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Industrial relevance

This research develops a thermodynamic model able to describe mass transfer and kiwifruit deformation during OD and using PEF as a pre-treatment. Moreover, a deep analysis of active and passive mechanisms transports affected by PEF was done. The results of this research have demonstrated that PEF used as a pre-treatment of OD accelerated water mass transfer and removes part of the fruit natives electrolytes, affecting the functionality of the cell homeostasis system. Therefore, the present work represents an opportunity in the design of new candying products (less calories and sweetness).

RESEARCH HIGHLIGHTS

> The usefulness of PEF as pre-treatment of OD of kiwifruit has been demonstrated.

> A thermodynamic approach able to analyze tissue deformation has been developed.

> The phenomenological coefficients of water and sucrose have been obtained.

> Samples pre-treated with PEF show higher water losses and less sugar gain.

> PEF removes part of the native electrolytes, reducing the activity of proteins pumps.

EFFECT OF PULSED ELECTRIC FIELDS PRE-TREATMENT ON MASS TRANSPORT DURING THE OSMOTIC DEHYDRATION OF ORGANIC KIWIFRUIT

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ABSTRACT

Recently, some authors have applied pulsed electric fields (PEF) as a pre-treatment of osmotic dehydration, showing a faster kinetics of dehydration. Osmotic dehydration of fruit tissue shows complex mass transfer mechanism associated with active and passive transports of the vegetal matrix, usually driven by electrolytes. The aim of this work was to analyze the effect of different PEF values (100, 250, 400 V/cm) as a pre-treatment of the osmotic dehydration (61.5 °Brix, up to 120 min) on mass transport mechanism of organic kiwifruit. A thermodynamic model able to describe the mass transfer and tissue deformation in kiwifruit was developed. It was

possible to conclude that pulsed electric field as a pre-treatment, remove a part of the native electrolytes, reducing the activity of protein active pumps, leaving alone the passive protein channels as a main mass transmembrane transport and therefore affecting to the regular functionality of cell homeostasis system.

Keywords: kiwifruit, Pulsed Electric Fields, osmotic dehydration, mass transfer, thermodynamics, phenomenological coefficients.

NOTATION

a_j	activity of the chemical specie j (-)
R	ideal gases universal constant (J mol $^{-1}$ K^{-1})
T	temperature (K)
S	entropy (J K^{-1})
P	absolute pressure (Pa)
F	Force (N)
F	Faraday Constant (C mol^{-1})
V	volume (m^3)
l	elongation (m)
L	Phenomenological coefficient (mol^2 J^{-1} s^{-1} m^{-2})
n	number of moles (mol)
M	mass (g)
Mr	molecular weight (g mol^{-1})
x	mass fraction (g g^{-1})
S	surface (m^2)
J	molar flux (mol s^{-1} m^{-2})

t	time (min)
G	Gibbs free energy (J)
e	charge (C)
s	molar partial entropy (J K^{-1} mol^{-1})
z	Valence of each electrolyte (-)
Greek Alphabet	
ψ	electric potential (J mol^{-1} C^{-1})
μ	chemical potential (J mol^{-1})
ν	molar partial volume of the specie j (L mol^{-1})
Subscripts	
w	water
t	treatment time
0	initial time
s	sucrose
i	principal chemical species
j	any chemical species
Superscripts	
s	surface
OD	osmotic dehydration solution
PT	passive transport
AT	active transport

1. Introduction

Osmotic dehydration (OD) is a widely used preservation technique which consists in the reduction of food water activity by immersing a biological tissue in hypertonic solutions (Castro-Giráldez, Fito, Dalla Rosa, & Fito, 2011a). The difference in water chemical potential between the internal liquid phase and external solution promotes the release of water from the food into the osmotic medium with the simultaneous incorporation of the solute into the product (Panarese et al., 2012).

Cellular systems evolve by free energy gradients known as passive transports (Tyerman, Bohnert, Maurel, Steudle, & Smith, 1999); however, occasionally biological systems require that the chemical species move in the opposite direction to these energy gradients; therefore, biological systems have developed transport mechanisms based on protein channels (Agre, Bonhivers, & Borgnia, 1998), which work with energy consumption as ATP (Ferrari, Sarantopoulos, Carmello-Guerreiro, & Hubinger, 2013). When a biological tissue is subjected to a dehydration process, the cells suffer water losses which produces cell stress. The mechanisms of the tissue to survive to this level of water stress are multifold. While cell is losing water by passive transport, driven by the water chemical potential gradient, multiple mechanisms to preserve the intracellular water content are developed, such as active water pump transport or the vesicles process formation (Tylewicz, Romani, Widell, & Galindo, 2013), maintaining cell homeostasis and protecting the function of the structure (Bohnert & Jensen, 1996).

Kiwifruit has a complex organized cellular structure where the cells are interconnected by plasmodesmatas, which allow them to generate solute and solvent fluxes by symplastic ways. The mass transfer throughout the extracellular space is

97 named apoplastic way. Finally, the transport between intra and extra cellular space is
98 the transmembrane transport where the passive water transport is given by protein
99 channels named aquaporins (Maurel & Chrispeels, 2001). The main active transports
100 pumps are: Ca^{2+}, Na^{+} and Na^{+}/K^{+}, which are the responsible of the transport of water,
101 sucrose and electrolytes, respectively.
102 It should be taking into account that OD treatment removes the water from materials
103 (fruits and vegetables) only partially (Rastogi, Eshtiaghi, & Knorr, 1999). Therefore,
104 the combined use of OD treatment with other techniques such as Pulsed Electric
105 Fields (PEF) represents a promising tool to improve mass transfer, increasing yields
106 and reducing processing times (Rastogi & Niranjan, 1998).
107 PEF is a non-thermal promising technology which consists on applying electric fields
108 pulsed through a material placed between two electrodes for very short periods of
109 time (microseconds to milliseconds) (Dellarosa et al., 2016; Parniakov, Lebovka,
110 Bals, & Vorobiev, 2015; Puértolas, Luengo, Álvarez, & Raso, 2012), increasing the
111 osmotic yield treatment (Baier, Bußler, & Knorr, 2015).
112 Cell membrane is a semipermeable barrier conformed by phospholipid bilayer with
113 native electric field, and is considered as a natural capacitor of the cell (Singh &
114 Heldman, 2001). However, when the system is subjected to an external electric field
115 bigger than the native one, changes in the electric conformation and also
116 reorganization of phospholipidic bilayer are produced. This phenomenon could be
117 cause of the cell membrane breakdown, and it is known as electroporation (Baier et
118 al., 2015), a representative diagram can be seen in Figure 1. Another way of
119 membrane breakdown is the electrocompression; when food is subjected to an
120 external electric field the electric charges (particularly electrolytes, such as Ca^{2+}, Na^{+}

or K^+) accumulate at both sides of the cell membrane generating a potential difference through it. These charges attract each other, therefore the membrane suffers a compression, and as a consequence its original thickness is reduced. The elastic forces of the membrane oppose to the electric compression, but when the charge accumulation exceed the limit point of elasticity, pores are generated due to the disruption of it (Calderón-Miranda, Fernanda, Martín, Barbosa-Cánovas, & Swanson, 1998).

According to the intensity of the applied electric field, the numbers of pulses, and the temperature, the electroporation could be reversible or irreversible (Knorr, Angersbach, Eshtiaghi, Heinz, & Lee, 2001). In order to estimate the critical electric field of membrane breakdown, Zimmermann, Pilwat, Beckers, & Riemann (1976) applied voltage gradients in a simulated cell membrane. They reported values between 5 mV to 1 V at 20 ºC and 1.2 V at 4 ºC as an electric potential difference to cell membrane breakdown. If the average thickness of the phospholipidic bilayer is 4 nm (Briegel et al., 2009) and it is considered as a parallel plates system, the critical electric field obtained are 12.5 kV/cm to 2.13 MV/cm at 20ºC and 3 MV/cm at 4ºC. However, some effects in chemical transport by using PEF at lower electric fields intensities used as pre-treatment of OD have been reported. Rastogi, Eshtiaghi, & Knorr, (1999) have been able to accelerate the water mass transfer of carrots by applying electric fields between 0.22 to 1.6 kV/cm at 40ºC; Taiwo, Angersbach, Ade-Omowaye, & Knorr, (2001) have increased the water loss with a minimal alteration of apples using an intensity electric field of 1.4 kV/cm at 40ºC. Finally, Tedjo, Taiwo, Eshtiaghi, & Knorr, (2002), have obtained a moisture reduction without altering the taste of mangos by applying 1 to 3 kV/cm at 40ºC.

145 Moreover, PEF application in food processing maintains the activity of vitamins
146 (Vega-mercado, Gongora-Nieto, Barbosa-Cánovas, & Swanson, 2007) and preserves
147 some physical properties, such as color, texture or fresh taste (Calderón-Miranda,
148 Fernanda, Martín, Barbosa-Cánovas, & Swanson, 1998).
149 The aim of this work was to analyze the effect of pulsed electric fields as a pre-
150 treatment of the osmotic dehydration of kiwifruit, and determine the transport
151 mechanism affected by the pre-treatment.
152

153 ## 2. Material and methods

154 ### 2.1. Raw material

155 Organic kiwifruits (*Actinidia deliciosa* cultivar ‘‘Hayward’’) were bought on a local
156 market located in Cesena (Italia) and stored at 4±1 ºC until their processing. The
157 fruits were tempered at 25 ºC, hand peeled and cut with a manual cork borer from the
158 outer pericarp in order to obtain cylinders with homogeneous size of 8 mm diameter
159 and a length of 10 mm (the core and the inner pericarp were removed). The
160 refractometric indexes of the fruits used for the experiment were 13±1 ºBrix.
161

162 ### 2.2. Experimental procedure

163 The fresh samples were characterized according the following parameters: mass,
164 volume, refractometric index (ºBrix), water activity and moisture by quadruplicate.
165 12 sample cylinders were used for each treatment (576 samples). They were placed
166 inside the Pulsed electric field (PEF) chamber and subjected to different electric
167 fields strengths. Immediately after, the samples were weighed and introduced to the
168 osmotic dehydration solution. Considering previous results, the OD treatment times

were 0, 10, 20, 30, 60 and 120 minutes. Due to the fact that the samples after treatments show concentration profiles, another batch of samples were reposed after the treatments at 4 ºC during 24 hours in decagon containers closed with parafilm® in order avoid the sample dehydration. Finally, mass, volume, ºBrix, water activity and moisture were measured as final determinations for fresh, treated and reposed samples.

2.3. Pulsed electric field (PEF) treatment

Pulsed electric field treatments were applied to the cylinders using a pulse generator equipment based on MOSFET technology and capacitors as energy tanks. The samples (12 cylinders per experiment) were placed in a rectangular treatment chamber equipped with two 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 field (100, 250 and 400 V/cm at 100 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.

2.4. Osmotic dehydration treatment

The OD was carried out by immersing the samples in 61.5 º Brix sucrose solution prepared with commercial sugar and distilled water at 25 ºC and maintaining a relationship 1:4 (w/w) between the fruit and the OD solution in order to avoid changes in the solution concentration during the treatment time of 0, 10, 20, 30, 60 and 120 min.

193 **2.5. Analytical determinations**

194 Mass was determined by using a Kern balance ABS 320-4N (±0.0001) (KERN &
195 SOHN GmbH, Germany), and a dew point Hygrometer Decagon (Aqualab®, series 3
196 TE) was used for measuring the water activity, with a precision ±0.003.
197 Volume was determined by an image analysis using Adobe© Photoshop© CS6
198 software (Adobe Systems Inc., San Jose, CA, USA) in order to get the diameter and
199 the thickness of the samples.
200 The analysis of the moisture was accomplished following the AOAC Method 934.06,
201 2000. Sugar content was determined by measuring the refractometric index with a
202 digital refractometer (KRÜSS Optronic© GmbH, Germany) calibrated with distilled
203 water at 25ºC. Refractometric index was measured in both kiwifruit samples and
204 agent solution after the treatment.
205 Analytical determinations described above were obtained by quadruplicate.
206

207 **3. Results and discussion**

208
209 During the osmotic treatments, kiwifruit suffers mass variations which involve the
210 total mass, the water mass losses and the sucrose mass gain and they can be
211 calculated using the following equations:
212

213 $$\Delta M = \frac{M_t - M_0}{M_0} \quad (1)$$

214 $$\Delta M_w = \frac{M_t x_{wt} - M_0 x_{w0}}{M_0} \quad (2)$$

215 $$\Delta M_s = \frac{M_t x_{st} - x_{s0} \,.\, M_0}{M_0} \quad (3)$$

216

217 Where M represents the mass (g), x the mass fraction (g/g), the subscripts w
218 represents the water, s the sucrose, t the treatment time and 0 the initial value.
219 Figure 2 shows the water and sucrose mass variation during the osmotic dehydration
220 of the kiwifruit PEF pre-treated at different electric fields (0, 100, 250 and 400
221 V/cm). In the figure, water mass decreases due to high water losses for all the
222 treatments, however, the water losses for samples that have not been pre-treated are
223 considerably less than the PEF pre-treated samples. In addition, no differences in
224 water losses between the samples pre-treated with 250 V/cm and 400 V/cm can be
225 appreciated. Nevertheless, the sucrose mass gain is ordered in inverse sense of water
226 losses; samples without PEF pre-treatment present the maximum sucrose mass gain.
227 Figure 3 shows the relationship between the overall mass variation and the water and
228 sucrose mass variation. The line with a slope equal to 1 represents the mass balance
229 $\Delta M = \Delta M_w + \Delta M_s$. No PEF samples are not fitted to the line which means that
230 other flux is present in the process and it is not considered, probably a flux of other
231 native solutes (sugar and electrolytes). However, the data of the samples pre-treated
232 with PEF (all electric fields intensities) are located on the line, confirming that the
233 kiwi mass variation is only due to the variation of water and sucrose (Castro-
234 Giraldez, Fito, & Fito, 2010).
235 It is important to highlight that besides the water and sucrose mass variation, the
236 native soluble solids present in the vegetal tissue should be considered, which can be
237 estimated as follows:

238 $$\Delta M_i = \Delta M - (\Delta M_w + \Delta M_s) \quad (4)$$

239 Where ΔM_i represents the mass variation of native soluble solids leaving the fruit
240 matrix to the osmotic solution.

241 Sugars present driving forces for mass gain as reported in Figure 2. However, as can
242 be seen in Figure 4, samples without PEF pre-treatment lost up to 4 % of native
243 soluble solids thus the nature of them has two characteristics: they are affected by the
244 applied electric field and they play an important role in the transport of water and
245 sugars. Therefore, these native compounds could be electrolytes. Throughout the
246 traditional osmotic treatment, fruit tissue losses part of the native electrolytes (Peiró,
247 Dias, Camacho, & Martínez-Navarrete, 2006), reducing the active transmembrane
248 transport; however the samples pre-treated with PEF start the osmotic treatment with
249 low amount of electrolytes.
250 In order to understand the different behaviors involved in the mass transfer, Figure 5
251 shows a scheme of a cellular system with the active and passive transports. Interface
252 sucrose solution/surface fruit is defined in order to develop the transport models.
253 Each chemical specie involved in the osmotic dehydration treatment has different
254 driving forces to move into the cell system. Particularly, water fluxes can be
255 generated by passive and active transports. Passive transport is driven by water
256 chemical potential gradients and it could be produced outside the cells by the
257 apoplastic pathways (Steudle & Frensch, 1996) and through transmembrane protein
258 channels by the aquaporins (Agre et al., 1998; Shiratake & Martinoia, 2007). On the
259 other hand, active transmembrane transport requires energy as ATP and is driven by
260 Ca^{2+} pump. In case of high water stress, the homeostatic cell system counteracts the
261 water losses by the aquaporins introducing water in cell by calcium pump (Moraga,
262 Moraga, Fito, & Martínez-Navarrete, 2009). Regarding the sucrose fluxes, they are
263 driven by passive transport in the apoplastic ways and by active transport throughout
264 the membrane, by the sodium pump (Zeuthen, 2010).

Electrolytes transmembrane transport is produced by the sodium/potassium pump (Jaitovich & Bertorello, 2006); however, the rest of active transports depend on the pass of some electrolytes such as Ca^{2+}, Na^{+}, K^{+} or Mg^{2+} throughout this pump.

In order to understand and quantify the passive transport, a non-equilibrium thermodynamic model based in Gibbs free energy has been developed (Talens, Castro-Giraldez, & Fito, 2016):

$$dG = -SdT + VdP + Fdl + \psi de + \sum_i \mu_i dn_i|_{P,T,n_i} \quad (5)$$

Where SdT corresponds to the thermic term, VdP and Fdl are the mechanical energies, ψde the electric term and finally $\sum_i \mu_i dn_i$ is the activity term and represents the addition of the chemical potentials of all the compounds in the system considering pressure and temperature constants, and without molecular interactions. Developing the chemical potential for i compound affected by j compounds, by using the equation 5, next equation is obtained:

$$d\mu_i = \frac{dG}{dn_i} = -s_i dT + v_i dP + F_i dl + \psi_i de + RTln\, a_i + \sum_j RTln\, a_j \frac{dn_j}{dn_i} \quad (6)$$

During the PEF treatment, cellular tissue was immersed in a water bath with two poles, inducing an electric field throughout the samples. Taking into account the interface tap water/fruit surface, the chemical fluxes were defined. In case of water and sugars only the activity terms induce chemical potential gradients to produce transports, because internal pressure and temperature are constant (no deformations appear and the system is tempered). Nevertheless, electrolytes (chemical species with high charge) are also affected by the external electric field, producing high gradients

289 of chemical potential and therefore ion fluxes leaving the tissue. Taking into account
290 only the PEF pre-treatment, the ion chemical potential throughout the interface
291 water/tissue can be defined as follows (Velázquez-Varela, Fito, & Castro-Giráldez,
292 2014):
293
294 $$\Delta\mu_i = \sum_i z_i F E \, \Delta n_i + \sum_j RT \, ln \frac{a_j^{ext}}{a_j^{int}} \, \Delta n_j \quad (7)$$
295
296 Where z is the valence of each electrolyte (with sign), F is the Faraday constant
297 (96485.3415 C/mol), E is the Electric field applied (V/m), Δn_i is the variation of
298 each ion and the subscripts i and j represent the electrolytic and chemical species,
299 respectively. The first term of the equation represents the electric term and the
300 second one is the activity term. Considering that the electric fields applied are
301 moderately high (100 to 400 V/cm) and the electrolytes concentrations are low (low
302 activity of each chemical specie) the driving force that governs the ion transport is
303 the electric term. Therefore, during the PEF pre-treatment electrolyte fluxes are
304 induced, leaving the tissue. Final quantity of electrolytes that will remain in the tissue
305 depends on the electric field strength. Depending on the amount of electrolytes with
306 physiological activity in the tissue, the water and sucrose transmembrane active
307 transport, during the osmotic treatment, will be affected.
308 In order to quantify the effect of the reduction of the amount of electrolytes, the
309 driving forces during the osmotic dehydration treatment must be defined by using
310 equation 6, fixing the interface between osmotic solution and fruit surface.
311 In the osmotic dehydration treatment, equation 6 could be transformed according to
312 the research developed by Castro-Giráldez, Fito, & Fito, (2011b) and Tylewicz, Fito,

313 Castro-Giráldez, Fito, & Dalla Rosa (2011). For this treatment, the thermal (SdT)
314 and electric (ψde) terms can be neglected because it is an isothermal process and the
315 amount of native ions is low. Therefore it is possible to obtain the water chemical
316 potential as follows:
317
318 $$\Delta\mu_w = \frac{\Delta G}{\Delta n_w} = v_w \Delta P + F_w \Delta l + RTln\frac{a_w^S}{a_w^{OD}} + RTln\frac{a_s^S}{a_s^{OD}}\frac{J_s}{J_w} \quad (8)$$
319
320 Where the superscript OD represents the osmotic dehydration solution (sucrose
321 solution), and superscript S represents the properties of fruit surface.
322 In order to understand the transports, it is necessary to calculate the water molar flux
323 with the following equation:
324 $$J_w = \frac{\Delta M_w \,.\, M_0}{\Delta t \,.S\,.Mr_w} \quad (9)$$
325
326 Where J_w is the water flux (mol/s m^2), ΔM_w represents the water mass variation
327 (dimensionless), M_0 is the initial mass of the sample (g), Δt is the process time (s), S
328 corresponds to the surface of the sample during the treatment (m^2) and Mr_w is the
329 molecular weight of water (18 g/mol).
330
331 Figure 6 shows the maximum water flux ordered by the PEF pre-treatment intensity.
332 The electric field applied before the osmotic treatment increases the water flux
333 because the pre-treatment removes a part of the basic electrolytes, reducing the
334 homeostatic cell system based on the Ca^{2+} pump.
335 Applying the first relation of Onsager (Traffano-Schiffo, Castro-Giráldez, Fito, &
336 Balaguer, 2014), the molar fluxes are related to the chemical potential, as a driving

force of the transport of the component i, by the phenomenological coefficient (L_i) (equation 10).

$$J_i = L_i \,.\Delta\mu_i \tag{10}$$

Where the component *i* represents the water or the sucrose. The phenomenological coefficient is the physical property than explains the overall transport of each chemical specie. Nevertheless, the chemical potential is needed in its estimation where mechanical forces induced by the tissue deformations increase the complexity in the calculation. Tissue deformation is produced by the plasmolysis cell process, thus, this effect is punctual and it affects in determined periods of the osmotic treatment. Therefore, it is necessary to analyze the tissue deformation in order to determine the periods without mechanical effects, in order to estimate the phenomenological coefficient.

In order to analyze the tissue deformation, volume and surface variation were calculated by using the following equations:

$$\Delta V = \frac{V_t - V_0}{V_0} \tag{11}$$

$$\Delta S = \frac{S_t - S_0}{S_0} \tag{12}$$

Where V corresponds to the volume (m^3), S is the surface (m^2) and the subscripts t and 0 correspond to the treatment time and the initial value (0 minutes), respectively.

In Figure 7, it is possible to observe the volume deformation during the osmotic treatment, where a shrinkage/swelling process occurs in two phases divided by the

plasmolysis process of the different tissues as was explained by (Castro-Giráldez, Tylewicz, Fito, Dalla Rosa, & Fito, 2011c) where activity terms are predominant in the shrinkage periods and mechanical terms are predominant in swelling periods (equation 8). The samples pre-treated by PEF show the critical point of plasmolysis before than the no pre-treated samples. This phenomenon could be accelerated, in the pre-treated samples, by higher water fluxes, and therefore higher intracellular shrinkage. The initial shrinkage is ordered according to the pre-treatment intensity. Consequently, at the initial shrinkage (10 min of OD), mechanical term could be considered neglected, therefore, the chemical potential could be estimated as follows:

$$\Delta\mu_w = RTln\frac{a_w^S}{a_w^{OD}} + RTln\frac{a_s^S}{a_s^{OD}}\frac{J_s}{J_w} \quad (13)$$

And for sucrose chemical potential:

$$\Delta\mu_S = RTln\frac{a_w^S}{a_w^{OD}}\frac{J_w}{J_S} + RTln\frac{a_s^S}{a_s^{OD}} \quad (14)$$

Applying equations 13 and 14, the phenomenological coefficients of water and sucrose were obtained (Table 1). The phenomenological coefficient has a physical meaning which describes the contribution of driving forces of the compounds according to the fluxes (Ferrando & Spiess, 2003). From literature, similar phenomenological coefficients values were reported for water transport; Castro-Giráldez et al., (2011c) obtained a value of $2.46 \cdot 10^{-5}$ mol^2/J s m^2 for OD of kiwifruit at 30ºC and using a 65% w/w sucrose solution; Segui, Fito, & Fito, (2012) obtained $L_w = 0.9 \pm 0.3 \cdot 10^{-4}$ mol^2/J s m^2 for apple isolated cells during OD at 30ºC using a

385 45% (w/w) sucrose solution, also Segui, Fito & Fito, (2013) obtained L_w = 1.3 ± 0.3
386 $\cdot 10^{-4}$ $mol^2/J\ s\ m^2$ for apple isolated cells during rehydration. In contrast, few data are
387 available for sucrose phenomenological coefficients (L_s).
388
389 In Table 1, it is possible to observe the increase of water phenomenological
390 coefficient according to the electric field intensity applied as pre-treatment. Water
391 transmembrane transport works with active and passive transport. The homeostatic
392 cellular system, in case of water stress, induces the activity of Ca^{2+} pump in opposite
393 way of aquaporins (passive transport). However, before the osmotic treatment, the
394 PEF pre-treatment removes the electrolytes, reducing the activity of Ca^{2+} pump,
395 affecting to the osmotic treatment and increasing the kinetics of the dehydration, as
396 the values of Table 1 show. The case of sucrose is the opposite; sucrose
397 transmembrane transport works by the Na^+ pump, therefore any reduction of the
398 overall quantity of the electrolytes reduces the sucrose transmembrane transport
399 maintaining the sucrose transport in the apoplastic ways.
400 Sorption isotherms describe the relationship between the surface water activity of the
401 samples and its moisture (in dry basis) (Traffano-Schiffo, Castro-Giraldez, Colom, &
402 Fito, 2015). Figure 8 shows the sorption isotherms after treatment (Fig. 8a) and after
403 reposed 24 h (Fig. 8b) at 4ºC for all the dehydrated samples at each PEF treatment
404 condition. Moreover, data of a pure solution of water and sucrose is shown (Starzak
405 & Mathlouthi, 2006). Surface water activity is a punctual value and moisture is an
406 average value, thus the distance between surface data and line of pure sucrose
407 solution explains the concentration profile inside sample (Castro-Giráldez et al.,
408 2011b). Samples fitted in pure sucrose solution line represent equilibrated samples

409 (no concentration profile), thus it is possible to rename this line to “equilibrated
410 sample line”. The relations between both isotherms permit to predict the internal
411 transport, strongly driven by the symplastic ways (Fisher & Oparka, 1996).
412 After osmotic treatment, samples are close the equilibrium line depending on the pre-
413 treatment intensity (see figure 8a). However, in Figure 8b it is possible to observe
414 that the no pre-treated samples and samples pre-treated at low electric field intensity
415 reach the equilibrium line at 24h, nevertheless the samples pre-treated with PEF are
416 far from the equilibrated sample line. It could be explained because sucrose
417 molecules, in samples without Na^+ pump working (affected by PEF pre-treatment),
418 equilibrate the sucrose content by the apoplastic ways. The symplastic transport of
419 sucrose, without active transport, does not work because symplastic transport needs
420 first a transmembrane transport. Therefore, samples pre-treated by PEF, increase the
421 water transport but reduce the sucrose transport.
422 Therefore, PEF pre-treatment opens an opportunity in osmotic dehydration
423 treatments in fruits, accelerating the water losses, but reducing the sugar gained in
424 fruit (less calories and sweetness).
425

426 **4. Conclusions**

427 The application of pulsed electric fields as a pre-treatment of the osmotic
428 dehydration in kiwifruit increase the water mass transfer and reduces the final sugar
429 concentration comparing with samples that have not been pre-treated. The water
430 phenomenological coefficient, in osmotic treatment, increases according to the
431 electric fields applied in the pre-treatment. Thus because, the application of electric
432 field prior to the osmotic treatment removes the electrolytes, reducing the activity of

433 Ca^{2+} pump, and leaving alone the aquaporins as a main protein channel of water
434 transmembrane transport and therefore affecting to the regular functionality of cell
435 homeostasis system. However, the sucrose phenomenological coefficient, in osmotic
436 treatment, decrease according to the electric field applied, because the sucrose
437 transmembrane transport is made by the Na^{+} pump, therefore, any reduction of the
438 overall quantity of the electrolytes reduces the sucrose content.
439 PEF pre-treatment opens an amazing opportunity in the design of new products of
440 candying fruits with high dehydration and less sugar content.
441
442
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453
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FIGURE CAPTIONS

Figure 1. Electroporation phenomenon of the lipid bilayer.

Figure 2. Water (ΔM_w) and sucrose (ΔM_s) mass variation through osmotic dehydration treatment pre-treated with PEF at different electric field intensities. (♦) corresponds to no PEF (0 V/cm), (■) 100 V/cm, (▲) 250 V/cm and (●) 400 V/cm.

Figure 3. Relation between the overall mass variation and the water and sucrose mass variation, where (♦) corresponds to no PEF (0 V/cm), (■) 100 V/cm, (▲) 250 V/cm and (●) 400 V/cm.

Figure 4. Native soluble solids variation during OD time, where (♦) corresponds to no PEF (0 V/cm), (■) 100 V/cm, (▲) 250 V/cm and (●) 400 V/cm.

Figure 5. Schematic representation of the cellular transports during osmotic dehydration treatment, where **PT**: passive transport and **AT**: active transport.

Figure 6. Water fluxes during OD treatment with PEF pre-treatment at different voltages, where (♦) corresponds to no PEF (0 V/cm), (■) 100 V/cm, (▲) 250 V/cm and (●) 400 V/cm.

Figure 7. Evolution of area (ΔS) and volume (ΔV) variation of the samples during OD treatment pre-treated with PEF at different voltages, where (♦) corresponds to no PEF (0 V/cm), (■) 100 V/cm, (▲) 250 V/cm and (●) 400 V/cm.

Figure 8. Sorption isotherm a) after osmotic dehydration treatment and b) after reposed 24 h, where (♦) corresponds to no PEF (0 V/cm), (■) 100 V/cm, (▲) 250 V/cm and (●) 400 V/cm and (–) sucrose solutions (obtained from Starzak & Mathlouthi, 2006).

602 **TABLE CAPTIONS**

603 **Table 1.** Phenomenological coefficient of water (L_w) and sucrose (L_s) for the first 10

604 minutes of the kiwifruit osmotic dehydration treatment.

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Figure 1
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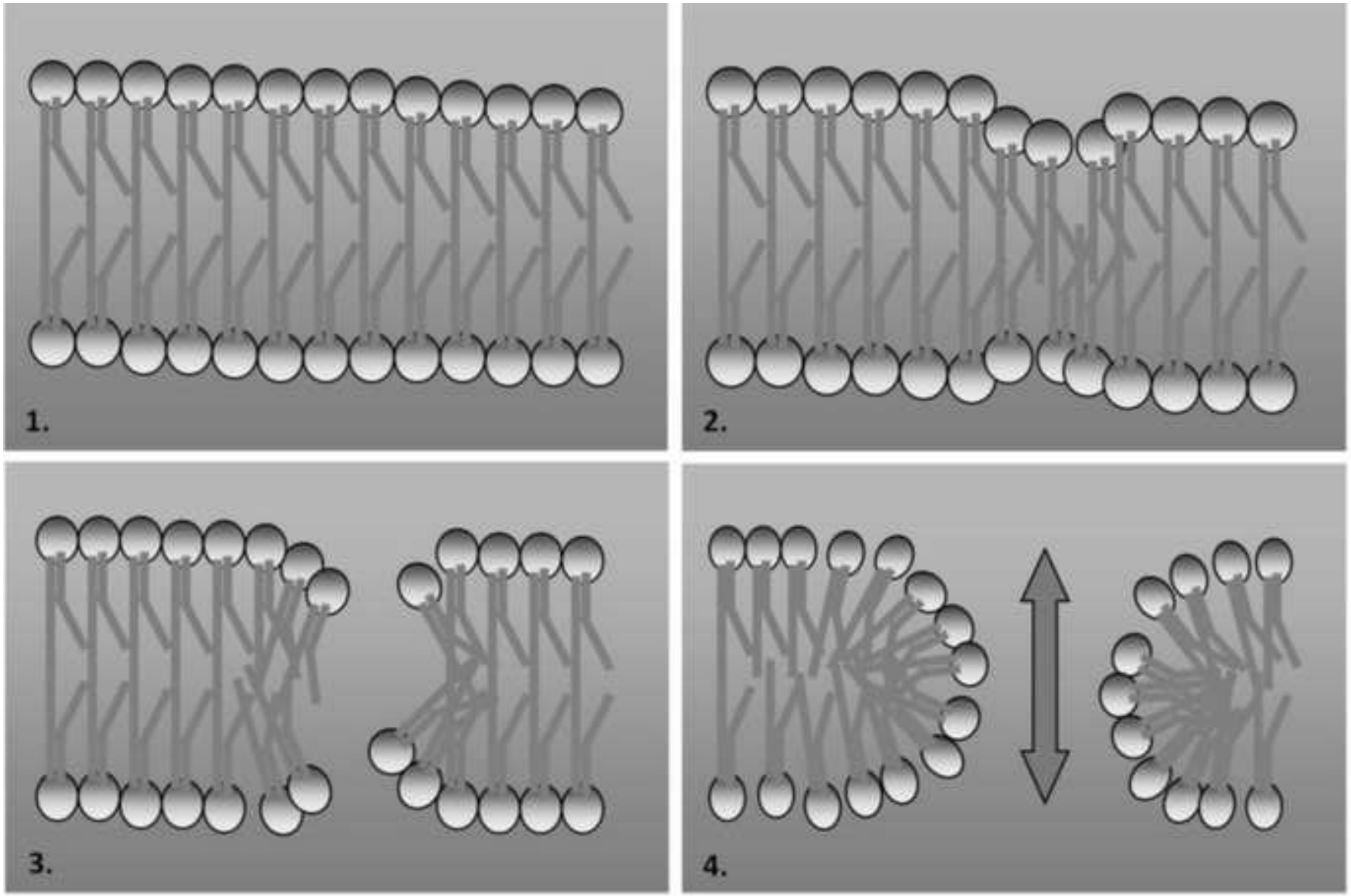

Figure 1.

Figure 2

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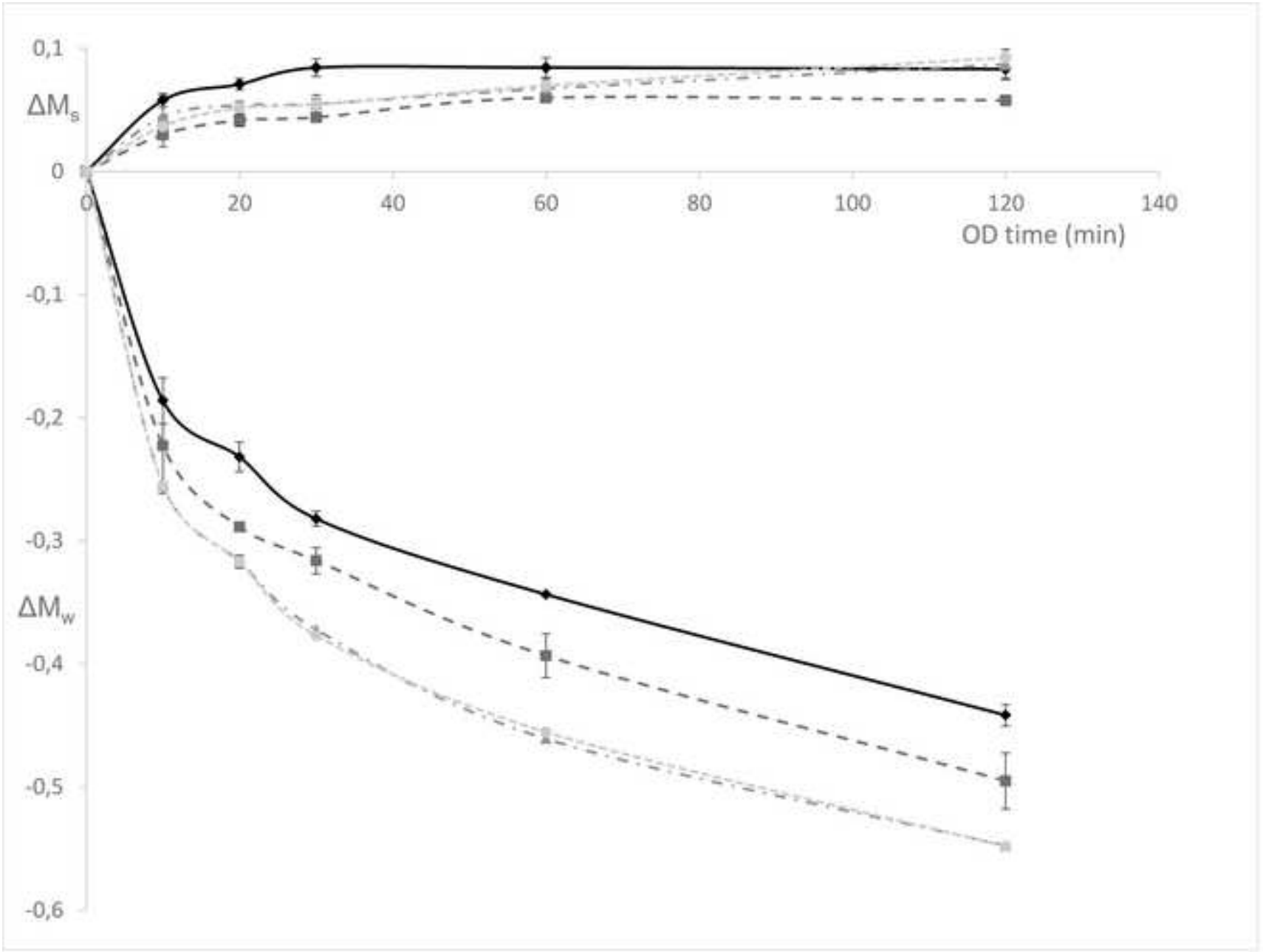

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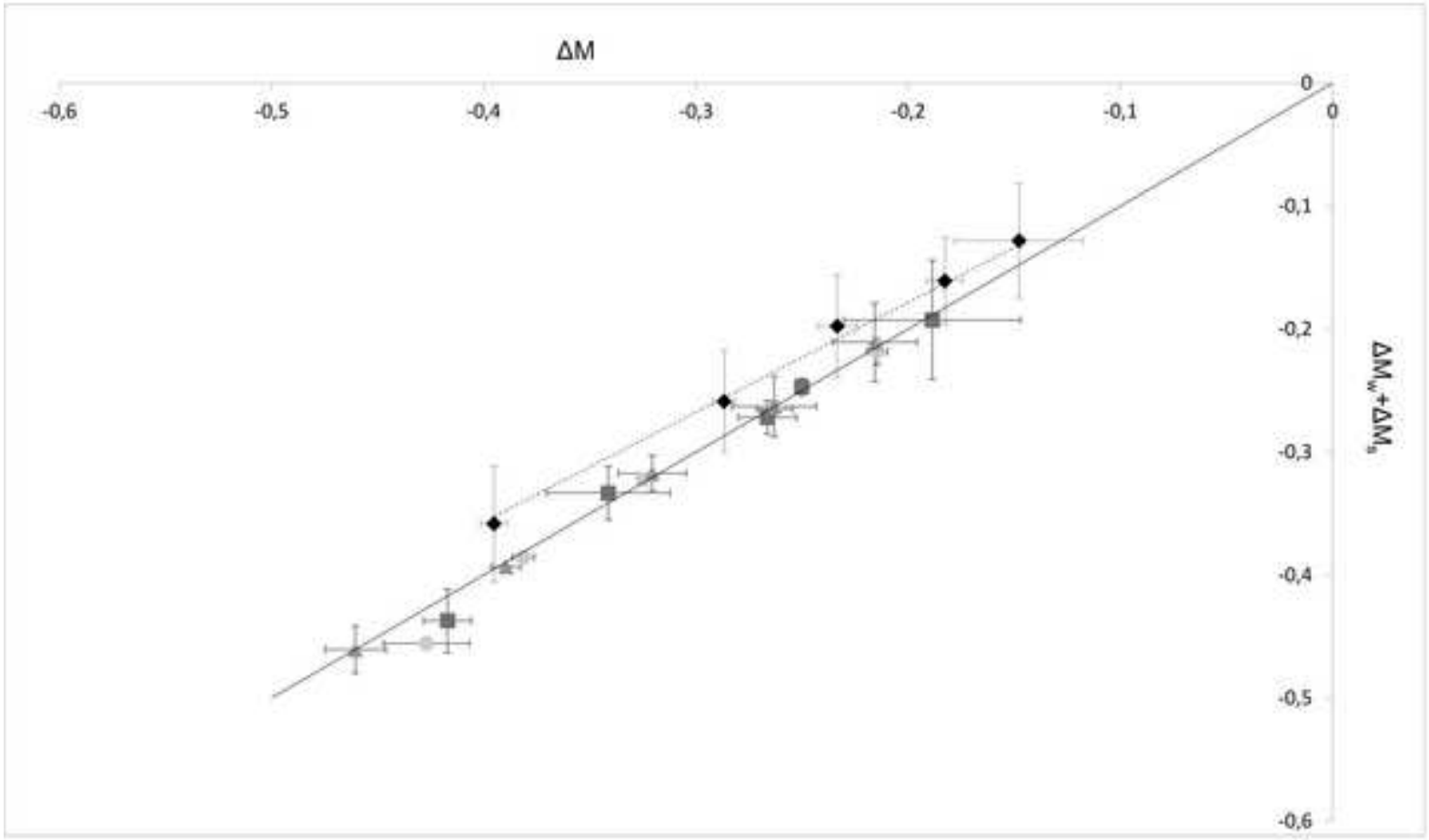

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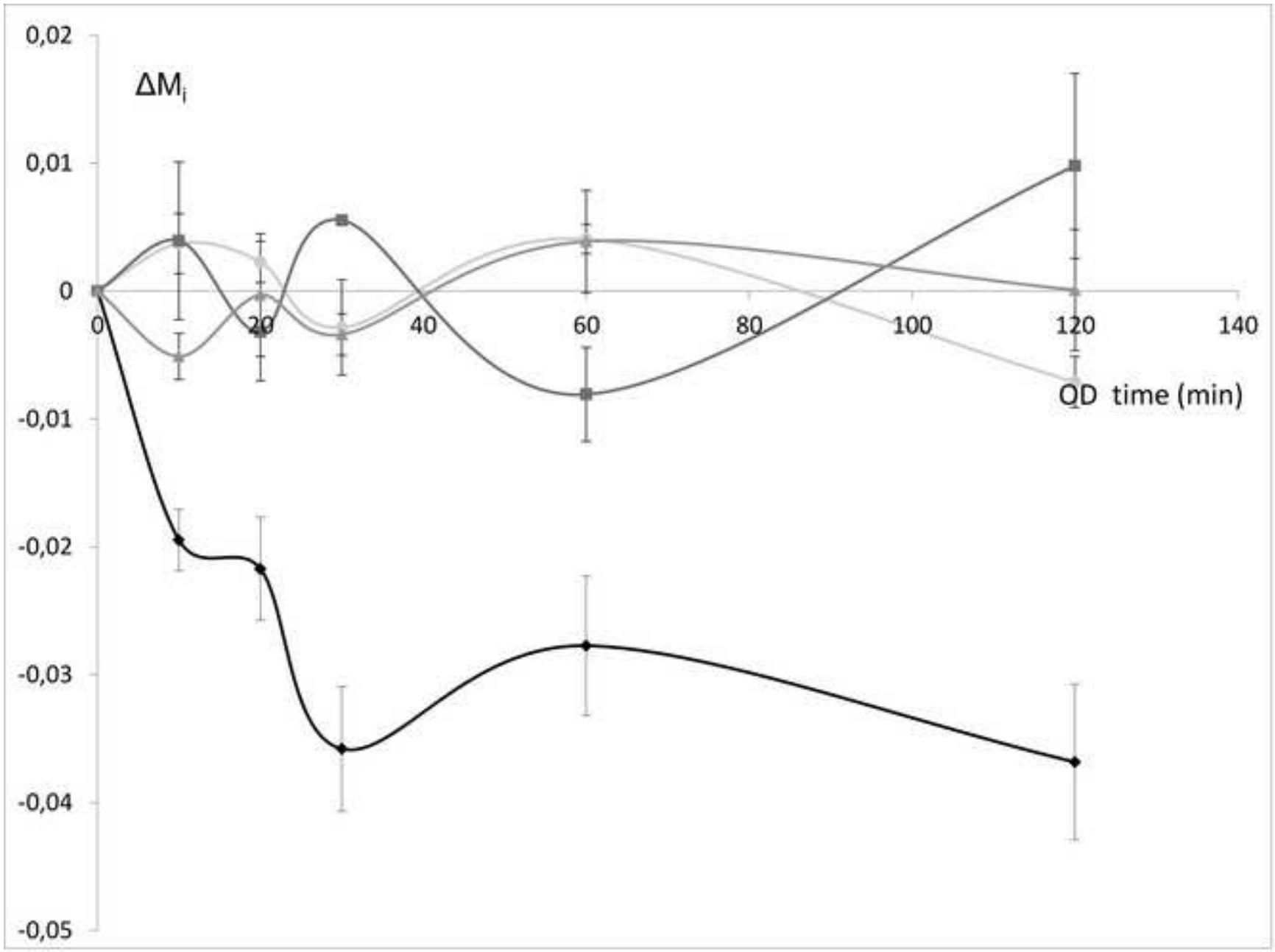

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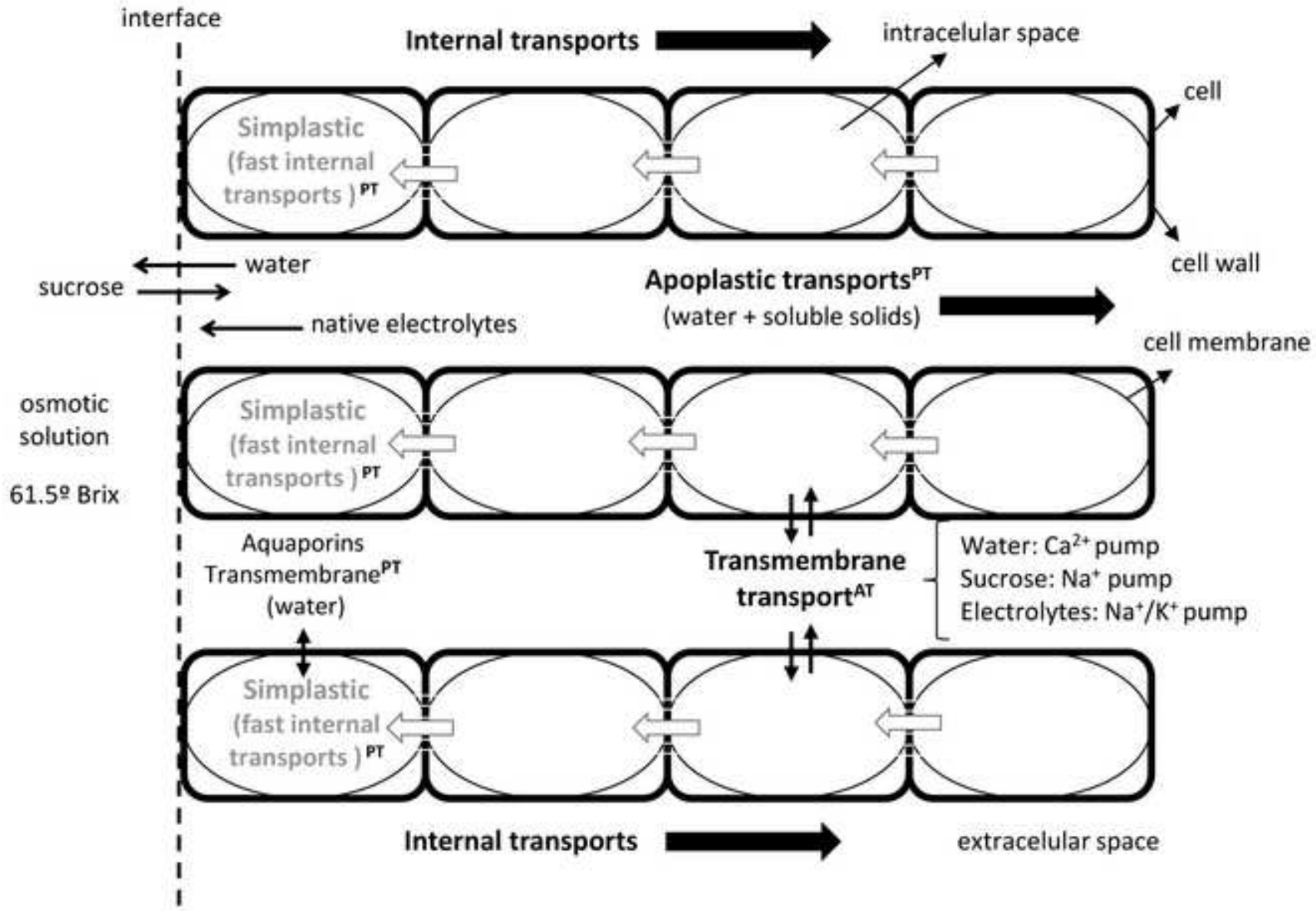

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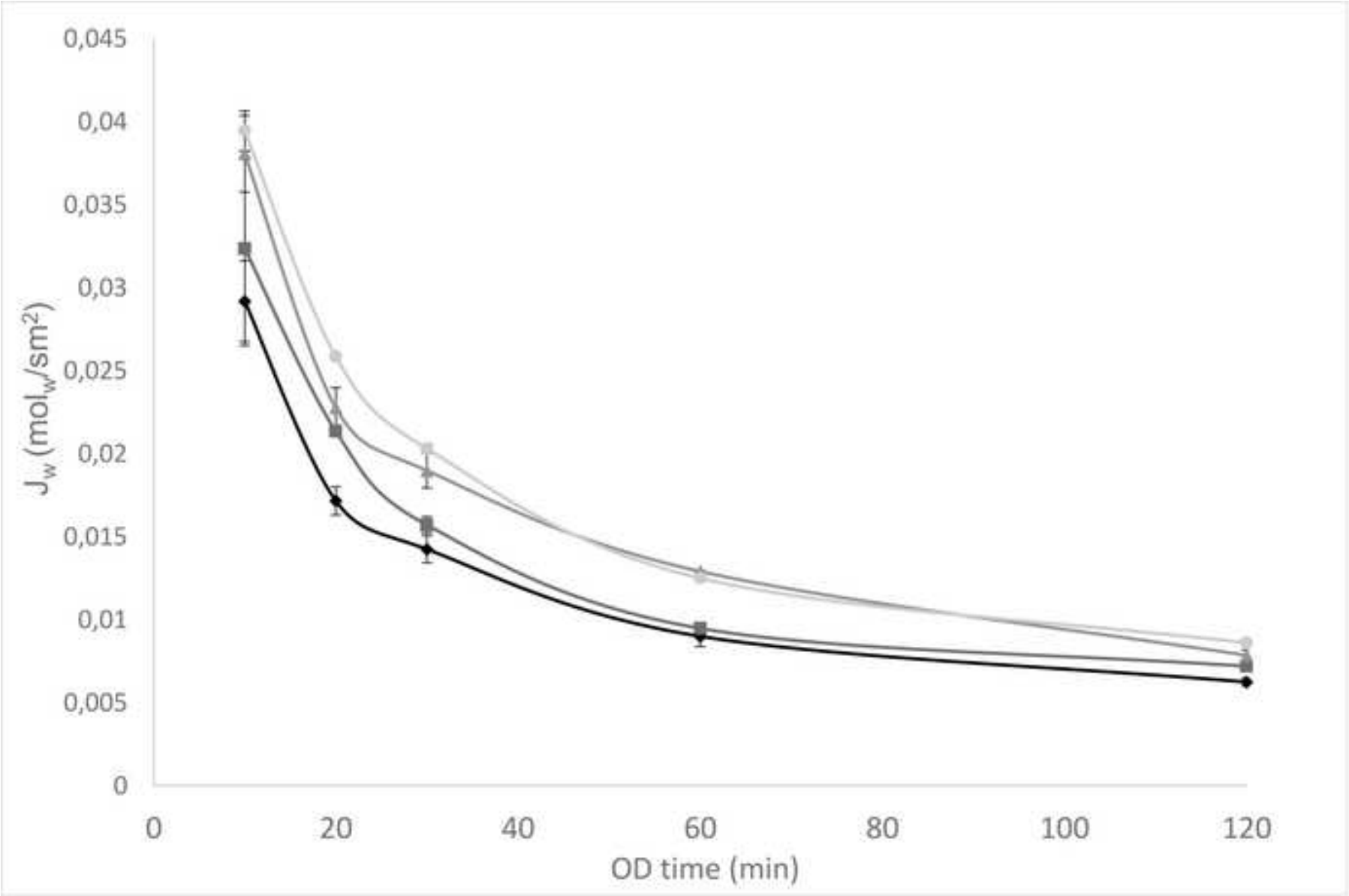

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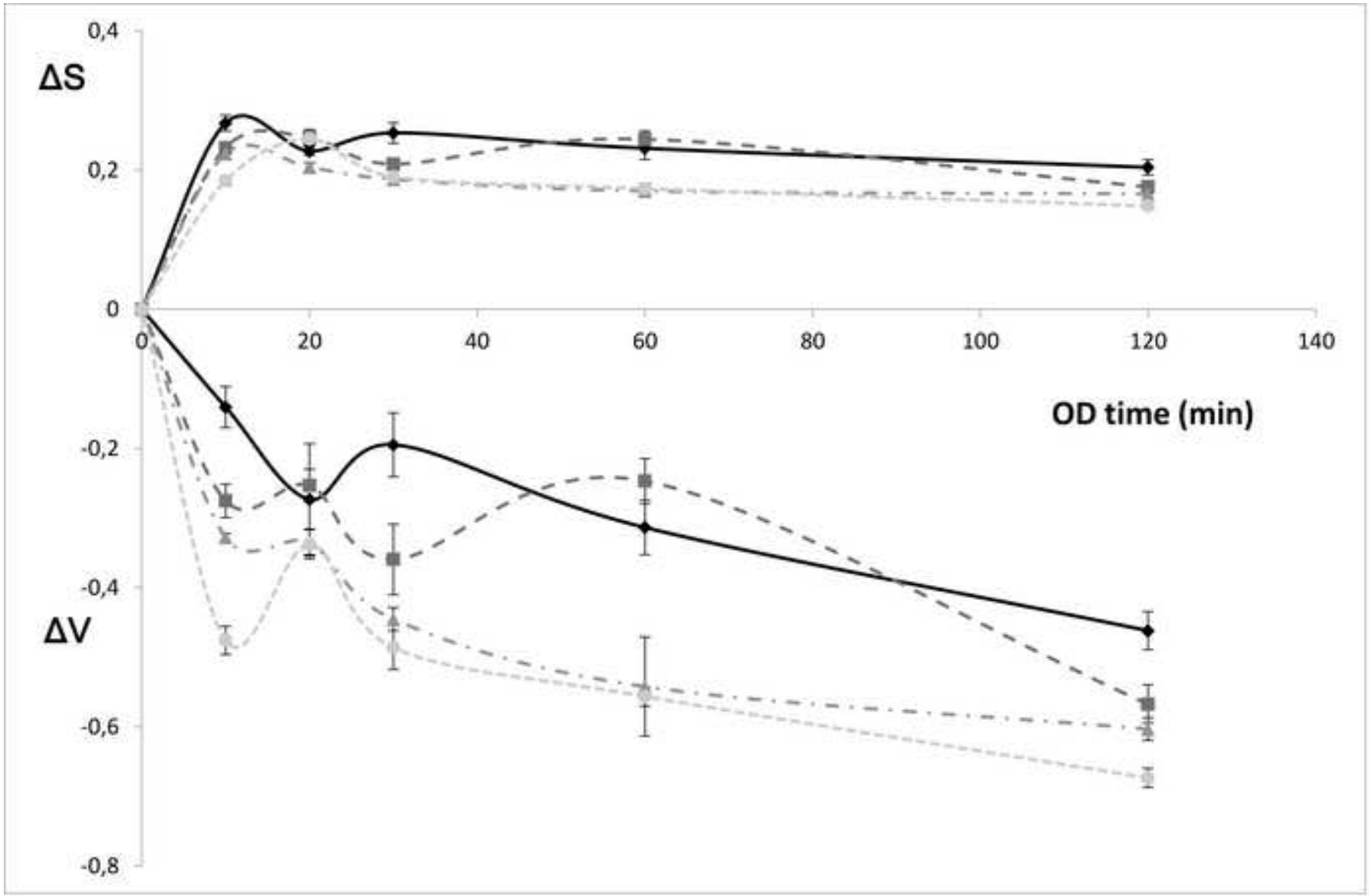

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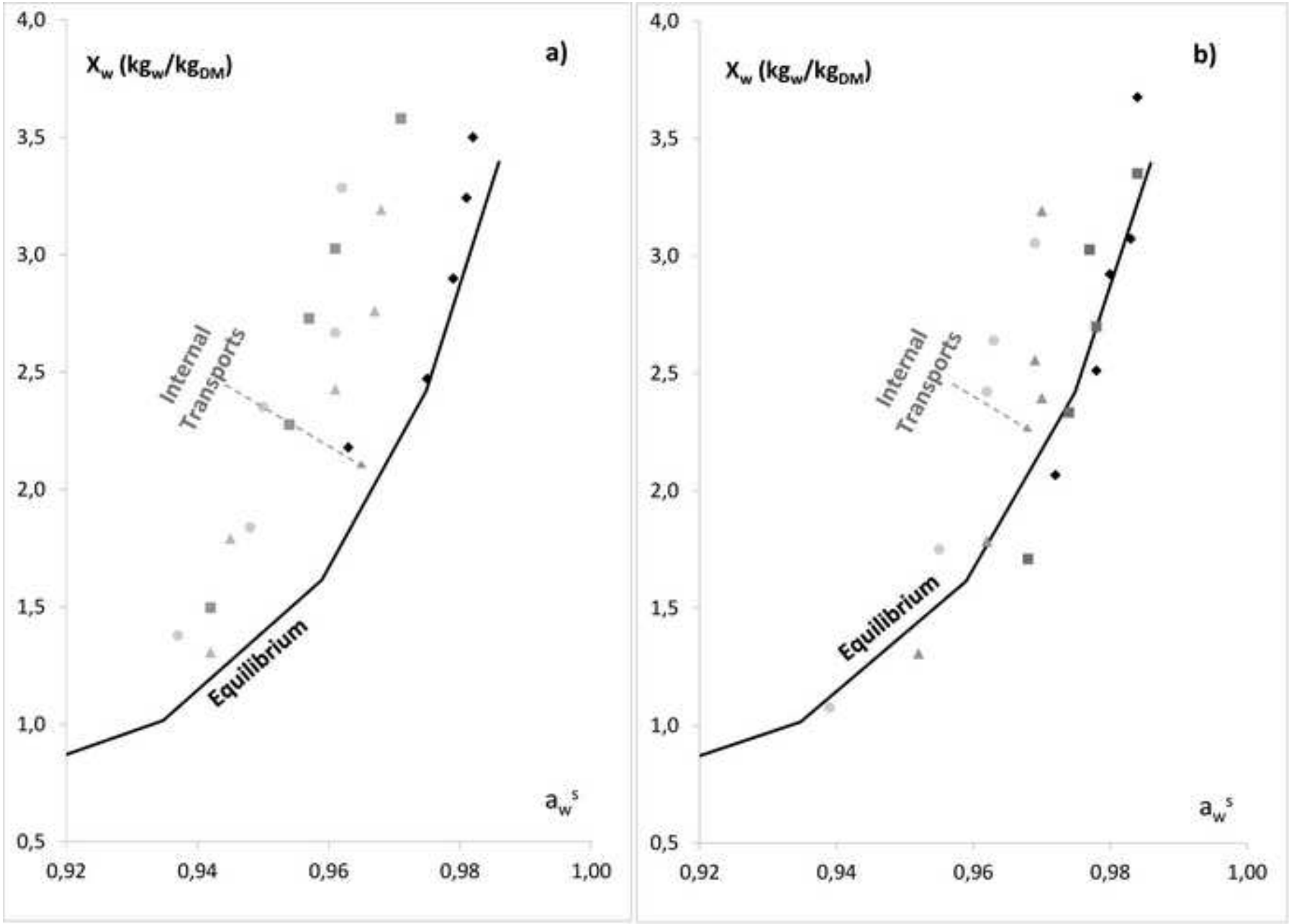

Figure 8.

Table 1

PEF (V/cm)	**L_w (10^{-4})** ($mol^2/J\ s\ m^2$)			**L_S (10^{-8})** ($mol^2/J\ s\ m^2$)		
0	1.7	±	0.4	8.5	±	3.8
100	1.83	±	0.15	1.5	±	0.5
250	2.04	±	0.7	2.9	±	1.7
400	2.4	±	0.5	1.75	±	0.5