013). The governing equation (Eq. 1) could be solved considering, as initial condition, that the moisture distribution inside the solid was uniform at the beginning of the process (Eq. 2). As boundary conditions, moisture distribution symmetry (Eq. 3), and the external mass transfer at the solid surface (Eq. 4) were considered.

$$W_{l_{(x,y,z)}} \Big|_{t=0} = W_0 \tag{2}$$

$$\frac{\partial W_{l_{(x,y,z)}}}{\partial x} \Big|_{x=0} = 0 \qquad \frac{\partial W_{l_{(x,y,z)}}}{\partial y} \Big|_{y=0} = 0 \qquad \frac{\partial W_{l_{(x,y,z)}}}{\partial z} \Big|_{z=0} = 0 \tag{3}$$

$$-D_e \rho_{dm} \frac{\partial W_{l_{(x,y,z)}}}{\partial x} \Big|_{x=L} = h_m (\varphi_e - \varphi_\infty)$$

$$-D_e \rho_{dm} \frac{\partial W_{l_{(x,y,z)}}}{\partial y} \Big|_{y=L} = h_m (\varphi_e - \varphi_\infty) \tag{4}$$

$$-D_e \rho_{dm} \frac{\partial W_{l_{(x,y,z)}}}{\partial z} \Big|_{z=L} = h_m (\varphi_e - \varphi_\infty)$$

The sorption isotherm reported by Figiel (2010) and the psychometric data were considered to complete the model.

COMSOL Multiphysics® 5.1 (COMSOL AB) was used to solve the mathematical model, applying the finite elements method (FEM). After the mesh independence test, a domain composed of about 2650 quadratic triangular elements, resulting in about 3500 degrees of freedom, was used. Matlab 2014a® (The Mathworks, Inc., Natick, USA) was used to develop the algorithm to identify both the effective diffusion (D_e) and the external mass transfer (h_m) coefficients from each drying curve through the minimization of the objective function (mean relative error) given by the Eq. 5.

$$MRE = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{W_{exp_i} - W_{cal_i}}{W_{exp_i}} \right| \tag{5}$$

2.4. Bioactive compounds and antioxidant activity determinations

Raw (R), frozen (F) and dried samples without (R0 and F0) and with ultrasound application (R1, R2, F1 and F2) were analyzed to determine their betaxanthins content (BXC), betacyanins content (BCC), total polyphenol content (TPC) and antioxidant activity (AA). Methanol extracts from beetroot samples were prepared according to the methodology described by Eim et al. (2013) with some modifications. Samples were accurately weighted (~2 g) and 20 mL of methanol extraction solvent was added. Mixture was homogenized using Ultra-Turrax© (T25 Digital, IKA, Staufen, Germany) at 13,000 rpm for 1 min at 4 °C, and then the obtained solution was refrigerated overnight. Mixtures were centrifuged at 4,000 rpm for 10 min, and then filtrated. The extracts were refrigerated at 4 °C until analysis. At least, six methanol extracts were prepared for each sample.

Betalain content was determined as betaxanthins (BXC) and betacyanins (BCC) contents, separately, according to Stintzing et al. (2005). Absorbance measurements were carried out at 25 °C in a UV/Vis/NIR spectrophotometer (UV-2401PC, Shimadzu, Kyoto, Japan) at 476 and 535 nm, respectively. The betalain content was expressed as mg indicaxantin equivalent (IE)/g dm for BXC and mg betanin equivalent (BE)/g dm for BCC.

Total polyphenol content (TPC) was determined by means of the Folin-Ciocalteu assay according to Eim et al. (2013). The antioxidant activity (AA) was determined by using FRAP, CUPRAC and ABTS assays according to González-Centeno et al. (2012). Absorbance measurements were carried out at 25 °C in a UV/Vis/NIR spectrophotometer (Thermo Scientific Multiskan Spectrum, Vantaa, Finland) at 745 (TPC), 593 (FRAP), 450 (CUPRAC) and 734 (ABTS) nm. Absorbance measurements were correlated with standard curves (0-250 ppm gallic acid for TPC and 0-400 ppm trolox for AA). The results were expressed as mg of gallic acid equivalent (GAE)/g dm for the TPC, while the AA was expressed as mg trolox equivalent (TE) /g dm.

2.5. Statistical analyses

Statistical analyses were carried out by using R[©] (GNU project) software. Data were averaged from replicates and reported as mean±standard deviation. Two-factor analysis of variance was applied to analyze the effects of freezing pre-treatment and ultrasound application on the total polyphenol content, antioxidant activity and betalain content. Means were compared by Tukey's test at p<0.05.

Additionally, the percentage of explained variance (Eq. 6) was used to evaluate the accuracy of the obtained simulation.

$$var = \left[1 - \frac{S_{xy}^2}{S_y^2}\right] x100 \tag{6}$$

3. RESULTS AND DISCUSSION

3.1. Microstructural Analysis

The study of the effect of pre-freezing treatment and of the use of ultrasound during drying on the microstructure of beetroot has been carried out by means of light microscopy. Parenchyma tissue was selected to observe changes and compare between different treatments due to its homogeneous pattern. The photographs of raw, pre-frozen and dried beetroots are shown in figure 1. Raw sample, which is shown in figure 1R, presented typical beetroot isodiametrical and polyhedral cells with few intercellular spaces as it has been reported by Nayak, Suguna, Narasimhamurthy, & Rastogi (2007) observing raw beetroot. During drying one of the most important phenomena is cell shrinkage, which leads to the major modification in the structure of the product and allows the release of water (Ramos, Silva, Sereno, & Aguilera, 2004). Comparing figures 1R (raw sample) and 1R0 (dried sample) it can be seen how shrinkage took place in dried samples during drying at 40 °C and 1 m/s of air velocity.

Figure 1F shows structure of the frozen beetroot sample (F) before drying. It can be observed a that freezing pre-treatment promoted disruptions and fissures on beetroot tissue as it has been reported on asparagus, zucchini and green beans industrial freezing treatment at −40 °C prior to boiling (Paciulli et al., 2015) and also on carrot freezing pre-treatment at −50 °C (Kidmose & Martens, 1999). Moreover, a freeze-thaw cycle seems promote cell collapses resulting in large intercellular spaces and the loss of cohesion as it has been observed on papaya tissue after the first freeze-thaw cycle at −25 °C and 4 °C (Phothiset & Charoenrein, 2014).

Regarding ultrasound application, it can be seen in figures 1R1 and 1R2 that the use of acoustic densities of 16.4 and 26.7 kW/m^3 during drying contributed to disrupt the cellular structure, presenting larger pores than in R0 samples. Moreover, the higher the acoustic density applied, the more disruption and larger pores were observed in samples. Similar effects were observed at the same drying conditions (at 40 °C and 1 m/s) by García-Pérez et al. (2012) on orange peel drying when acoustic density of 37 kW/m^3 was applied and Rodríguez et al. (2014) on apple drying when acoustic density of 30.8 kW/m^3 was applied. Both studies concluded that ultrasound application during drying produced an even more intense disruption than conventional drying creating micro-channels and making easier the water pathway.

Figure 1F0 shows the pre-frozen dried sample without ultrasound application. It can be observed a remarkable cellular damage and cells irregular shapes in the structure of this sample, together with cell shrinkage due to drying process. Finally, figures 1F1 and 1F2 show the pre-frozen dried sample with ultrasound application at the two acoustic densities tested. Those samples presented a sum of freezing, drying and ultrasound application effects previously described.

3.2. Drying kinetics

The initial moisture content of raw beetroot in this study was of 8.7±0.1 kg/kg dm within the range proposed in the literature by Kaleta & Górnicki (2010) (between 6 and 8 kg/kg dm) and by Figiel (2010) (10.2 kg/kg dm) for the same vegetable. No significant differences were observed between initial moisture content of raw and frozen samples, therefore the freezing pre-treatment did not significantly change the initial moisture content as it has been also reported after freezing at −20 °C for broccoli, carrots and green beans (Howard, Wong, Perry, & Klein, 1999) and blueberries (Zielinska et al., 2015).

Figure 2 shows the experimental drying curves obtained for raw and pre-frozen beetroot cubes without and with ultrasound application at 40 °C and 1 m/s, from the initial moisture content down to ca 0.45±0.02 kg/kg dm of final moisture content. The drying time for this final moisture content of the raw sample when ultrasounds were not applied (R0) was approximately of 5.4 h, and of the pre-frozen beetroot when ultrasounds were not applied (F0) was approximately of 3.0 h, 46% shorter than that of the R0 sample. This fact suggests that the freezing pre-treatment promoted an improvement of the water removal during the drying process. Zielinska et al. (2015) reported drying time reductions of 13 and 20% when pre-frozen (at −20 °C) blueberries were dried at 60 and 80 °C, respectively, compared to the raw sample.

A similar reduction of drying time (40%) was observed when pre-frozen (at −20 °C) carrots were dried at 60 °C (Ando et al., 2016).

When an acoustic densities of 16.4 kW/m^3 (R1) and 26.7 kW/m^3 (R2) were applied, reductions of the drying time of 36 and 43% were observed, respectively, compared to the raw sample. It is difficult to analyze the effects of different ultrasonic devices because the efficiency is very dependent on the characteristics of the vibrating element. Thus, the comparison of drying experiments carried out with the same aluminum cylindrical vibrating element and air conditions (40 °C and 1 m/s) is more appropriate (Ozuna, Cárcel, García-Pérez, & Mulet, 2011). When an acoustic density of 30.8 kW/m^3 was applied to carrot cubes drying, a drying time reduction of 30% was observed (Cárcel et al., 2011); in potato cubes drying, the application of 37 kW/m^3 promoted a drying time reduction of 40% (Ozuna et al., 2011). All these time reductions were similar to those observed in the present work. Carrot, potato and beetroot could be considered "low porosity" products (their porosity values "ε" are lower than 0.050) (Boukouvalas, Krokida, Maroulis, & Marinos-Kouris, 2006) and might be less-sensitive to the effects of the ultrasound application. The effect of ultrasound application on the mass transport has been linked to the alternative expansions and compressions produced in the material by ultrasonic waves, the "sponge effect" (De la Fuente-Blanco et al., 2006). Other products, like apple or eggplant ("medium-high porosity" products, their porosity values "ε" are higher than 0.100) (Boukouvalas et al., 2006) seemed to be more sensitive to the "sponge effect" exhibiting reductions of 54 and 75%, respectively, at 37 kW/m^3 of acoustic density under the same air drying conditions (40 °C and 1 m/s) (Puig, Pérez-Munuera, Cárcel, Hernando, & García-Pérez, 2012; Sabarez, Gallego-Juárez, & Riera, 2012).

Similarly, the ultrasound application during drying of pre-frozen samples also promoted a decrease of the drying time, being of 55% (F1) and 58% (F2) in comparison to raw sample. According to these results, both the freezing pretreatment and the ultrasound application (at 16.4 kW/m^3 and 26.7 kW/m^3) during drying enhanced the mass transfer and consequently reduced the drying time. Comparing with other combined method, reductions of the drying time (11-39%) have been reported when pre-frozen rice (at −20 °C) was dried (110-185 °C) with micro-wave assistance (850 W) which also enhanced the mass transfer process (Sripinyowanich & Noomhorm, 2013).

In order to evaluate the existing drying periods, the water flux (kg/kg dm m^2 s) was estimated and represented vs the average moisture content for all samples in figure 3. In this figure no constant rate period was observed and the entire drying curves fell within the falling rate period except for the first moments of frozen samples drying. This behavior of raw samples has also been reported by other authors for the convective drying of different fruits and vegetables, like eggplant (Puig et al., 2012) and orange peel (García-Pérez et al., 2012); among others. In the case of frozen samples, water flux was very low at the beginning of the process while these samples were thawing (induction period). Similar behavior has been reported for pre-frozen (at −30 °C) apple slices prior to drying at 65 °C and 1.2 m/s (Ramírez, Troncoso, Muñoz, & Aguilera, 2011). During the first 4 min of drying process, an increment in the mass flux was observed by these authors, as the surface temperature of apple slices increased. It can be also seen in figure 3 that the water flux was higher when samples were pre-frozen and/or ultrasounds were applied during drying.

3.3. Modelling

In order to better study the effect of both the freezing pre-treatment and the ultrasound application on the mass transfer phenomenon, mathematical modeling was used as a tool for explaining and quantifying the observed enhancement of water removal during drying. A first attempt of modeling the drying curves was made assuming that the external resistance to mass transfer could be neglected, thus considering that the solid surface was at equilibrium with the drying air from the early stages of the drying process. However, the simulation of the drying curves under these conditions did no provide satisfactory results (results not shown).

Therefore, both, the external mass transfer (h_m) and the effective diffusion (D_e) coefficients were simultaneously identified by minimizing the differences between the experimental drying curves of beetroot and the simulated ones. The identified figures for these parameters (h_m and D_e) are summarized in table 1 for each drying experiment. As it can be observed in this table, there were important effects of both the freezing pre-treatment and the ultrasound application on the effective diffusion coefficient while only the ultrasound application affected the mass transfer coefficient.

The identified h_m was of 2.18×10^{-4} kg/m^{2}s for R0 sample, which is similar to the one observed in potato cubes when drying at 40 °C and 1 m/s (2.03×10^{-4} kg/m^{2}s) (Ozuna et al., 2011). As expected, the freezing pre-treatment did not increase the h_m coefficient which was of 2.18×10^{-4} kg/m^{2}s equal to R0 sample. The external mass transfer coefficient is, in fact, a parameter that takes into account the conditions in the external resistance to mass transfer (the layer of fluid, air, that is all about the sample undergoing drying). Different is the case when ultrasound waves are applied: in this case, in fact, ultrasound waves influence the external resistance too and the h_m increased up to 2.79×10^{-4} kg/m^{2}s in R1 sample (when an acoustic density of 16.4 kW/m^3 was applied) and to 3.24×10^{-4} kg/m^{2}s in R2 sample (26.7 kW/m^3), thus, compared to R0 increases of 28 and 49% were respectively observed. When acoustic densities of 18.5 and 37 kW/m^3 were applied during orange peel slabs drying at 40 °C and 1 m/s important increments on h_m were also observed (47 and 108%) (García-Pérez et al., 2012). Undoubtedly these results indicate that the ultrasound application may induce decreases not only on the internal resistance, but also on the external resistance to the mass transfer probably due to pressure variations at the solid/gas interfaces, and therefore increasing the surface moisture evaporation rate (Rodríguez et al., 2014). Moreover, acoustic energy create turbulences, oscillating velocities and microstreaming at the interfaces, which leads to a reduction of the boundary layer thickness (Gamboa-Santos, Montilla, Cárcel, Villamiel, & Garcia-Perez, 2014). When samples were pre-frozen and dried with ultrasound application, h_m increased up to 2.79×10^{-4} kg/m^{2}s for F1 sample (16.4 kW/m^3) equal to R1 sample and to 3.24×10^{-4} kg/m^{2}s for F2 sample (26.7 kW/m^3) equal to R2 sample. Identified h_m figures for frozen samples were equal to respective raw samples, indicating that freezing pre-treatment did not affect external resistance.

The identified D_e was of 3.07×10^{-10} m^2/s for R0 sample drying, which was in the range of the observed in carrot cubes and lemon peel slabs drying at 40 °C and 1m/s (1.20 and 4.95×10^{-10} m^2/s) (García-Pérez et al., 2009). The freezing pre-treatment promoted an important increase of the D_e up to 7.93×10^{-10} m^2/s (158% increment in comparison to the R0 sample) probably due to the freezing cellular tissue damage which improved the water transport throughout the

solid. This effect was also reported for pre-frozen (at −30 °C) apple slices drying at 65 °C and 1.2 m/s where identified initial effective diffusivity increased a 30% in comparison to the raw sample (Ramírez et al., 2011). This parameter (D_e) also increased due to ultrasound application up to 4.92×10^{-10} m^2/s in R1 sample (16.4 kW/m^3) and 5.32×10^{-10} m^2/s in R2 sample (26.7 kW/m^3) thus, compared to R0, increases of 60 and 73% were respectively observed. When acoustic densities of 16 and 25 kW/m^3 were applied during lemon peel slabs drying at 40 °C and 1 m/s, similar increases on D_e were observed (49 and 99%) (García-Pérez et al., 2009). No significant differences were observed between both identified D_e figures for R1 and R2. When samples were pre-frozen and dried with ultrasound application, D_e increased up to 9.32×10^{-10} m^2/s in F1 sample (16.4 kW/m^3) and 9.54×10^{-10} m^2/s in F2 sample (26.7 kW/m^3), thus, compared to R0 sample increases of 204 and 211% were respectively observed. No significant differences were observed between both identified D_e figures for F1 and F2. These figures indicated that not only the freezing pre-treatment promoted increases of D_e, but also the ultrasound application did it.

Although more experimentation should be done, the variation of the h_m coefficient with the acoustic density (AD) appeared to be linear with a determination coefficient of 0.99 (Ec. 7). This trend was less evident for the variation of the effective diffusion coefficient (D_e) with the applied ultrasound acoustic density the determination coefficients being lower in this case (equations not shown).

Raw samples $\qquad h_m = 5.31 \times 10^{-5}\, AD + 2.21 \times 10^{-4} \quad r^2 = 0.992$ $\qquad\qquad$ (7)

By using the identified D_e and h_m figures, the drying curves were simulated. In order to evaluate the simulation, the predicted moisture content has been represented vs the experimental one for all the experiments in figure 4. This figure also shows the regression analysis and the prediction bounds at a 95% confidence. As it can be seen in this figure, good agreement between both groups of data (predicted and experimental) was obtained for both raw and frozen samples dried without or with ultrasound application. The goodness of the simulation was corroborated by the regression analysis. The y-intercept and the slope figures were close to zero and to unity, respectively, and the coefficient of determination, which describes the good correlation of the predicted concentrations with their experimental values, was higher than 0.99. To mathematically evaluate the simulation, the mean relative error (Ec. 5) and the percentage of explained variance (Ec. 6) were calculated for each experiment. Results are also shown in table 1. As it can be seen in this table, MRE was lower than 4.7% and the %var was higher than 99.7% for the simulation of all the experiments (Table 1). It could be concluded from figure 4 and table 1 that the drying curves of beetroot were satisfactory simulated by using the proposed model.

3.4. Bioactive compounds and antioxidant activity determinations

With the aim of evaluating the effects of processing on the bioactive compounds of beetroot, betaxanthins content (BXC), betacyanins content (BCC), total polyphenol content (TPC) and antioxidant activity (AA) were determined in raw and pre-frozen samples before and after convective drying. To achieve a more complete view, three methods were used to evaluate the antioxidant activity (AA) of the samples: FRAP, CUPRAC and ABTS analyses. Due to the fact that

each method is based on a different chemical system and/or reaction, different results of AA could be expected depending on the method used (González-Centeno et al., 2012). The selection of different methods allows a better understanding of the wide variety and range of action of antioxidant compounds present in beetroots.

Figure 5 shows betaxanthins (figure 5 a), betacyanins (figure 5 b) and the total polyphenol (figure 5 c) contents, of raw and pre-frozen beetroot cubes before and after drying with and without ultrasound application as averages and standard deviations. Figure 6 shows the antioxidant activity (measured by FRAP (figure 6 a), CUPRAC (figure 6 b) and ABTS (figure 6 c) methods) of beetroot cubes before and after drying with and without ultrasound application as averages and standard deviations. Both freezing pre-treatment and ultrasound application exhibited significant effects ($p<0.05$) on BC, TPC and AA (FRAP, CUPRAC and ABTS methods). Therefore, Tukey's multiple range test analysis was carried out considering all samples simultaneously. Results of the Tukey's multiple range test analysis are also shown with different lowercase letters in the same figure when samples are significantly different at a significance level of $p<0.05$.

Initial values of raw beetroot (R) were of 2.34±0.03 mg IE/g dm, 2.34±0.17 mg BE/g dm, 6.5±0.2 mg GAE/g dm and 13.4±0.4, 31.5±0.9 and 19.1±1.0 mg TE/g dm of BXC, BCC, TPC and AA according to FRAP, CUPRAC and ABTS methods, respectively. These initial values were in the range of those proposed by Wruss et.al. (2015) for seven beetroots varieties: 1.5±0.2-2.4±0.3 mg IE/g dm for BXC, 2.3±0.2-3.9±0.5 mg BE/g dm for BCC, 4.1±0.7-6.3±0.9 mg GAE/g dm for TPC and 21.1±4.9-45.0±7.5 mg TE/g dm for the AA (FRAP method). BXC, BCC, TPC and AA according to FRAP method of frozen samples significantly ($p<0.05$) increased about 57, 57, 16 and 37% compared to raw sample (R). Freezing pre-treatment seemed to affect the beetroot cell structure accelerating the reaction between different substances to generate free forms. Similar behavior has been previously observed in the total polyphenol content (59% increase) of black garlic after freezing pre-treatment at −18 °C (Li, Lu, Pei, & Qiao, 2015) and in the total polyphenol content and antioxidant activity (FRAP method) (30 and 18% increase) of broccoli florets after freezing at −26 °C (Cai et al., 2016). However, no significant changes (less than 4%) were observed in the AA of the frozen sample (F) in comparison to the raw sample (R) according to CUPRAC and ABTS methods.

After the drying process, BXC, BCC, TPC and AA of the R0 sample decreased in comparison to the initial values (R sample) by 47%, 54%, 10% and 13±5% (according to FRAP, CUPRAC and ABTS methods), respectively. Convective drying process caused an intensive oxidation that occurred during long exposition to hot air. Betacyanins and betaxanthins, are sensitive pigments to temperature as it has been demonstrated previously by Fernández-López & Almela (2001) with prickly pear fruits. Therefore, convectively dried samples exhibited lower antioxidant compounds than raw sample. Moreover, convective drying process seemed to destroy beetroot antioxidant compounds as it has been reported by Figiel (2010) when beetroot was dried at 60 °C and 1.8 m/s. At this study, beetroot cubes antioxidant activity (measured by FRAP method) decreased a 29% after drying process, comparing to raw sample. Regarding pre-frozen sample after the drying process (F0), BXC, BCC, TPC and AA decreased in comparison to the initial values (R sample) by 58%, 61%, 28% and 47±8% (according to FRAP, CUPRAC and ABTS methods), respectively. No significant differences were observed in the final

betaxanthins and betacyanins contents between R0 and F0 samples. Thus, as a result, betalain content of beetroot cubes after drying was not modified when samples were pre-frozen before drying. However, TPC and AA according to FRAP, CUPRAC and ABTS methods of the pre-frozen sample (F0) significantly decreased in comparison to R0 sample.

Significant effects ($p < 0.05$) of the use of ultrasounds during drying on the BXC, BCC, TPC and AA of beetroot were observed in the case of the raw samples. When ultrasound energy was applied to drying at 16.4 kW/m^3 (R1 sample) and 26.7 kW/m^3 (R2 sample) of acoustic density, BXC, BCC, TPC and AA decreased by 68-72%, 73-81%, 43-51% and 39±6-55±3% (according to FRAP, CUPRAC and ABTS methods), respectively. No significant differences were observed between BXC and BCC of R1 and R2 samples. Therefore betalain content of beetroot cubes when ultrasounds were applied during drying was not modified at the two acoustic densities tested. However, significant differences between R1 and R2 samples TPC and AA were observed. Thus the ultrasound application promoted higher TPC and AA losses, mainly when the highest acoustic density (26.7 kW/m^3) was applied. These results could be related to the cellular damage induced by the combination of the drying temperature and the ultrasound application. Similar behavior was observed in drying of apple at 70 °C and 1 m/s of air velocity. TPC loss was higher (39% of loss) when the higher acoustic density tested was applied (30.8 kW/m^3) (Rodríguez et al., 2014).

Similarly, in the case of pre-frozen samples (F1 and F2), the use of ultrasounds promoted significant effects ($p < 0.05$). Higher BXC, BCC, TPC and AA decreases in comparison to the initial values (R sample) were observed when ultrasound energy was applied to drying of pre-frozen samples at 16.4 kW/m^3 (F1 sample) and 26.7 kW/m^3 (F2 sample) of acoustic density: 71-76%, 70-79%, 56-50% and 55±2-56±7% (according to FRAP, CUPRAC and ABTS methods), respectively. No significant differences were observed between BXC and BCC of F1 and F2 samples, although significant differences between F1 and F2 samples TPC and AA were observed. TPC and AA (FRAP method) were significantly higher at F2 sample than at F1 sample. Thus, when samples were pre-frozen, TPC, BXC, BCC and AA (FRAP method) were preserved when drying was carried out at the highest acoustic density tested: 26.7 kW/m^3, probably due to hot air exposition time reduction since polyphenols, betaxanthins and betacyanins are sensitive pigments to temperature. Similar behavior has been observed at beetroot cubes drying at 60 °C and 1.8 m/s when powers of 240 and 480W vacuum-microwave were applied. Antioxidant activity (measured by FRAP method) was preserved when vacuum-microwave power was applied during drying because thermal degradation was decreased due to hot air exposure time reduction (Figiel, 2010). However, higher losses of F2 than F1 were observed in AA in comparison to the raw sample (R) according to the CUPRAC and ABTS methods.

4. CONCLUSIONS

Significant microstructural changes were observed after freezing pre-treatment and after drying with and without ultrasound application. Also, disruptions and fissures on beetroot tissues were more extensive when samples were pre-frozen and drying was carried out by using ultrasounds. Drying time of beetroot decreased when ultrasounds were applied during drying (36-43% decrease) and also when samples were frozen before drying without (46% decrease) or with ultrasound application (55-58% decrease). Thus, both pre-freezing and

ultrasound application during drying enhanced the mass transfer and reduced the drying time a maximum of 58% for 26.7 kW/m^3 of acoustic density. By using a diffusional model, taking into account both the external and the internal mass transfer resistances, the drying curves without and with ultrasound application, of raw and pre-frozen beetroot cubes were satisfactorily simulated (average MRE was of 2.9±0.9%). Ultrasound application during drying induced important increases in both the effective diffusion (60 and 73% increases with respect to raw sample (R) when an acoustic densities of 16.4 kW/m^3 (R1) and 26.7 kW/m^3 (R2) were applied) and the external mass transfer (28 and 49% increases with respect to raw sample (R) when an acoustic densities of 16.4 kW/m^3 (R1) and 26.7 kW/m^3 (R2) were applied) coefficients, meanwhile freezing pre-treatment induced increases only in internal coefficient (158% increases with respect to raw sample (R) for frozen sample (F0)). Therefore, not only freezing pre-treatment but also ultrasound application was suitable for the intensification of the drying kinetics of beetroot. With regard to the effects of processing on the bioactive compounds of beetroot, important effects of freezing pre-treatment, convective drying and ultrasound application on the total polyphenol content, betalain content and antioxidant activity of beetroot were observed. While freezing promoted significant increases in the TPC (16%), BC (57%) and AA (37% according to FRAP method), probably due to the release of free forms of active compounds from the food matrix, drying exhibited the opposite effect (10-28% decrease in TPC, 47-61% in BC and 8-52% in AA). Moreover, when ultrasounds were applied during drying, decreases were higher (43-56% in TPC; 68-81% in BC; 32-61% in AA). Thus, although freezing pre-treatment and ultrasound application during drying could be used to increase the mass transfer rate, processing can affect the bioactive compounds stability and availability.

5. ACNOWLEDGMENTS

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Table 1.Identified figures for the external mass transfer (h_m) and the effective diffusion (D_e) coefficients, mean relative error (MRE) and percentage of explained variance (% var) obtained by comparison between the experimental and simulated drying curves of beetroot at 40 °C and 1 m/s.

SAMPLE			h_m (10^{-4}kg/m^{2}s)	D_e (10^{-10}m^2/s)	MRE (%)	var (%)
Without Ultrasound	Raw	R0	2.18±0.03	3.07±0.13	3.0±0.2	99.9±0.1
	Frozen	F0		7.93±0.40	2.8±0.2	99.9±0.1
Ultrasound (16.4 kW/m^3)	Raw	R1	2.79±0.04	4.92±0.24	1.8±0.1	99.9±0.1
	Frozen	F1		9.32±0.34	2.3±0.1	99.9±0.1
Ultrasound (26.7 kW/m^3)	Raw	R2	3.24±0.04	5.32±0.26	4.7±0.3	99.7±0.1
	Frozen	F2		9.54±0.37	2.6±0.2	99.9±0.1

Figure 1. Light microscope photographs of raw (R), pre-frozen (F) and dried beetroot cubes at 40 °C and 1m/s , without (0) and with ultrasound application at 16.4 kW/m^3 (1) and 26.7 kW/m^3 (2): R, R0, R1, R2, F, F0, F1, and F2. Legend: is= intercellular spaces, s=shrinkage, f=fissure, d=disruptions, m=micro-channels

Figure 2. Drying curves of raw (R) and pre-frozen (F) beetroot cubes at 40 °C and 1m/s, without (0) and with ultrasound application at 16.4 kW/m^3 (1) and 26.7 kW/m^3 (2). Average value± standard deviation.

Figure 3. Variation of mass flux vs average moisture content during convective air-drying (40 °C, 1 m/s) of raw (R) and pre-frozen (F) beetroot cubes without (0) and with ultrasound application at 16.4 kW/m^3 (1) and 26.7 kW/m^3 (2). Average value± standard deviation.

Figure 4. Predicted vs. experimental average moisture content. Drying experiments carried out with raw (R) and pre-frozen (F) beetroot cubes at 40 °C and 1m/s, without (0) and with ultrasound application at 16.4 kW/m^3 (1) and 26.7 kW/m^3 (2).

Figure 5. Total polyphenol (a), betaxanthins (b) and betacyanins (c) contents (mg GAE or IE or BE/g dm) of raw (R;---) and pre-frozen (F;—) beetroot cubes and dried at 40 °C and 1m/s , without (0) and with ultrasound application at 16.4 kW/m^3 (1) and 26.7 kW/m^3 (2). Average value± standard deviation. Means with different letter for total polyphenol or betaxanthins or betacyanins contents show significant differences according to Tukey's test ($p<0.05$).

Figure 6. Antioxidant activity (AA): FRAP (a), CUPRAC (b) and ABTS (c) methods of raw (R;---) and pre-frozen (F;—) beetroot cubes and dried at 40 °C and 1m/s , without (0) and with ultrasound application at 16.4 kW/m^3 (1) and 26.7 kW/m^3 (2) (mg TE/g dm). Average value± standard deviation. Means with different letter for antioxidant activity show significant differences according to Tukey's test ($p<0.05$)
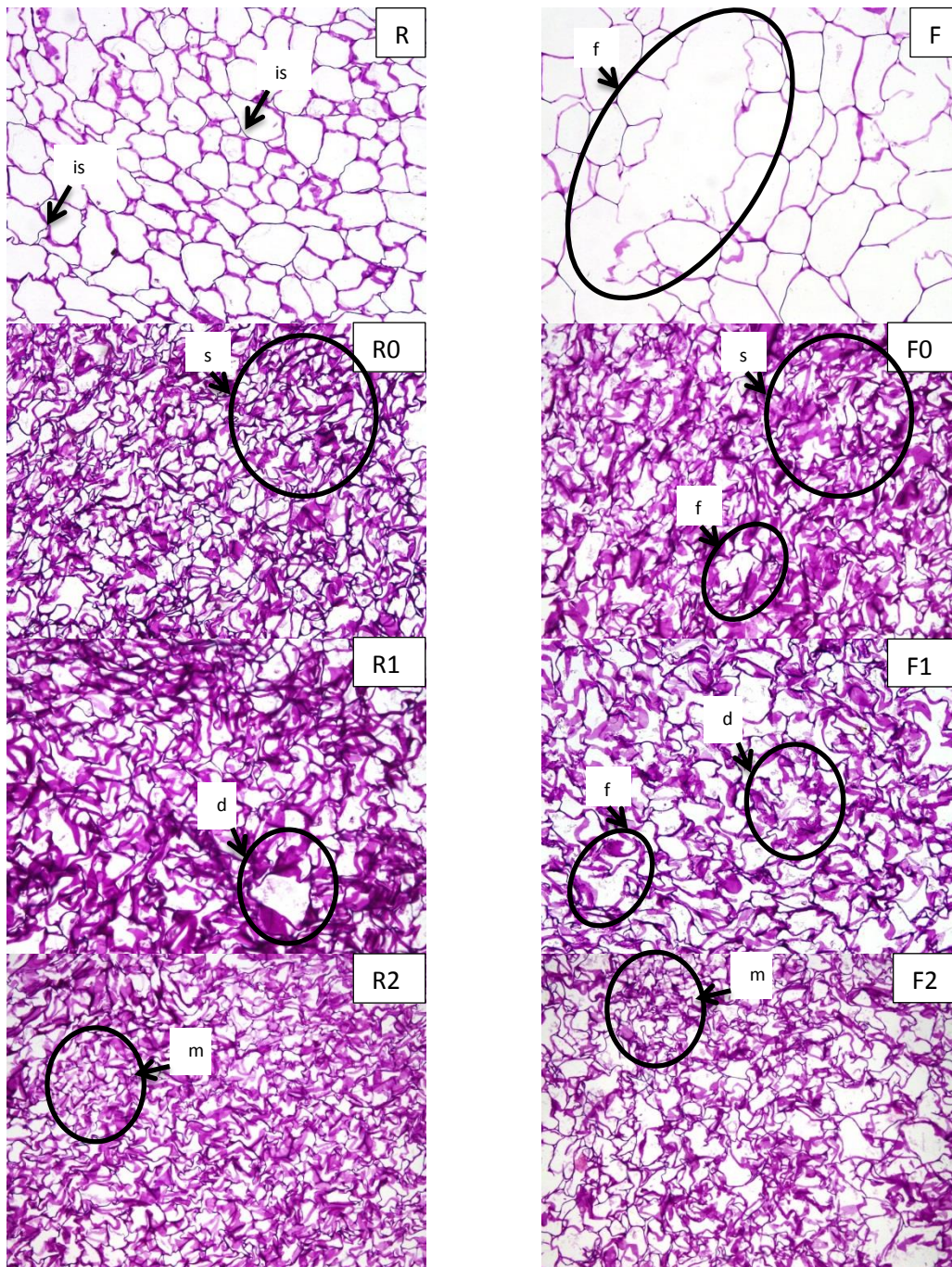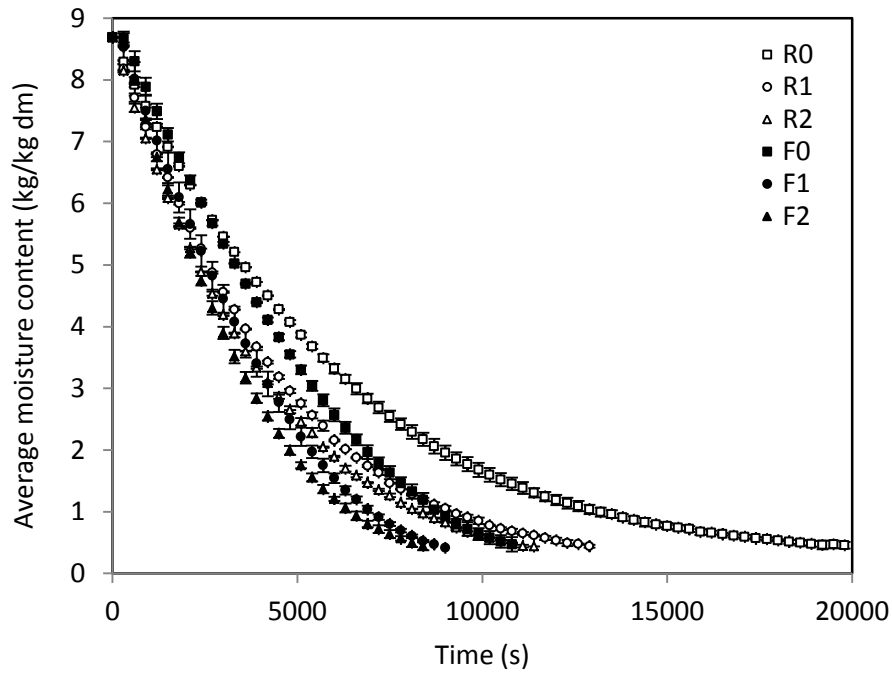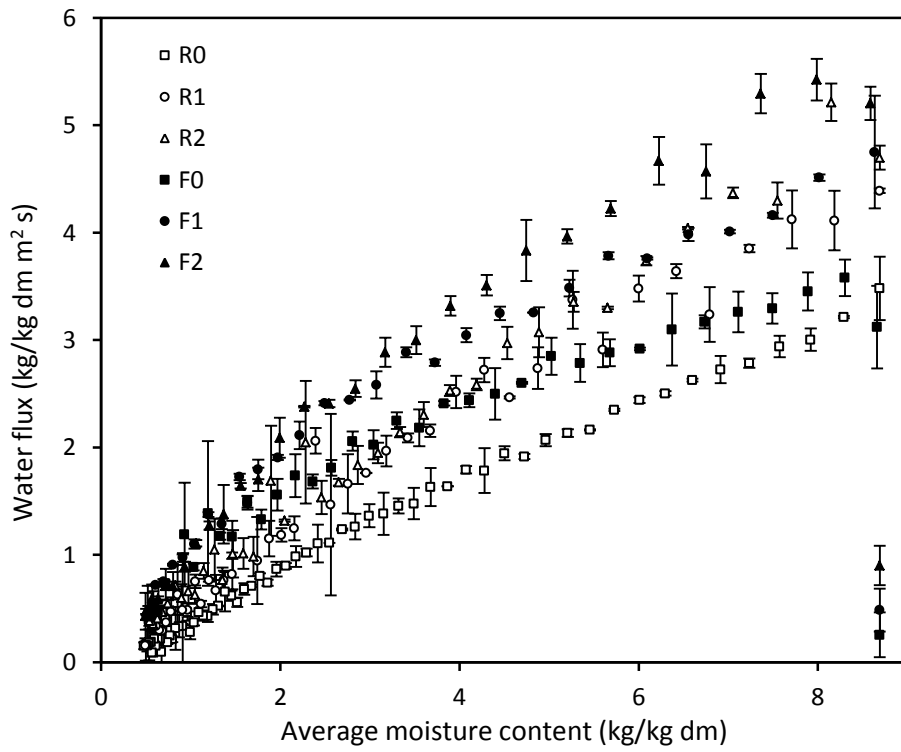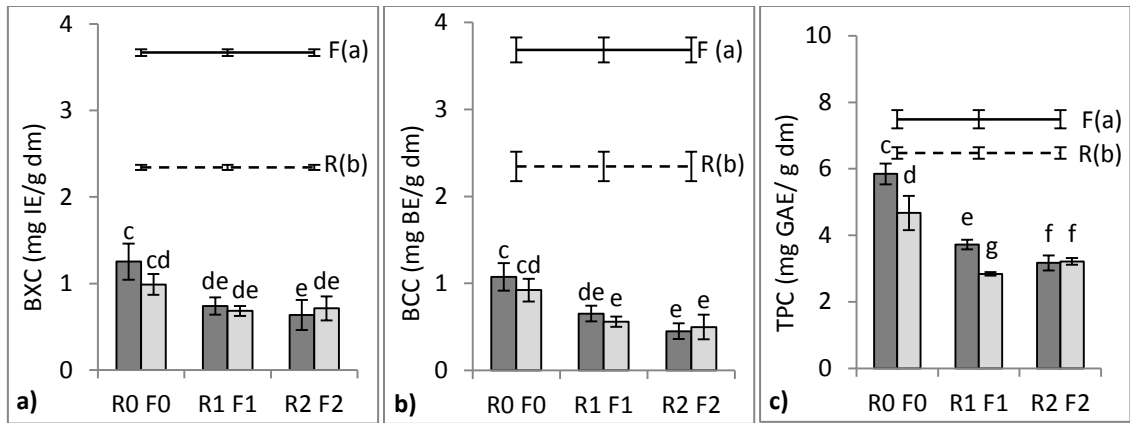
Figure 1

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Figure 6