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Abstract: Osmotic dehydration is a widely used preservation technique that consists in the reduction in food water activity by the immersion of the biological tissue in hypertonic solutions. The aim of this work was to analyze the effect of Pulsed Electric Fields in mass transfer as a pre-treatment of the OD using NMR. In this sense, PEF pre-treatments were done using three different voltages (100,250 and 400 V/cm) and 60 number of pulse. The OD of kiwifruit was carried out in 61.5% of sucrose solution at 25°C, for a contact period from 0 to 120min. The water distribution into the cellular tissue was studied by NMR relaxometry. In conclusion, NMR is an excellent technique for quantifying water molecules according to their interactions in the fruit tissue, obtaining the adsorbed water and opening the possibility to apply the BET model to fit the adsorbed isotherm over the whole range of water activity.

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OSMOTIC DEHYDRATION OF ORGANIC KIWIFRUIT PRE-TREATED BY PULSED ELECTRIC FIELDS AND MONITORED BY NMR

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ABSTRACT

Osmotic dehydration (OD) is a widely used preservation technique that consists in the reduction in food water activity by the immersion of the biological tissue in hypertonic solutions. The aim of this work was to analyze the effect of Pulsed Electric Fields (PEF) in mass transfer as a pre-treatment of the OD using NMR. In this sense, PEF pre-treatments were done using three different voltages (100, 250 and 400 V/cm) and 60 number of pulse. The OD of kiwifruit was carried out in 61.5% of sucrose solution at 25 ºC, for a contact period from 0 to 120 min. The water distribution into the cellular tissue was studied by NMR relaxometry. In conclusion, NMR is an excellent technique for quantifying water molecules according to their

interactions in the fruit tissue, obtaining the adsorbed water and opening the possibility to apply the BET model to fit the adsorbed isotherm over the whole range of water activity.

Keywords: Kiwifruit, Pulsed Electric Fields, Osmotic dehydration, TD-NMR, Water distribution.

1. Introduction

Kiwifruit is well known as a source of vitamin C besides its high levels of fiber, minerals, antioxidants and other bioactive substances that present beneficial effects on health (Diamante, Savage, & Vanhanen, 2012). It is constituted by three distinct types of tissues: outer pericarp, inner pericarp and core, which have structural and compositional differences (Castro-Giráldez, Tylewicz, Fito, Dalla Rosa, & Fito, 2011a).

Osmotic dehydration (OD) is a conservation process commonly used to increase the shelf-life of fruits. It consists in the immersion of the biological tissue in a hypertonic solution, which generates fluxes of water and solutes and, as a consequence, the water activity of the product is reduced (Moraga, Moraga, Fito, & Martínez-Navarrete, 2009). From a thermodynamic point of view, the difference in the chemical potentials (water and sucrose) between the sample and the dipping solution promotes the water release from the fruit to the osmotic solution and the simultaneous solutes inflow from the external solution to the fruit (Castro-Giráldez, Fito, & Fito, 2011b). In order to increase yields and to reduce processing times, different techniques coupled to OD treatment have been studied, such as ultrasound (Ahmed, Qazi, & Jamal, 2016; Nowacka, Tylewicz, Laghi, Dalla Rosa, & Witrowa-Rajchert, 2014; Li, Zhao, Guo, An, Ding, & Wang, 2012), pulsed-vacuum (Corrêa, Pereira, Vieira, & Hubinger, 2010; Rastogi, Raghavarao, Niranjan, & Knorr, 2002) and pulsed electric fields (Wiktor, Śledź, Nowacka, Chudoba, & Witrowa-Rajchert, 2014; Amami, Vorobiev, & Kechaou, 2006).

Pulsed electric fields (PEF) is a non-thermal and preservation technology which consists in applying electric pulses through a biological tissue placed between two electrodes for very short periods of time (micro- to milli-seconds) (Dellarosa, Ragni, Laghi, Tylewicz, Rocculi, & Dalla Rosa, 2016; Faridnia, Burritt, Bremer, & Oey, 2015; Toepfl, Heinz, & Knorr, 2005), causing structural changes in the cell membrane (Angersbach, Heinz, & Knorr, 2000). This phenomenon could be classified as electroporation or electrocompression and according to the electric field strength they could be reversible or irreversible. Electroporation is produced when the external electric field induces conformational changes and the reorganization of the phospholipidic bilayer, generating pores (Liu, Han, Zeng, Sun, & Aadil, 2016; Baier, Bußler, & Knorr, 2015). On the other hand, the electrocompression is produced due to the charges (electrolytes) accumulation at both sides of the cell membrane, which attracts each other, compressing it. When this compression exceeds the elastic restoration force, the disruption of the membrane is produced generating pores (Traffano-Schiffo, Tylewicz, Castro-Giraldez, Fito, Ragni, & Dalla Rosa, 2016; Saulis, 2010; Calderón-Miranda, González, Barbosa-Cánovas, & Swanson, 1998).

In a previous work about the use of a coupled treatment (PEF/OD) in organic kiwifruit (Traffano-Schiffo el at., 2016) it has been demonstrated that water losses have increased and accelerated compared to samples which had not been pretreated with PEF. In addition, it has been demonstrated that the pulse electric field produces electrolytes mass losses, affecting the active transmembrane transports, inducing changes on the overall transport. However, this study could not explain the water distribution inside the cell and the internal transports. Due to this, Time Domain

Nuclear Magnetic Resonance (TD-NMR) represents a valuable tool able to study the redistribution of the water during sample processing (Santagapita, Laghi, Panarese, Tylewicz, Rocculi, & Dalla Rosa, 2013), the state of the cell membranes disruption, protoplast and tonoplast (Aguiló-Aguayo, Downey, Keenan, Lyng, Brunton, & Rai, 2014) and the block of water and sucrose active pumps due to the electric pulses (Traffano-Schiffo el at., 2016).

TD-NMR is a fast, non-destructive and non-invasive technique able to determine the relaxation times parameters, such as the spin-lattice or longitudinal relaxation (T_1) and the spin-spin or transverse relaxation (T_2) of protons differentiating vacuoles, cytoplasm/extracellular spaces and cell wall (Santagapita, Tylewicz, Panarese, Rocculi, & Dalla Rosa, 2016; Tylewicz et al., 2011). Panarese, Laghi, Pisi, Tylewicz, Dalla Rosa, & Rocculi, (2012) were able to separately observe, in the pericarp of kiwifruit, water located in extracellular spaces and cytoplasm, water located in vacuole and protons ascribable to water tightly bound to the most rigid biopolymers.

The aim of this work was to analyze the effect of PEF used as a pre-treatment of the OD of organic kiwifruit (*Actinidia deliciosa cv Hayward*) in water redistribution by NMR.

2. Material and methods

Organic kiwifruits (*Actinidia deliciosa cv Hayward)* with the same ripeness and similar size were bought on a supermarket located in Cesena (Italy) and kept refrigerated at 4 ± 1 ºC until use. The fruits were tempered at 25 ºC, peeled and cylinders (8 mm diameter and 10 mm length) were obtained from the parenchymatic

part of the tissue. The initial refractometric indexes (º Brix) of the fruits used were 13 ± 1 ºBrix.

Fresh kiwifruits were characterized by mass, volume, soluble solids content (ºBrix), water activity (a_w), moisture (kg_w/kg_T) and TD-NMR by quadruplicate. 12 sample cylinders were used for each treatment (considering all OD times and the triplications for each measurement, the total number of treated samples was 576). They were placed inside the PEF chamber avoiding free spaces between them and subjected to different electric fields strengths (12 extra samples were used as control, without PEF-treatment). After, the samples were weighed and introduced into the osmotic dehydration solution. According to previous results, the selected OD treatment times were 0, 10, 20, 30, 60 and 120 minutes (Traffano-Schiffo et al., 2016).

Due to the fact that the samples after treatments show concentration profiles (non-equilibrated samples), another batch of samples were treated and reposed at 4 ºC during 24 hours in decagon containers closed with parafilm® (equilibrated samples). Finally, mass, volume, soluble solids, a_w, soluble solids content and TD-NMR were measured as final determinations for non-equilibrated and equilibrated samples. In addition, at each osmotic time, an aliquot of sucrose solution was taken to measure a_w and soluble solids content.

2.1. Pulsed electric field (PEF) treatment

Pulsed electric field treatments were applied to the samples using monopolar pulse generator equipment based on MOSFET technology and capacitors as energy tanks (Dellarosa et al., 2016). The cylinders of organic kiwifruit were placed in a

rectangular treatment chamber equipped with two stainless steel electrodes (20 x 20 mm^2) with a separation between them of 30 mm and filled with 5 mL of tap water with known conductivity at 25 ºC.

PEF pre-treatments were done by applying three different pulsed electric fields (100, 250 and 400 V/cm at 50 Hz) with near-rectangular shape pulses, a train of 60 pulses, a fixed pulse width of 100 ± 2 μs and a repetition time of 10.0 ± 0.1 ms.

2.2. Osmotic dehydration treatment

The osmotic solution at 61.5% (w/w) was prepared with commercial sucrose (Eridana SpA, Bologna, Italia) and distilled water at 25 ºC. Samples were immersed into the sucrose solution maintaining a relationship of 1:4 (w/w) between the fruit and the solution.

2.3. Analytical determinations

A dew point Hygrometer Decagon (Aqualab™, series 3 TE) was used for measuring the water activity (a_w), with a precision ± 0.003. Mass was determined by using a Kern balance ABS 320-4N (±0.0001) (KERN & SOHN GmbH, Germany).

Volume was determined by image analysis using Adobe® Photoshop® CS6 software (Adobe Systems Inc., San Jose, CA, USA). Moisture was determined following the AOAC Method 934.06, 2000.

Soluble solid content was determined by measuring the refractometric index with a digital refractometer (KRÜSS Optronic© GmbH, Germany) calibrated with distilled water at 25 ºC. Refractometric index was measured in both kiwifruit samples and agent solution after the treatment.

Analytical determinations described above were obtained by quadruplicate.

2.4. TD-NMR measurements

Proton transverse relaxation time (T_2) decay was measured for each sample by applying the CPMG pulse sequence (Meiboom & Gill, 1958), using a Bruker 'The Minispec' spectrometer (Bruker Corporation, Germany) operating at 20 MHz, as described by Dellarosa et al. (2016). Each measurement comprised 32000 echoes, with an interpulse spacing of 0.08 ms and a recycle delay of 10 s, which allowed the measurement of proton decays included between 1 and 3000 ms and avoided sample overheat. Each acquisition was performed over 8 scans giving rise to a total time of analysis around 90 s. The registered spectra were normalized to unitary area and analyzed by UpenWin software (Borgia, Brown, & Fantazzini, 1998) to give quasi-continuous distributions of relaxation time. The number of output relaxation times, sampled logarithmically in the 1–3000 ms range, was set to 100. To obtain quantitative information from the T_2-weighted decay curves, signals were fitted using a discrete multi-exponential curve. The fitting was run using the 'Levenberg–Marquardt nonlinear least squares' algorithm implemented in 'R' software (R Foundation for Statistical Computing, Austria). Unlike Santagapita et al. (2013), the optimum number of exponential curves for each tested treatment was found to be three, without removing any initial T_2 weighted point.

2.5. Desorption isotherm

The desorption isotherm of the adsorbed water was fitted following the BET model using equation 1 (Brunauer, Emmett, & Teller, 1938).

$$X_w^{ADS} = \frac{X_{w0} C\, a_w}{(1- a_w)(1+(C-1)\, a_w)} \quad (1)$$

Where: X_w^{ADS} corresponds to the kiwifruit adsorbed moisture (kg_w/kg_{dm}), X_{w0} is the monomolecular moisture layer (kg_w/kg_{dm}) and C is the energy constant (dimensionless). BET model was fitted by using a non-linear regression with the Statgraphics Centurion XVI software (Statgraphics, Virgina, U.S.A.).

3. Results and discussion

During the osmotic treatments, kiwifruit suffers mass variations which involve the water losses and the sucrose gain. Each chemical specie involved in the osmotic dehydration treatment has different driving forces and ways to move into the cell system. Particularly, water fluxes can be generated by passive and active transports. Passive transport is driven by water chemical potential gradients and it could be produced outside the cells by the apoplastic pathways (Steudle, & Frensch, 1996), through transmembrane protein channels by the aquaporins (Agre, Bonhivers, & Borgnia, 1998) and across the plasmodesmata channels between cells by the symplastic pathways. On the other hand, active transmembrane transport is produced by Ca^{2+} pump and requires energy as ATP. In case of high water stress, the homeostatic cell system counteracts the water losses by the aquaporins introducing water in cell by calcium pump (Moraga et al., 2009). Transmembrane transports (active or passive) are affected by the quantity of water molecules adsorbed in the membrane, especially in treatments with high water liquid phase (Fito, Fito, Betoret, Argüelles & Chenoll, 2011).

In Figure 1 it is possible to observe the relation between moisture expressed in dry matter and the surface water activity, for equilibrated and non-equilibrated samples

pre-treated at different intensities of pulsed electric field. Taking into account that moisture is an average value of the whole sample and the water activity is a surface value, the non-equilibrated samples are far from the sucrose pure solution curve because they have concentration profiles, however, the equilibrated samples will approximate to the pure sucrose solution curve as a function of the amount of water that they have in liquid phase.

The equilibrated samples seem to be ordered as a function of the intensity of the pretreatment, observing that the higher the pre-treatment the less quantity of water in the liquid phase the samples present.

In order to know the water distribution and to quantify the amount of water molecules that are not in liquid phase, NMR measurements have been performed.

Figure 2a shows an example of the distribution of T_2-weighted signals obtained by TD-NMR in parenchyma tissue of fresh and pre-treated with PEF at 250 V/cm kiwifruit. Three protons population observed in the non pre-treated samples presented T_2 of 1170, 425, and 53 ms. Moreover, Figure 2b shows the intensity (area of distribution T_2-weight) by the T_2 for each molecular water group and pre-treatment. The smaller the T_2, the lower the mobility of the water molecule, for this reason it is possible to determine the origin of each group of molecules in function of the different motion capacity that the water molecules have in the tissue.

The lower value of T_2 corresponds to water molecules with less mobility, in this group most of water molecules in parenchyma tissue are the molecules subjected to electrical adsorption forces. This group is adsorbed on the cell wall and on the cell membrane (protoplast and tonoplast). The remaining groups might correspond to the different liquid phases that make up the parenchyma, from the interior of the cell

mostly occupied by the vacuole (higher T_2 and higher intensity), to the cytoplasm and external liquid phase or intra liquid phase produced in the plasmolization process (intermediate T_2).

PEF treatment caused, for each of the intensities applied, a decrease of average T_2 of vacuole and cytoplasm protons populations. Chemical exchange between water (with a T_2 around 2s) and exchangeable sites of the biopolymers of the structures (with a T_2 of milliseconds) dominates T_2 of these protons populations, as demonstrated for kiwifruit (Panarese et al., 2012) and other fruits (Mauro et al., 2016). The simultaneous shortening of the T_2 of both compartments suggests therefore that in both cases exchangeable protons of carbohydrates induced increase their contribution to the overall protons populations upon PEF treatment, but in minimum sense considering negligible. It is worth noticing that the T_2 decrease was not proportional to the voltage applied, with 100 V/cm giving rise to marginal modifications, and the stronger treatments giving rise to similar and much higher T_2 decreases. The T_2 of each group does not converge to the same value, this suggests that the liquid phase of samples are not mixed, remaining in each compartment.

It is possible to define a proportionality variable to describe the relation between the intensity of each group of water molecules and overall measured intensity; this relation follows the next equation:

$$r_I^j = \frac{I_j}{I_T} \quad (2)$$

Where r_I^j is the relative intensity of water group j (1: water adsorbed; 2: external liquid phase, 3: vacuole liquid phase), I_j is the intensity of water group, and I_T is the overall measured intensity.

Figure 3 shows the relative intensity along osmotic treatment for the samples treated with increasing PEF voltage (non-equilibrated and equilibrated samples). Non-equilibrated samples show the state of the three populations of water just after the osmotic dehydration process when the samples present internal profiles; the equilibrated samples show the distribution of water populations when the transports have finished. On the other hand, samples skipping PEF treatment allow observing the fate of the three populations upon osmosis only, while Santagapita et al. (2013) showed that the cell wall population was poorly affected by osmotic treatment. In the present work it reached a relative intensity around 20-25% and, consequently, confirming the contribution from extracellular protons suggested by the data obtained with no osmosis applied.

As it is described by some authors (Lauffer, 1987; Otting & Wuethrich, 1989; Tsukahara, Hibara, Ikeda, & Kitamori, 2007), the intensity is proportional to the induced protons. When induction occurs at a fixed frequency that only affects the protons of a specific molecule, in this case water, the intensity is proportional to the overall number of water molecules present in the tissue. Therefore, the relative intensity will be a parameter of proportionality of the water mass distribution, and the distribution of water will follow the next equation:

$$x_w^j = x_w \cdot r_I^j \quad (3)$$

Where x_w^j is the water mass fraction of water group j ($kg_{w\ in\ j}/kg_T$) and x_w is the water mass fraction (kg_w/kg_T). Thus, it is possible to segregate the low mobility water molecules, adsorbed to the surface of the cell matrix, from the rest of water molecules, as follows:

$$X_w^{ADS} = X_w \cdot r_I^1 \quad (4)$$

285 Where X_w^{ADS} is the adsorbed moisture expressed in dry matter (kg_w/kg_{dm}) and X_w is
286 the moisture expressed in dry matter (kg_w/kg_{dm}).
287 Figure 4 shows the adsorbed moisture of kiwifruit samples at different PEF pre-
288 treatment with regard to the surface water activity. It is possible to observe that PEF
289 pre-treatment produces an increase of adsorbed moisture and a reduction of the water
290 activity. This is because the electric field increases the surface electrical energy of
291 the cell membrane (protoplast and tonoplast) and the cell wall, increasing the surface
292 free energy available for molecular adsorption. This means that the number of layers
293 of adsorbed water molecules increased, reducing the number of water molecules in
294 the liquid phase. For this reason, increasing adsorbed moisture reduces water
295 activity.
296 The moisture and relative intensity were measured after the treatment (non-
297 equilibrated samples) and in equilibrium, thus, the adsorbed moisture of the non-
298 equilibrated samples may undergo variations due to the internal water chemical
299 potential gradients. Nevertheless, the adsorbed moisture of the equilibrated samples
300 may be valid to obtain the sorption isotherm fitted by BET model in the whole range
301 of water activity.
302 Figure 5 shows the adsorbed moisture with regard to the surface water activity for
303 equilibrated samples fitted by BET model. The correlation coefficients (R^2) obtained
304 adjusting the BET model for each PEF treatment (0, 100, 200 and 400 V/cm) were
305 0.90, 0.96, 0.92, 0.91 respectively. Moreover, it is possible to observe how the
306 samples are sorted in function of the pre-treatment.
307 From the adsorbed moisture fitting by BET model, it is possible to obtain two
308 parameters with physic sense: the moisture monomolecular layer (X_{w0}) related with

the minimum water adsorbed in the surface of matrix and the C parameter related with the isosteric heat by next equation (Labuza & Altunakar, 2007):

$$Q_c = RT \ln C \quad (5)$$

Where Q_c is the isosteric heat of sorption (kJ/mol), R is ideal gas constant (J/mol K) and T is absolute temperature (K).

Figure 6 shows the moisture monomolecular layer and the isosteric heat with regard the electric field applied throughout the tissue. As the figure shows, the electric field charges the surface of the tissue increasing its energy of adsorption or isosteric heat. This fact produces an addition amount of water adsorbed and, therefore, a hydration of the tissue. This induces a reduction of water in the liquid phase and changes in the transmembrane transport mechanisms that are shown in an increase of the water fluxes during the osmotic treatment.

Therefore, the use of NMR to quantify the water distribution in the tissue allows estimating the sorption isotherms of the absorbed moisture in the whole range of water activities; this allows quantifying the electrical energy stored in the tissue in form of energy of adsorption.

4. Conclusions

NMR is a suitable technique for quantifying water molecules according to their situation in the fruit tissue. This technique allows us to obtain the adsorbed water and open the possibility to apply the BET model over the whole range of water activity. It has been demonstrated that the application of electric fields across the plant tissue causes a storage of electrical energy that is converted into free energy to attract and retain water molecules on the surface of membranes and cell walls.

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6. References

Agre, P., Bonhivers, M., & Borgnia, M. J. (1998). The aquaporins, blueprints for cellular plumbing systems. *Journal of Biological Chemistry*, 273(24), 14659-14662.

Aguiló-Aguayo, I., Downey, G., Keenan, D. F., Lyng, J. G., Brunton, N., & Rai, D. K. (2014). Observations on the water distribution and extractable sugar content in carrot slices after pulsed electric field treatment. *Food Research International*, 64, 18-24.

Ahmed, I., Qazi, I. M., & Jamal, S. (2016). Developments in osmotic dehydration technique for the preservation of fruits and vegetables. *Innovative Food Science & Emerging Technologies*, 34, 29-43.

Amami, E., Vorobiev, E., & Kechaou, N. (2006). Modelling of mass transfer during osmotic dehydration of apple tissue pre-treated by pulsed electric field. *LWT-Food Science and Technology*, 39(9), 1014-1021.

Angersbach, A., Heinz, V., & Knorr, D. (2000). Effects of pulsed electric fields on cell membranes in real food systems. *Innovative Food Science & Emerging Technologies*, 1(2), 135-149.

AOAC. (2000). AOAC, Association of Official Analytical Chemist Official Methods of Analysis. Washington, D.C.

Baier, A. K., Bußler, S., & Knorr, D. (2015). Potential of high isostatic pressure and pulsed electric fields to improve mass transport in pea tissue. *Food Research International*, 76, 66-73.

Borgia, G. C., Brown, R. J. S., & Fantazzini, P. (1998). Uniform-penalty inversion of multiexponential decay data. *Journal of Magnetic Resonance*, 132(1), 65-77.

Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American chemical society*, 60(2), 309-319.

Calderón-Miranda, M. L., González, M. F. S. M., Barbosa-Cánovas, G. V., & Swanson, B. G. (1998). Métodos no térmicos para procesamiento de alimentos: Variables e inactivación microbiana. *Brazilian Journal of Food Technology*, 1, 3-11.

Castro-Giráldez, M., Fito, P. J., & Fito, P. (2011b). Application of microwaves dielectric spectroscopy for controlling long time osmotic dehydration of parenchymatic apple tissue. *Journal of Food Engineering*, 104(2), 227-233.

Castro-Giráldez, M., Tylewicz, U., Fito, P. J., Dalla Rosa, M., & Fito, P. (2011a). Analysis of chemical and structural changes in kiwifruit (Actinidia deliciosa cv

Hayward) through the osmotic dehydration. *Journal of Food Engineering*, 105(4), 599-608.

Corrêa, J. L., Pereira, L. M., Vieira, G. S., & Hubinger, M. D. (2010). Mass transfer kinetics of pulsed vacuum osmotic dehydration of guavas. *Journal of Food Engineering*, 96(4), 498-504.

Dellarosa, N., Ragni, L., Laghi, L., Tylewicz, U., Rocculi, P., & Dalla Rosa, M. (2016). Time domain nuclear magnetic resonance to monitor mass transfer mechanisms in apple tissue promoted by osmotic dehydration combined with pulsed electric fields. *Innovative Food Science & Emerging Technologies*, 37, 345-351.

Diamante, L. M., Savage, G. P., & Vanhanen, L. (2012). Optimisation of vacuum frying of gold kiwifruit slices: application of response surface methodology. *International Journal of Food Science & Technology*, 47(3), 518-524.

Faridnia, F., Burritt, D. J., Bremer, P. J., & Oey, I. (2015). Innovative approach to determine the effect of pulsed electric fields on the microstructure of whole potato tubers: Use of cell viability, microscopic images and ionic leakage measurements. *Food Research International*, 77, 556-564.

Fito, P., Fito, P. J., Betoret, N., Argüelles, A. & Chenoll, C. (2011).Thermodynamic approach to equilibrium isotherms in salted structured food. *Journal of Food Process Engineering*, 34, 623–638.

Labuza, T. P., Altunakar, B. (2007). Water Activity Prediction and Moisture Sorption Isotherms. In G. V. Barbosa-Cánovas, A. J. Fontana, S. J. Schmidt, & T. P. Labuza (Eds.), *Water Activity in Foods: Fundamentals and Applications* (Vol. 109-154). Iowa, USA: IFT Press and Blackwell Publishing.

Lauffer, R. B. (1987). Paramagnetic metal complexes as water proton relaxation agents for NMR imaging: theory and design. *Chemical Reviews*, 87(5), 901-927.

Li, H., Zhao, C., Guo, Y., An, K., Ding, S., & Wang, Z. (2012). Mass transfer evaluation of ultrasonic osmotic dehydration of cherry tomatoes in sucrose and salt solutions. *International Journal of Food Science & Technology*, 47(5), 954-960.

Liu, Z. W., Han, Z., Zeng, X. A., Sun, D. W., & Aadil, R. M. (2016). Effects of vesicle components on the electro-permeability of lipid bilayers of vesicles induced by pulsed electric fields (PEF) treatment. *Journal of Food Engineering*, 179, 88-97.

Mauro, M. A., Dellarosa, N., Tylewicz, U., Tappi, S., Laghi, L., Rocculi, P., & Dalla Rosa, M. (2016). Calcium and ascorbic acid affect cellular structure and water mobility in apple tissue during osmotic dehydration in sucrose solutions. *Food Chemistry*, 195, 19-28.

Meiboom, S., & Gill, D. (1958). Modified spin-echo method for measuring nuclear relaxation times. *Review of Scientific Instruments*, 29(8), 688-691.

Moraga, M. J., Moraga, G., Fito, P. J., & Martínez-Navarrete, N. (2009). Effect of vacuum impregnation with calcium lactate on the osmotic dehydration kinetics and quality of osmodehydrated grapefruit. *Journal of Food Engineering*, 90(3), 372-379.

Nowacka, M., Tylewicz, U., Laghi, L., Dalla Rosa, M., & Witrowa-Rajchert, D. (2014). Effect of ultrasound treatment on the water state in kiwifruit during osmotic dehydration. *Food Chemistry*, 144, 18-25.

Otting, G., & Wuethrich, K. (1989). Studies of protein hydration in aqueous solution by direct NMR observation of individual protein-bound water molecules. *Journal of the American Chemical Society*, 111(5), 1871-1875.

426 Panarese, V., Laghi, L., Pisi, A., Tylewicz, U., Dalla Rosa, M., & Rocculi, P. (2012).
427 Effect of osmotic dehydration on Actinidia deliciosa kiwifruit: A combined NMR
428 and ultrastructural study. *Food Chemistry*, 132(4), 1706-1712.
429 Rastogi, N. K., Raghavarao, K. S. M. S., Niranjan, K., & Knorr, D. (2002). Recent
430 developments in osmotic dehydration: methods to enhance mass transfer. *Trends in*
431 *Food Science & Technology*, 13(2), 48-59.
432 Santagapita, P. R., Tylewicz, U., Panarese, V., Rocculi, P., & Dalla Rosa, M. (2016).
433 Non-destructive assessment of kiwifruit physico-chemical parameters to optimise the
434 osmotic dehydration process: A study on FT-NIR spectroscopy. *Biosystems*
435 *Engineering*, 142, 101-109.
436 Santagapita, P., Laghi, L., Panarese, V., Tylewicz, U., Rocculi, P., & Dalla Rosa, M.
437 (2013). Modification of transverse NMR relaxation times and water diffusion
438 coefficients of kiwifruit pericarp tissue subjected to osmotic dehydration. *Food and*
439 *Bioprocess Technology*, 6(6), 1434-1443.
440 Saulis, G. (2010). Electroporation of cell membranes: the fundamental effects of
441 pulsed electric fields in food processing. *Food Engineering Reviews*, 2(2), 52-73.
442 Steudle, E., & Frensch, J. (1996). Water transport in plants: role of the apoplast.
443 *Plant and Soil*, 187(1), 67-79.
444 Toepfl, S., Heinz, V., & Knorr, D. (2005). Overview of pulsed electric field
445 processing for food. In D. W. Sun (Ed.), *Emerging technologies for food processing*
446 (pp. 69–99). Oxford, UK: Elsevier.
447 Traffano-Schiffo, M. V., Tylewicz, U., Castro-Giraldez, M., Fito, P. J., Ragni, L., &
448 Dalla Rosa, M. (2016). Effect of pulsed electric fields pre-treatment on mass

449 transport during the osmotic dehydration of organic kiwifruit. *Innovative Food*
450 *Science & Emerging Technologies*, 38, 243-251.
451 Tsukahara, T., Hibara, A., Ikeda, Y., & Kitamori, T. (2007). NMR study of water
452 molecules confined in extended nanospaces. *Angewandte Chemie International*
453 *Edition*, 46(7), 1180-1183.
454 Tylewicz, U., Panarese, V., Laghi, L., Rocculi, P., Nowacka, M., Placucci, G., &
455 Dalla Rosa, M. (2011). NMR and DSC water study during osmotic dehydration of
456 Actinidia deliciosa and Actinidia chinensis kiwifruit. *Food Biophysics*, 6(2), 327-
457 333.
458 Wiktor, A., Śledź, M., Nowacka, M., Chudoba, T., & Witrowa-Rajchert, D. (2014).
459 Pulsed electric field pretreatment for osmotic dehydration of apple tissue:
460 Experimental and mathematical modeling studies. *Drying Technology*, 32(4), 408-
461 417.
462

FIGURE CAPTION

Figure 1. Relation of moisture in dry basis vs. surface water activity of treated samples; left plot: non-equilibrated samples; right plot: equilibrated samples, where: (▫) corresponds to no PEF (0 V/cm), (○) 100 V/cm, (Δ) 250 V/cm, (◊) 400 V/cm and (solid black line) pure sucrose solution.

Figure 2. a) T_2-weighted signal distribution, normalized to unitary area, registered on fresh samples treated by PEF at 0 (solid line) and 250 V/cm (dashed line). b) T_2 and intensity of the signals from vacuole, cytoplasm + extracellular space and cell wall + membrane protons at 0 (▫), 100 (○), 250 (Δ) and 400 (◊) V/cm for samples before OD treatment. For both T_2 and intensity, bars highlight standard deviation around mean.

Figure 3. Relative intensity of the three proton populations identified by TD-NMR for non-equilibrated and equilibrated samples, where: (▫) corresponds to no PEF (0 V/cm), (○) 100 V/cm, (Δ) 250 V/cm and (◊) 400 V/cm, being a) and d) vacuole, b) and e) cytoplasm and extracellular liquid phase, c) and f) cell wall and membrane.

Figure 4. Pre-treated fresh samples (without OD): where adsorbed moisture (■) and surface water activity (♦) at different PEF (V/cm) pre-treatments.

Figure 5. Adsorbed water content of equilibrated samples with regard to the surface water activity at different PEF pre-treatments, where experimental points (▫) 0 V/cm, (○) 100 V/cm, (Δ) 250 V/cm and (◊) 400 V/cm and calculated BET model (—) 0 V/cm, (— · —) 100 V/cm, (– –) 250 V/cm and (- -) 400 V/cm.

484 **Figure 6.** Relationship between the moisture monomolecular layer (X_{w0}) and the
485 Isosteric heat (Qc) with the PEF pre-treatment.
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487

Figure 1

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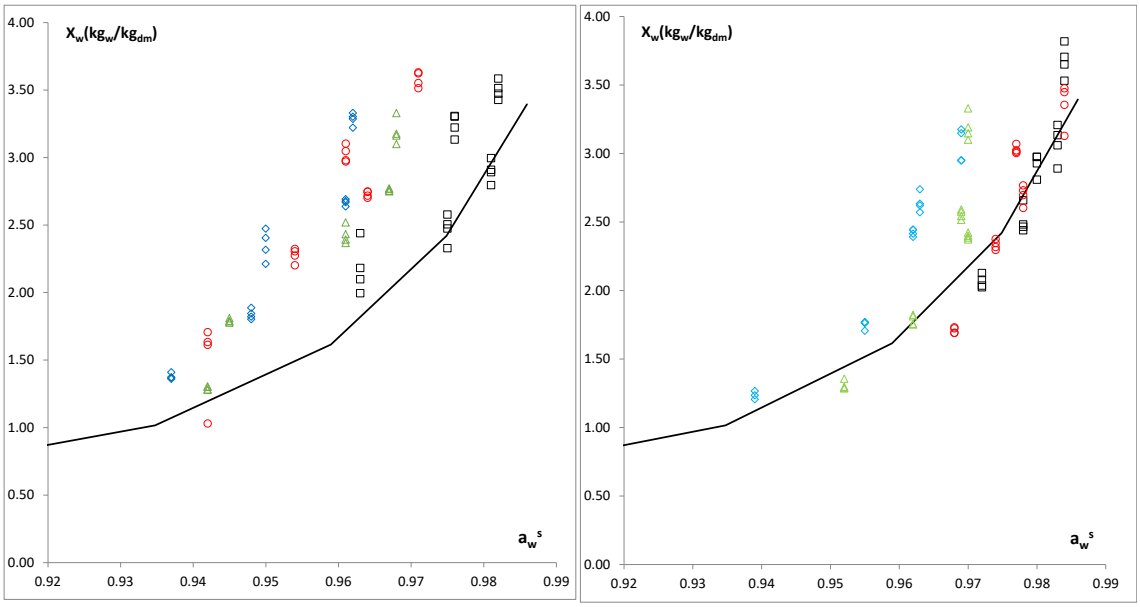

Figure 1.

Figure 2

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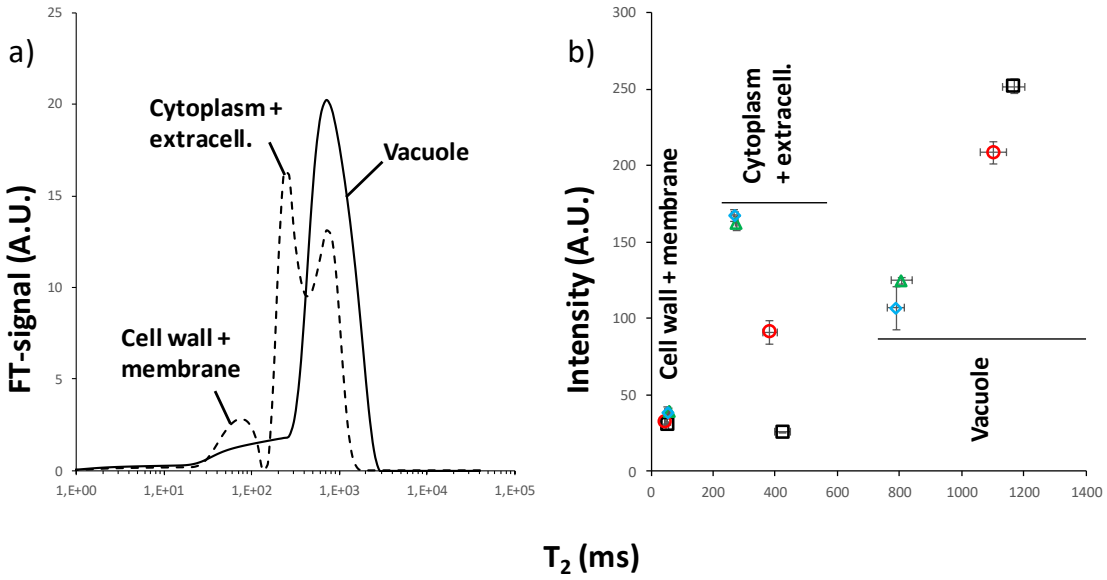

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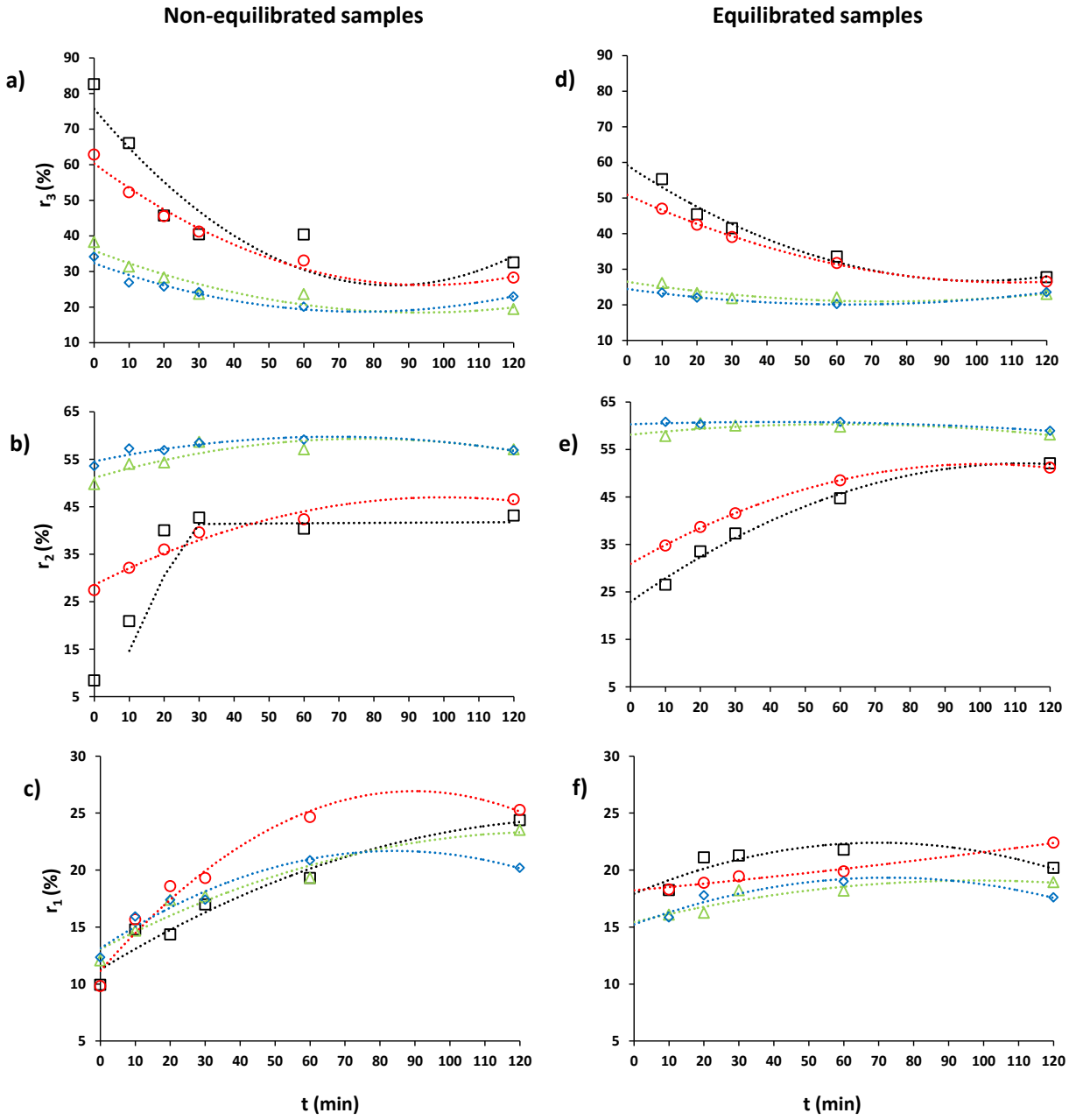

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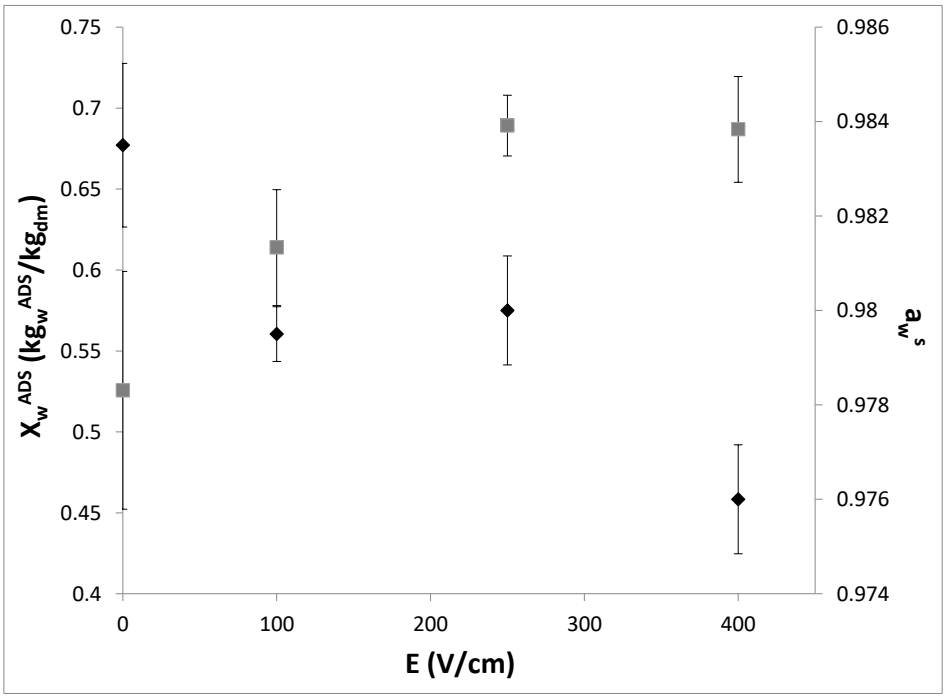

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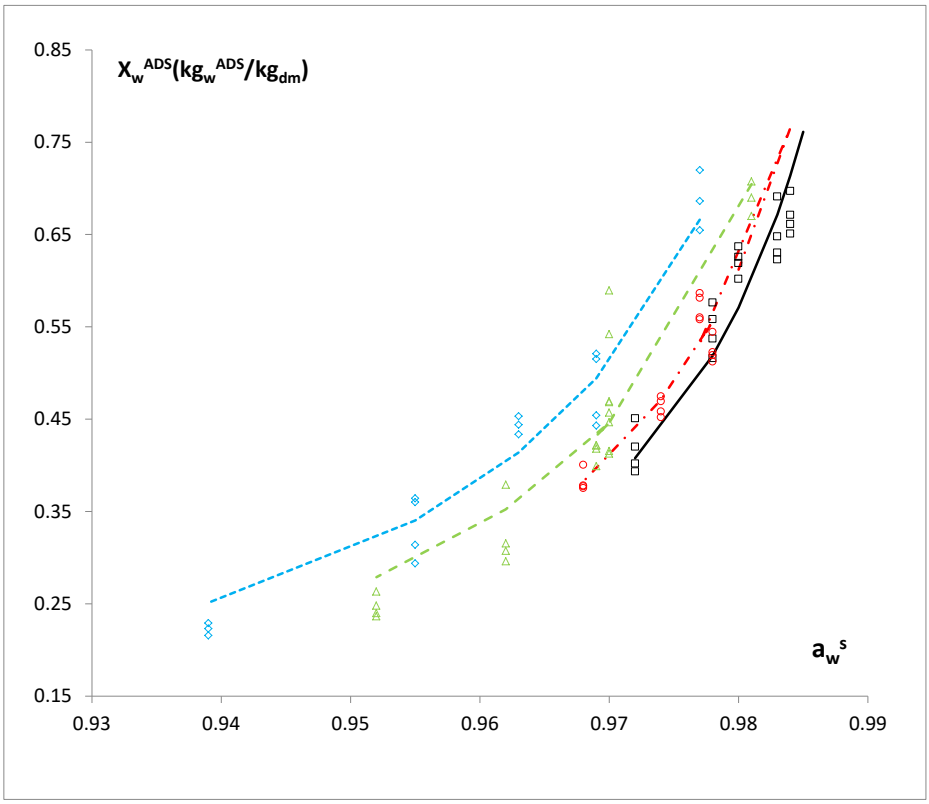

Figure 5.

Figure 6

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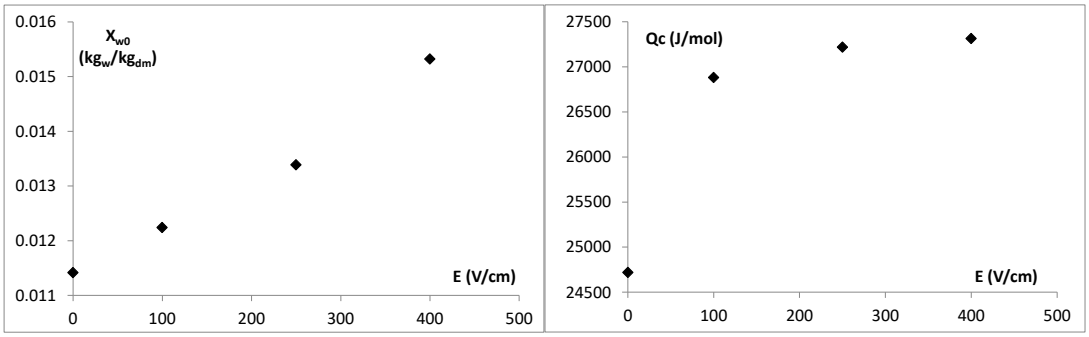

Figure 6