Recovery of lycopene from industrially derived tomato processing by-products by pulsed electric fields-assisted extraction

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Abstract

The influence of pulsed electric fields (PEF) pre-treatment at different field strength (E=1–5 kV/cm) and energy input (W_T =5-10 kJ/kg) on the recovery yield of lycopene in either acetone or ethyl lactate from industrial tomato peels residues, was investigated. The rate of lycopene extraction in both solvents decreased with time and was predicted rather satisfactorily (R^2=0.96–0.99) by the Peleg's model. Micrograph of tomato peels showed that PEF induced size reduction and separation between the plant cells likely due to pore formation and leakage of intracellular matter. Coherently, PEF treatment (5 kV/cm, 5 kJ/kg) significantly enhanced the extraction rate (27-37%), the lycopene yields (12-18%) and the antioxidant power (18.0-18.2%) in either acetone and ethyl lactate extracts, as compared with untreated samples. However, acetone gave the highest lycopene yield. HPLC analyses revealed that all-trans lycopene was the main carotenoid extracted and no degradation/isomerization phenomena occurred. The results obtained in this work suggest that the application of PEF prior to solid-liquid extraction with environmentally friendly solvents could represent a sustainable approach for the valorization of industrial tomato peels residues.

Keywords: Tomato processing by-products; pulsed electric fields (PEF); extraction; lycopene; antioxidant; HPLC.

1. Introduction

Tomato (*Solanum Lycopersicon*) is among the most consumed vegetables in the world, being a low caloric source of many traditional nutrients and a predominant source of bioactive compounds with functional and health beneficial properties, especially carotenoids (Lu, Wang, Gao, Fe, & Zhao, 2019; Pataro, Sinik, Capitoli, Donsì, & Ferrari, 2015; Strati & Oreopoulou, 2014).

In terms of global production, around 180 million tons of tomatoes are produced each year (FAOSTAT, 2016), of which about 80% are processed to obtain products such as peeled tomato

(whole, diced, or sliced), paste, juices, sauce and ketchup, whose manufacture often requires peel removal (Arnal et al., 2018; Rock, Yang, Goodruch-Schneider, & Feng, 2012). Peeling is, therefore, a key unit operation in the industrial transformation of tomatoes prior to further processing. It typically involves the use of hot lye (e.g., sodium hydroxide) solutions or a steam peeling process, which consists of a rapid steam blanching of the whole tomato fruits coupled with vacuum cooling prior to mechanical removal of peels (Arnal et al., 2018; Rock et al., 2012).

Thus, industrial processing of tomatoes unavoidably generates large amount of by-products, accounting for approximately 2-5 % in weight of the total processed tomato fruits (Knoblich, Anderson, & Latshaw, 2005), whose constitution depends on the form of the final product and the peeling method applied (Lu et al., 2019). For example, in the case of peeled tomatoes for canning, tomato by-products is only composed of peels, while the manufacturing of homogenized products, such as juice and paste, typically generates a mixture of peels, seeds as well as a small amount of pulp (Lu et al., 2019).

These by-products represent a major disposal problem for tomato processing companies, where they currently find low-added value uses as animal feed or compost (Knoblich et al., 2005; Strati & Oreopoulou, 2014), or are directly sent to landfill (Rossini et al., 2013).

However, the previous research revealed that tomato by-products retain, among others, large amount of natural carotenoid compounds with high antioxidant activity which, therefore, seem to withstand to industrial processing methods and whose recovery might bring significant economic and environmental benefits (Juric, Ferrari, Velikov, & Donsì, 2019; Lu et al., 2019; Pataro et al., 2018, Pataro, Carullo, & Ferrari, 2019; Strati & Oreopoulou, 2014). Lycopene, a bright red pigment, is the most abundant carotenoid in tomato processing by-products. It accumulates in the peels (Strati & Oreopoulou, 2014) at concentrations about five times higher than in tomato seeds (Knoblich et al., 2005) and pulp (Luengo, Alvarez, & Raso, 2014). Because of its superior antioxidant activity, lycopene has been found to have significant beneficial effect on human health in reducing the risk of cardiovascular diseases, atherosclerosis, prostate cancer and cognitive impairment (Giovannucci,

1999; Giovannucci, Rimm, Liu, Stampfer, & Willett, 2002; Song et al., 2017; Story, Kopec, Schwartz, & Harris, 2010). Therefore, in addition to its use as natural pigment in the dyeing of various kinds of food products (Strati & Oreopoulou, 2014), lycopene has been proposed, or is already used, in a wide range of industrial applications as food supplement or nutraceutical ingredient in the formulation of food products (Lu et al., 2019), as well as in the preparation of skin cosmetic for its antiaging properties (Lenucci et al, 2015), up to the more recent pharmaceutical uses (Mussagy, Winterburn, Santos-Ebinuma, & Pereira, 2019). This large number of applications of lycopene as high-added value product, combined with its abundance in tomato peels, and the growing consumer's demand for natural food additives, justifies the greater interest of researchers and manufacturers in the recovery of lycopene from tomato processing by-products, which are discarded from the peeling operation (Juric et al., 2019; Lu et al., 2019).

As most of the carotenoid compounds, lycopene is a highly hydrophobic molecule that is found predominantly in the chromoplast of plant tissues (Pataro et al., 2015; Juric et al., 2019). Because of these reasons, conventional methods used to recovery lycopene from tomato peels with sufficiently high yield typically require intensive pre-treatments of the raw material, mainly comminution and drying (Knoblich et al., 2005; Luengo et al., 2014; Pataro et al., 2018; Strati & Oreopoulou, 2014), as well as excessive usage of organic solvents, which are very often toxic and harmful, thus with negative effects in terms of environmental sustainability and on human health due to the uncompleted solvent removal from the final product (Ishida & Chapman, 2009; Lu et al., 2019; Strati & Oreopoulou, 2014).

In light of these drawbacks of conventional solvent extraction methods, in recent studies alternative, more sustainable, environmental friendly and food safety approaches were proposed, such as those based on the implementation of wet disruption methods of plant cells, such as pulsed electric field (PEF), prior to the extraction process (Grimi et al., 2014; Liu, Zeng, & Ngadi, 2018; Luengo et al, 2014; Pataro et al., 2018, 2019; Rocha et al., 2018), as well as on the usage of low impact solvents (Ishida & Chapman, 2009; Strati & Oreopoulou, 2011b).

More specifically, it has been shown that PEF pre-treatment of moderate electric field intensity (0.5-10 kV/cm) and relatively low energy input (1-10 kJ/kg) has beneficial effects on the permeabilization of membranes of plant cells, thus enabling high recovery yields of intracellular compounds of interest from a wide range of food processing wastes and by-products (Puértolas & Barba, 2016), while reducing the energy costs, the solvent consumption and shortening the treatment time (Rajha et al., 2019; Rocha et al., 2018; Sarkis, Boussetta, Tessaro, Marczak, & Vorobiev, 2015; Yu, Gouyo, Grimi, Bals, & Vorobiev, 2016).

Nevertheless, as per literature survey, only few works deal with the use of PEF as an intensification pre-treatment in the extraction of carotenoids from tomato peels, which were achieved at laboratory level after either peeling of untreated (Luengo et al., 2014) or PEF treated fresh tomato fruits (Pataro et al., 2018), or after steam blanching of tomatoes (Pataro et al., 2019). However, none of them was addressed to demonstrate the potential of PEF to intensify the extractability of carotenoids from peels derived from industrial steam peeling operation of tomato fruits, which might potentially induce thermal damages at cuticular level, thus making the subsequent PEF treatment useless.

The main objective of this work was to demonstrate the potential of PEF to intensify the extractability of carotenoids, especially lycopene, from peels derived from industrial steam peeling of tomato fruits in two different extraction solvents. Specifically, solvents with lower environmental impact and toxicity like acetone, listed in Class 3 by the U.S. Food and Drug Administration ("regarded as less toxic and of lower risk to human health"), and ethyl lactate, an environmental friendly solvent fully biodegradable in CO_2 and water, which is miscible with both hydrophilic and hydrophobic compounds **(**Amaro et al., 2015; Strati & Oreopoulou, 2011b), were selected for this work. Firstly, the effect of different combinations of field strength (E) and total specific energy input (W_T) on the extraction kinetics of lycopene was examined in each solvent with the aim to define optimal PEF pre-treatment conditions and extraction time. Then, the effect of the PEF-assisted extraction process carried out under optimal conditions on the total content and composition of carotenoids, as well as on the antioxidant activity of the extracts, was assessed.

2. Materials and methods

2.1. Tomato by-products

Tomato-processing by-products, mainly composed of peels, were gently provided by FPD s.r.l, a processing factory located in Fisciano (Salerno, Italy). For this work, tomato peels were obtained upon industrial steam peeling of tomato fruits (*Solanum lycopersicum*) of the "*Taylo*r" variety, which were field-grown in Apulia region (Southern Italy) in season 2018. The fresh fruits, having an almost cylindrical shape (4.4 ± 0.3 cm in diameter, 7.9 ± 0.5 cm in length), were harvested at red-ripening stage (Hue angle = 46.89 ± 2.27, total soluble solids = 4.83 ± 0.32 °Brix, titratable acidity = 0.43 ± 0.01 g citric acid/100g fresh weight tomatoes, moisture content = 93.2 ± 0.5%), transported to the FPD Company and processed within one day to obtain canned whole peeled tomatoes, according to the flow sheet depicted in the supplementary material (Figure S1). Briefly, after washing and sorting, tomato fruits entered the thermo-physical peeling phase, where the fruits were steam blanched in a scalder by pressurized steam (P = 120 kPa, t = 13 s), before being vacuum cooled (P = 54 ± 5 kPa, t = 2 s) and conveyed onto pinch rollers to facilitate complete peel removal. Whole peeled tomatoes were then canned and sterilized, while the produced tomato processing by-products (peels) were currently used as feed for animals. In this work, a sample of about 20 kg of these tomato peels was collected in plastic containers and immediately transported to the laboratories of ProdAl Scarl (Fisciano, Italy) and stored under refrigerated conditions (T = 4°C) until use, within 7 days from production. The moisture content of tomato-processing peels was determined upon arrival at the laboratory and found to be 64.2±1.5 %

2.2 Chemicals

HPLC grade methanol and acetonitrile as well as acetone, ethyl lactate, all-trans lycopene standard, iron chloride hexahydrate (FeCl3•6H2O), citric acid, and 2,4,6-tripyridyl-s-triazine (TPTZ) were

purchased from Sigma-Aldrich (Steinheim, Germany). Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) was obtained from Acros Organics (Geel, Belgium), while sodium acetate and acetic acid were purchased, respectively, from Panreac (Panreac Quimica, Barcelona, Spain) and Fisher (Fisher Scientific, Rodano, Italy).

2.3 PEF equipment

PEF treatments of tomato peels before solvent extraction were carried out using a laboratory scale batch system previously described by Bobinaitė et al. (2015). Briefly, the system consisted of a high voltage pulsed power (25 kV-500 A) generator (Modulator PG, ScandiNova, Uppsala, Sweden) able to deliver monopolar square wave pulses with different pulse width (3-25 μs) and frequency (1-450 Hz) through the plant tissue placed between two parallel plate cylindrical electrodes (3 cm in diameter, electrode gap up to 5 cm) of a batch treatment chamber. High voltage and current probes, connected to an oscilloscope, measured the actual voltage and current signals at the treatment chamber. The maximum electric field intensity (E, kV/cm) and total specific energy input (W_T, kJ/kg) were calculated as reported in Bobinaitė et al. (2015).

2.4 PEF-assisted extraction experiments

During PEF-assisted extraction experiments, samples of approximately 10 g of tomato peels, randomly selected after manual mixing of the initial sample (20 kg), were loaded into the treatment chamber with an inter-electrode gap of about 1.4 ± 0.1 cm. The PEF treatments were carried out at variable electric field strength (E = 1, 3 and 5 kV/cm) and total specific energy input (W_T = 5 and 10 kJ/kg) at a constant pulse repetition frequency (10 Hz) and pulse width (20 μs). The specific energy input per pulse (W_P) was equal to 0.012 kJ/kg, 0.160 kJ/kg and 0.475 kJ/kg, when the field strength was set at 1, 3 and 5 kV/cm, respectively, and the number of pulses applied ranged between 10 and 833. In all PEF experiments, the initial temperature of the samples was 20 ± 2 °C and no appreciable

163 temperature increase was detected due to the low energy input delivered during the treatment. All the
164 PEF treatments were performed in triplicate.
165 After the electro-permeabilization treatment, tomato peels were immediately placed into a 500 mL
166 Pyrex flask, where the extraction solvent (acetone or ethyl lactate) was added at a constant solid to
167 liquid ratio (1:40 g/mL). The flasks were then introduced in an orbital incubator S150 (PBI
168 international, Milan, Italy) set at 25°C where the extraction process was carried out under constant
169 shaking at 160 rpm for different diffusion times (0-1440 min).
170 According with previous findings (Pataro et al., 2019), extraction temperatures higher than 25°C were
171 not tested, since they seemed not to contribute to a significant increase in the extraction yield of
172 carotenoid compounds from peels of steam blanched tomatoes.
173 For the sake of comparison, untreated (control) tomato peels, achieved after industrial steam peeling
174 of tomato fruits, were subjected to conventional solid-liquid extraction process using the same
175 extraction protocol but without the application of the PEF pre-treatment.
176 To examine the effect of extraction time, two replicates of 1 mL extract of either untreated or PEF-
177 treated samples were removed from the flasks at different diffusion times (10, 20, 30, 45, 60, 120,
178 180, 240, 360 and 1440 min). The extracts were immediately centrifuged at 5700 x *g* (PK121R model,
179 ALC International, Cologno Monzese, IT) for 10 min at 4°C to separate the supernatant, which was
180 then filtered through 0.45 µm syringe filters. The final extracts were then stored at -20 °C until further
181 analysis.
182 According with the findings of Poojary & Passamonti (2014), the extraction kinetics data of lycopene
183 concentration (*LyC*) in each solvent were mathematically described using the empirical equation (Eq.
184 1) proposed by Peleg (1988), whose applicability on the extraction kinetic of intracellular compounds
185 from different food matrices has been extensively demonstrated (Bucic-Kojic, Planinic, Tomas, Bilic,
186 & Velic, 2007; Odriozola-Serrano, Soliva-Fortuny, Gimeno-Ano, & Martin-Bellozo, 2008; Poojary
187 & Passamonti, 2014).

$$LyC = \frac{t}{\frac{1}{v_0} + \frac{t}{LyC_\infty}} \quad (1)$$

where t is the extraction time (in min), v_o (in mg kg^{-1} of dry weight (DW) min^{-1}) refers to extraction rate at the very beginning ($t = t_0$), while LyC_∞ (in mg kg^{-1}DW) refers to the maximum concentration of lycopene in the extracts, that is, the equilibrium concentration of total extracted analyte when $t \rightarrow \infty$ (Poojary & Passamonti, 2014).

2.5 Optical microscopy analysis of tomato peel tissues

The effect of steam peeling and PEF treatment on the morphology and organization of the plant cells of tomato peel tissues was investigated by optical microscopy. The microscopic images were acquired with an inverted optical microscope (Nikon Eclipse TE2000-S) at 20 × magnification. In each experiment, 15 images from three different samples were analysed for tomato peels achieved upon hand peeling of fresh fruits, industrial steam peeling, and industrial steam peeling followed by PEF treatment.

2.6 Determination of lycopene content

The lycopene content of the supernatants of either acetone or ethyl lactate extracts achieved from untreated and PEF treated tomato peels was measured spectrophotometrically (V-650 UV-Vis, Jasco Inc., Easton, USA) in a 1-cm light path (l) cuvette at the wavelength of maximum absorption (λ_{max}) for lycopene in acetone (473 nm) and ethyl lactate (478 nm) against the corresponding solvent as blank. The λ_{max} values were determined experimentally from the spectra of pure lycopene in each solvent (data not shown). The following equations were used to calculate the lycopene concentration (LyC, in mg lycopene per kg DW tomato peels) in acetone (Eq. 2) and ethyl lactate (Eq. 3) extracts:

$$LyC = \frac{A_{473}}{l \cdot \varepsilon_{AC}} 40 \quad (2)$$

$$LyC = \frac{A_{478}}{l \cdot \varepsilon_{EL}} 40 \quad (3)$$

where A_{473} and A_{478} are the absorbances at λ_{max} in each solvent, ε_{AC} and ε_{EL} are the extinction coefficients of lycopene in acetone (90.82 L mg^{-1} cm^{-1} at 473 nm) and ethyl lactate (129.96 L mg^{-1} cm^{-1} at 478 nm), respectively, and 40 is the liquid to solid ratio adopted during the extraction process. The extinction coefficients were determined experimentally from the calibration curves for lycopene standard in either acetone or ethyl lactate in a concentration range comprised between 1 and 100 mg L^{-1}. All the assays were performed in triplicate.

2.7 HPLC analysis

The identification and quantification of lycopene molecules contained in either acetone or ethyl lactate extracts was carried out by High Performance Liquid Chromatographic (HPLC - DAD) analysis, using the method described by Pataro et al. (2018), with some modifications.

Carotenoids were separated using a Waters 1525 series HPLC system, equipped with a Water 2996 photodiode array detector (DAD) (Waters Corporation, USA). Analytical separation of carotenoids was carried out in a Waters Spherisorb C18 reverse phase column (5 μm ODS2, 4,6 mm x 150 mm, Water Corporation, USA). The temperature of the HPLC column was set at 30°C. Before the injection, tomato peels extracts were filtered with 0.20 μm filters. The mobile phase consisted of acetonitrile/methanol (10:90, v/v) and 9 mM TEA (triethilamine). The flow rate of the mobile phase through the column and the injection volume were 1 mL/min and 5 μL, respectively. The absorbance detection wavelength was set at 473 nm for acetone extracts and at 478 nm for ethyl lactate extracts. Lycopene was identified by comparing its HPLC retention time and visible absorption spectra with those of commercial standard. All-trans lycopene was dissolved in either acetone and ethyl lactate to generate five-point external standard calibration curves (concentration range was from 10 to 100

231 mg/L), whose linearity was acceptable (R^2= 0.9924 for acetone, and R^2= 0.9934 for ethyl lactate).
232 The content of lycopene in the extracts was expressed as mg lycopene per kg of DW tomato peels.

233

234 *2.8 Ferric Reducing Antioxidant Power (FRAP) assay*

235 FRAP assay of extracts from untreated and PEF treated tomato peels was carried out according to
236 the method described by Benzie & Strain (1996), modified as described by Pataro et al. (2018). The
237 FRAP working solution was prepared by freshly mixing 0.3 M sodium acetate buffer, 10 mM TPTZ
238 solution, and 20 mM ferric solution at a ratio of 10:1:1 (v/v/v). For the evaluation of the antioxidant
239 power of acetone extracts, 2.5 mL of freshly prepared FRAP working solution and 0.5 mL of
240 undiluted extract were mixed and incubated for 10 min at ambient temperature. The change in
241 absorbance due to the reduction of ferric-tripyridyltriazine (Fe III-TPTZ) complex by the
242 antioxidants contained in the samples was monitored at 593 nm using a V-650 UV-Vis
243 spectrophotometer (Jasco Inc., Easton, USA). The absorptions of blank samples (applying the same
244 analysis conditions) were tested each time before and after analysis. For the ethyl lactate extracts,
245 instead, prior to FRAP assay, the samples were evaporated to dryness by using a R-200/205
246 Rotavapor (BÜCHI Labortechnik AG, Flawil, Switzerland) set at 30°C; residues were then
247 resuspended in the same volume of acetone for spectrophotometric analysis.
248 Trolox was used as the standard for calibration curve and the FRAP values were expressed as mmol
249 of trolox equivalents (mmol TE) per kg of DW tomato peels. All the assays were performed in
250 triplicate.

251

252 *2.9 Statistical analyses*

253 All experiments and analysis, unless otherwise specified, were performed in triplicate and the mean
254 and standard deviation (SD) of the experimental values were calculated. Statistically significant

differences ($p \leq 0.05$) among the averages were evaluated using one-way analysis of variance (ANOVA) and the Tukey's test ($p < 0.05$). Statistical analysis were carried out using IBM SPSS Statistics 20 software (SPSS Inc., Chicago, USA). SigmaPlot 10.0 (Systat Software, Inc) was used for nonlinear regression analysis by Eq. 1 of the data obtained from the experiments conducted to assess the effects of extraction time and PEF processing conditions on the kinetic parameters v_0 and LyC_∞. The goodness of model fitting was evaluated by calculating the determination coefficient (R^2).

3 Results and discussion

3.1 Effect of PEF pre-treatment and type of solvent on extraction kinetic of lycopene from tomato peels

Acetone and ethyl lactate have been used by different scientists as effective and low environmental impact solvents for the recovery of carotenoids from tomato processing by-products (Ishida & Chapman, 2009; Luengo et al., 2014; Pataro et al., 2018, 2019; Strati & Oreopoulou, 2011a, b). In this work, the effect of PEF pre-treatment on intensifying the extractability of carotenoids, especially lycopene, from peels derived from industrial processing of tomato fruits, was investigated in both these solvents. Figures 1 and 2 show the influence of a PEF pre-treatment application at different electric field strength (1 - 5 kV/cm) and total specific energy input (5 - 10 kJ/kg) on the extraction kinetics of lycopene from tomato peels in acetone and ethyl lactate, respectively. The kinetic experimental data from untreated and PEF treated tomato peels were fitted by the Peleg's model (Eq.1). The calculated parameters of this model, namely v_o and LyC_∞, and values of determination coefficients R^2 are shown in Table 1 (for acetone extracts) and Table 2 (for ethyl lactate extracts). It should be noted that a greater v_o value in Eq. (1) implies a faster rate of the process, whilst a greater LyC_∞ value in Eq. (1) indicates a greater extraction yield (Poojary & Passamonti, 2014).

As it can be seen, the determination coefficients ranged between 0.968 and 0.989, indicating that the Peleg's model could be applied rather satisfactorily in the prediction of the extraction rate of lycopene

280 in these solvents. This is consistent with findings previously reported by other scientists on the
281 extraction of intracellular compounds like polyphenols or carotenoids from different plant tissues.
282 (Bucic-Kojic et al., 2007; Odriozola-Serrano et al., 2008; Poojary & Passamonti, 2014).
283 Moreover, as shown in Figures 1 and 2, regardless of PEF pre-treatment application and type of
284 solvent, *LyC* strongly depended on extraction time. Specifically, *LyC* rised rapidly during the initial
285 stage of extraction, when the solvent penetrates into the solid matrix, due to the high concentration
286 gradient developed between solid and liquid phases (Poojary & Passamonti, 2014). Then the
287 extraction rate gradually decreased with time, likely due to both the decrease in concentration driving
288 force between the solid and liquid phases and the decrease in concentration of the analytes in the solid
289 phase (Poojary & Passamonti, 2014), until an almost equilibrium condition was approached.
290 Independently of the extracting solvent, the majority of the carotenoid compounds were recovered
291 approximately during the first 240 min of extraction, while longer diffusion times did not produce
292 any substantial increment of the amount of total lycopene.
293 In agreement with previous findings (Luengo et al., 2014; Pataro et al., 2019; Strati & Oreopoulou,
294 2011a,b), the results of Figures 1 and 2 also highlight that acetone and ethyl lactate are good extraction
295 solvents, because they are able to penetrate the plant cells of tomato peel tissues, where carotenoids
296 are enclosed, and to dissolve substantial amount of them (Luengo et al., 2014; Strati & Oreopoulou,
297 2011a,b). However, it is likely that the ability of both these solvents to penetrate the plant cells of
298 tomato peel tissues detected in this work was further enhanced by the partial cell disintegration
299 induced at cuticular level by the industrial steam peeling treatment of tomato fruits. This is
300 corroborated by the findings of Pataro et al. (2018), who quantified the thermal damages induced at
301 the cuticular level upon steam blanching treatment of tomato fruits, through the evaluation of the cell
302 disintegration index (Z_p). The latter is widely considered as a reliable macroscopic indicator of the
303 degree of cell damages in diverse fruits and vegetable tissues (Bobinaite et al., 2015; Donsì, Ferrari,
304 & Pataro, 2010; Luengo, Alvarez, & Raso, 2013; Puértolas, Cregenzan, Luengo, Alvarez, & Raso,
305 2013), where it assumes a value ranged between 0 (for intact tissue) and 1 (for fully permeabilized

306 tissue). Specifically, the authors found that the Z_p values of tomato peel tissues achieved after hand
307 peeling of steam blanched tomato fruits in a lab-scale scalder for 1 min, significantly increased from
308 0.2 to 0.57 when the blanching temperature was increased from 50 to 70 °C.
309 Additionally, it is worth noting that the initial extraction rate and concentration at equilibrium were
310 considerably higher in acetone (Figure 1, Table 1) than in ethyl lactate (Figure 2, Table 2). For
311 instance, the extraction time required to achieve a given concentration of lycopene (8280± 322 mg/kg
312 DW) in acetone and ethyl lactate was 32 min and 240min, respectively. On the other hand, the
313 amounts of lycopene recovered from the untreated tomato peels after 240 min extraction was 13945±
314 610 mg/kg DW in acetone and 8280± 322 mg/kg DW in ethyl lactate.
315 In contrast with these findings, when Strati & Oreopoulou (2011b) studied the effect of the type of
316 solvent on the recovery of carotenoids from dried powder of tomato wastes (skins and seeds), they
317 found that ethyl lactate allowed a remarkable recovery of carotenoids, whose extent was 5-fold greater
318 than that observed when using acetone. Similarly, Ishida & Chapman (2009) found that ethyl lactate
319 achieved to extract more effectively tomato carotenoids from dried powder of tomato wastes than
320 acetone.
321 Although any comparison with data found in current literature is very difficult, this different
322 behaviour could be in part explained taking into account that the rate of extraction, and consequently
323 the approach to equilibrium, depend on the complex interaction between the solvent properties and
324 characteristics of the solid material.
325 Firstly, the solubilizing capacity of the solvent plays a very important role in the extraction process
326 (Luengo et al., 2014; Strati & Oreopoulou, 2011b). In this line, results of Figures 1 and 2 could be in
327 part explained by the slightly lower polarity of acetone in comparison with ethyl lactate (Amaro et al,
328 2015; Jessop, 2011), which likely makes acetone more adequate solvent to extract non polar
329 carotenoids (e.g., lycopene). In addition to solubility, the capacity of penetration or diffusion of the
330 solvent into the solid matrix also has an important role in the extraction efficiency (Luengo et al.,
331 2014; Strati & Oreopoulou, 2014). To this purpose, acetone is generally reported to be a good solvent

and a wetting material that penetrates easily inside the plant cells where carotenoids are enclosed (Luengo et al., 2014; Strati & Oreopoulou, 2011a). Moreover, it should be also considered that, while acetone is an aprotic solvent, ethyl lactate is a protic solvent due to the presence of a hydroxyl group, which should make ethyl lactate more hydrophilic and water-soluble than acetone. This may have two opposite effects on extraction efficiency of ethyl lactate, whose relative importance may depend on the fact that a wet or a dry solid matrix is used. In fact, from one side, the higher solubility of ethyl lactate in water in comparison with acetone might enhance its penetration capacity into the solid matrix when extraction is conducted in wet tomato peels residues like in this work, which is consistent with findings of previous scientists (Lin & Chen, 2003; Luengo et al., 2014; Strati & Oreopoulou, 2011a). On the other hand, the interaction of ethyl lactate with water molecules of a wet solid matrix through the formation of hydrogen bonds might decrease the penetration capacity or diffusion coefficient of this solvent into the plant cells, thus negatively affecting the extraction yield. An opposite behavior should be noted, instead, in the case of a dried solid matrix where unbounded molecules of ethyl lactate might penetrate more easily inside the intracellular space. The predominance of one or other effect might explain the results observed in the experimental data shown in Figures 1 and 2 in comparison with those achieved by other scientists when using dried tomato wastes (Ishida & Chapman, 2009; Strati & Oreopoulou, 2011b). However, more work is required in order to better elucidate the role and interaction between the properties of the solvent affecting the extraction efficiency and the characteristics of the solid matrix.

The application of PEF treatments at different field strength (1-5 kV/cm) and total specific energy input (5-10 kJ/kg) to the industrially tomato peel residues before solvent extraction with either acetone or ethyl lactate markedly enhanced the extraction rate (by 27-37%) and the recovery yields (by 12-18%) of lycopene, as compared with untreated samples (Figures 1 - 2, Tables 1 - 2). However, at a fixed energy input of 5 kJ/kg, significant differences ($p \leq 0.05$) were detected only when the field strength was increased at 5 kV/cm, as compared with the control extraction (Figures 1a and 2a).

357 Further increments of the total specific energy input up to 10 kJ/kg scarcely influenced the
358 extractability of lycopene, independently of the field strength applied (Figures 1b and 2b).
359 This indicates that, in our case, a field strength of 5 kV/cm and an energy input of 5 kJ/kg were
360 sufficient to significantly intensify the extractability of lycopene from tomato peels in both the
361 investigated solvents. However, it is worth noting that the effect of PEF was more evident when the
362 extraction was made with acetone, while resulted less important when ethyl lactate was used as
363 solvent. In this latter case, it is likely that, in spite of the electropermeabilization effect induced by
364 PEF application, the slightly higher polarity of ethyl lactate in comparison with acetone along with
365 the reduced penetration capacity of the water-bounded molecules of this solvent, was still limiting its
366 extraction efficiency.
367 The positive impact of PEF pre-treatment on extraction of carotenoids from tomato peels was also
368 previously observed by other scientists, even thought, to date, no previous works dealt with the use
369 of peels derived from the industrial steam peeling of tomato fruits. For example, Luengo et al. (2014)
370 found that the extraction of carotenoids from tomato peels in acetone was significantly improved by
371 the application of a 90 μs PEF treatment up to 5 kV/cm, while a further increase in the intensity of
372 the electric field strength up to 7 kV/cm scarcely affected the extraction yield. However, differently
373 from this work, the authors used a different tomato variety and applied PEF pre-treatment to peels
374 obtained from hand peeling of fresh tomatoes. Pataro et al. (2019) evaluated the impact of PEF pre-
375 treatment on the cell structure of tomato peel tissues in terms of cell disintegration index (Z_p) and the
376 subsequent recovery of carotenoid compounds in acetone, but using peels obtained after steam
377 blanching of tomato fruits at 70°C for 1 min in a lab-scale scalder. Nevertheless, similarly to our
378 results, the authors found that a PEF (5 kV/cm, 5 kJ/kg) pre-treatment of steam blanched samples was
379 sufficient to significantly enhance the Z_p value (up to 0.54) and, consequently, the extraction yield of
380 total carotenoids (up to 47%), as compared with the control samples.
381 The increase in carotenoids (especially lycopene) extraction can be explained by the fact that the
382 electroporation effect induced by PEF treatment has the potential to further enhance the degree of cell

383 disintegration induced at cuticular level by the previous steam peeling treatment, as previously shown
384 by Pataro et al. (2019). This likely facilitated the penetration of the solvent into the cytoplasm of the
385 plant cell and the subsequent mass transfer of the solubilized intracellular compounds, thus
386 intensifying the extractability of carotenoids (Luengo et al., 2014; Pataro et al., 2019).
387 This is also corroborated by the microscopic pictures of tomato peel tissues achieved after hand
388 peeling of fresh fruits, industrial steam peeling, and industrial steam peeling followed by PEF
389 treatment (E = 5 kV/cm; W_T = 5 kJ/kg), presented in Figure 3. In particular, it can be noted that the
390 tissue of fresh tomato peels (Figure 3a) showed cells that were compacted, regularly shaped and red
391 colored likely due to the high lycopene content of the peels of ripe tomato fruits. The thermal damages
392 occurring at cuticular level during the steam peeling operation, apparently induced a slight reduction
393 in size and red colour intensity of plant cells of tomato peels, which also appeared slightly more
394 separated (Figure 3b). The application of PEF treatment to peels of steam peeled tomato further
395 reduced the size and separation between the plant cells, while preserving their original shape (Figure
396 3c). It is also worth noting that the plant cells of PEF treated samples showed a marked loss of the
397 initial red coloration likely due to the leakage of lycopene. The probable explanation of these effects
398 is pores formation in the cell membranes that causes leakage of cell fluids into the extracellular gap
399 between the plant cells. A similar effect was previously noted by other scientists, who observed that
400 PEF treatment induced significant size reduction and separation between muscle cells of salmon and
401 chicken as well as collagen leakage into the extracellular space, which was attributed to the
402 consequent pore formation in the cell membranes of the muscle cells (Gudmundsson & Hafsteinsson,
403 2001).
404 According to the results shown so far, further investigations aimed at studying the influence of PEF
405 pre-treatment on the carotenoids composition and antioxidant power of the acetone and ethyl lactate
406 extracts from industrial tomato peel residues, were carried out with the PEF conditions set at 5 kV/cm
407 and 5 kJ/kg and the extraction time set at 240 min.
408

3.2 *Effect of PEF pre-treatment and type of solvent on composition and antioxidant activity of tomato peel extracts*

The composition of acetone and ethyl lactate extracts in terms of the main carotenoid compounds, obtained from untreated and PEF (5 kV/cm, 5 kJ/kg) treated industrial tomato peels after 240 min of extraction, was assessed via HPLC-DAD analysis. The resulting chromatograms profiles detected at 473 nm for acetone and 478 nm for ethyl lactate extracts are presented in Figures 4 and 5, respectively. As it can be seen, the profiles of the extracts from untreated samples appeared to be similar, independently on the type of solvent (Figures 4a and 5a). Only one major peak corresponding to all-trans lycopene (peak 1) was clearly detected at an elution time of 8.3 min in acetone and 9.5 min in ethyl lactate extracts. However, one minor and unidentified compound (peak 2), was also detected immediately after the elution time of all-trans lycopene peak, which could be probably attributed to one of the possible cis-isomers of lycopene, as similarly reported by Ishida, Ma & Chan (2001). These results are perfectly coherent with the fact that lycopene is the most abundant carotenoid in tomato processing peels (Pataro et al., 2018, 2019; Strati & Oreopoulou, 2011a,b), and that about 90% of the lycopene in dietary sources is found in the linear, all-trans conformation (Boileau, Boileau, & Erdman, 2002).

Moreover, HPLC analysis showed that the concentration of all-trans lycopene detected in acetone and ethyl lactate extracts of untreated samples was 11820±141 mg/kg DW and 6311±254 mg/kg DW, respectively, which is consistent with results achieved via spectrophotometric assay after the same extraction time (Figures 1 and 2). This also confirmed that acetone achieved to extract more effectively lycopene from wet tomato peels, as compared with ethyl lactate, and that a substantial amount of lycopene was still retained in the industrial tomato processing peels. It is likely that the short exposure time (13 s) of tomato fruits at the relatively high temperature (123°C) used during the industrial steam peeling process, was allowing to avoid any degradation or isomerization of lycopene from all-trans to cis-isomers. Apparently in contrast with this conclusion, when Chen, Shi, Xue & Ma

434 (2009) examined the stability of lycopene under thermal treatment they found that heating at 80 and
435 100°C did not affect the stability, whereas heating at 120 and 140°C increased isomerization of
436 lycopene and resulted in the degradation of total lycopene and cis-isomers. This can be explained by
437 the fact that the authors investigated cooking times in the range between 1 and 4 h, which were well
438 above those used in this work.
439 Additionally, HPLC analysis of our extracts indicated that, regardless of the type of solvent, the
440 electrical pre-treatment neither promoted the selective extraction of specific compounds nor caused
441 isomerization or degradation reactions. This is in agreement with the observations reported by other
442 authors (Luengo et al., 2013, 2014; Lopez, Puertolas, Hernandez-Orte, Alvarez, & Raso, 2009; Pataro
443 et al., 2017, 2018, 2019; Puértolas et al., 2013), who found that PEF treatment did not significantly
444 alter the HPLC chromatogram profiles of different plant tissues extracts, probably due to the relatively
445 mild intensity of the applied treatment (Mahnic-Kalamiza, Miklavcic, & Vorobiev, 2014).
446 However, it is worth noting that, in comparison with the control sample, PEF pre-treatment increased
447 the peak area of all-trans lycopene (peak 1), whereas no appreciable changes could be detected in the
448 peak area of the unidentified compound (peak 2). In particular, coherently with the results of Figures
449 1 and 2, the application of PEF pre-treatment caused a remarkable increment of the concentration of
450 all-trans lycopene by 18% and 23% in acetone and ethyl lactate extracts, respectively, as compared
451 with control extraction.
452 The abundance of all-trans lycopene detected in the tomato peel extracts might be of particular
453 importance, as it has been demonstrated to be helpful for the stability and color intensity of the extract,
454 even though the all-trans form appears to be less bioavailable than its cis-isomers. (Boileau et al.,
455 2002).
456 Additionally, it has been demonstrated that lycopene molecules show several beneficial properties
457 for human health due to their superior antioxidant capacity (Giovannucci, 1999; Giovannucci et al.,
458 2002; Song et al., 2017; Story et al., 2010). For this reason, in this work, the effect of PEF pre-
459 treatment on the antioxidant potential of the acetone and ethyl lactate extracts was assessed using the

FRAP assay. As shown in Table 3, regardless the application of PEF pre-treatment, acetone extracts possessed significantly ($p < 0.05$) higher FRAP values (65.5 % on average) than ethyl lactate extracts. In addition, in comparison with control extracts, PEF treated samples exhibited a stronger antioxidant power, which rose approximately by 18.0% and 18.2%, when extraction was carried out in acetone and ethyl lactate, respectively. These findings suggest that carotenoids, especially lycopene, strongly contribute to the antioxidant power of tomato peel extracts, as previously found in some other literature works, in which it was observed a highly positive correlation between total carotenoids, lycopene content and antioxidant activity of peel extracts (Luengo et al., 2014; Pataro et al., 2018, 2019).

4 Conclusions

The results of this work demonstrated that the application of PEF pre-treatment of moderate intensity (5 kV/cm) and relatively low energy input (5kJ/kg) before solvent extraction process with either acetone or ethyl lactate, can represent a sustainable, environmental friendly and food safety approach to intensify the extractability of carotenoids, especially lycopene, from industrial tomato peels residues.

The higher lycopene yield and antioxidant power of acetone extracts in comparison with ethyl lactate extracts indicates a better capability of this solvent to penetrate the plant cells of wet tomato peel tissue and to solubilize a greater amount of intracellular lipophilic compounds.

HPLC analyses revealed that all-trans lycopene is the most predominant carotenoid in the peel extracts, hence responsible for their antioxidant power, and no isomerization or degradation of lycopene occurred upon the application of PEF.

This work demonstrates the potential of PEF as a gentle and effective cell disintegration pre-treatment of wet plant tissues, such as industrial tomato peels residues, alternative to conventional extraction

485 methods, which require energy intensive pre-treatments of the raw material (e.g., comminution and
486 drying), large amount of organic solvents, high extraction temperatures and long extraction time.
487 However, comparative studies at preindustrial scale should be performed in order to validate the
488 results of the present research as well as to evaluate from an economical and environmental point of
489 view the advantages of PEF-assisted extraction against conventional extraction processes.
490
491
492 **Acknowledgments**
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494

495 **References**

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618

Figure Captions

Figure 1 Extraction kinetics of lycopene in acetone solvent from untreated (E = 0 kV/cm) and PEF treated tomato peel samples at variable field strength (E) and for two different total specific energy input (W_T): (a) 5 kJ/kg and (b) 10 kJ/kg. Extraction temperature was set at 25°C.

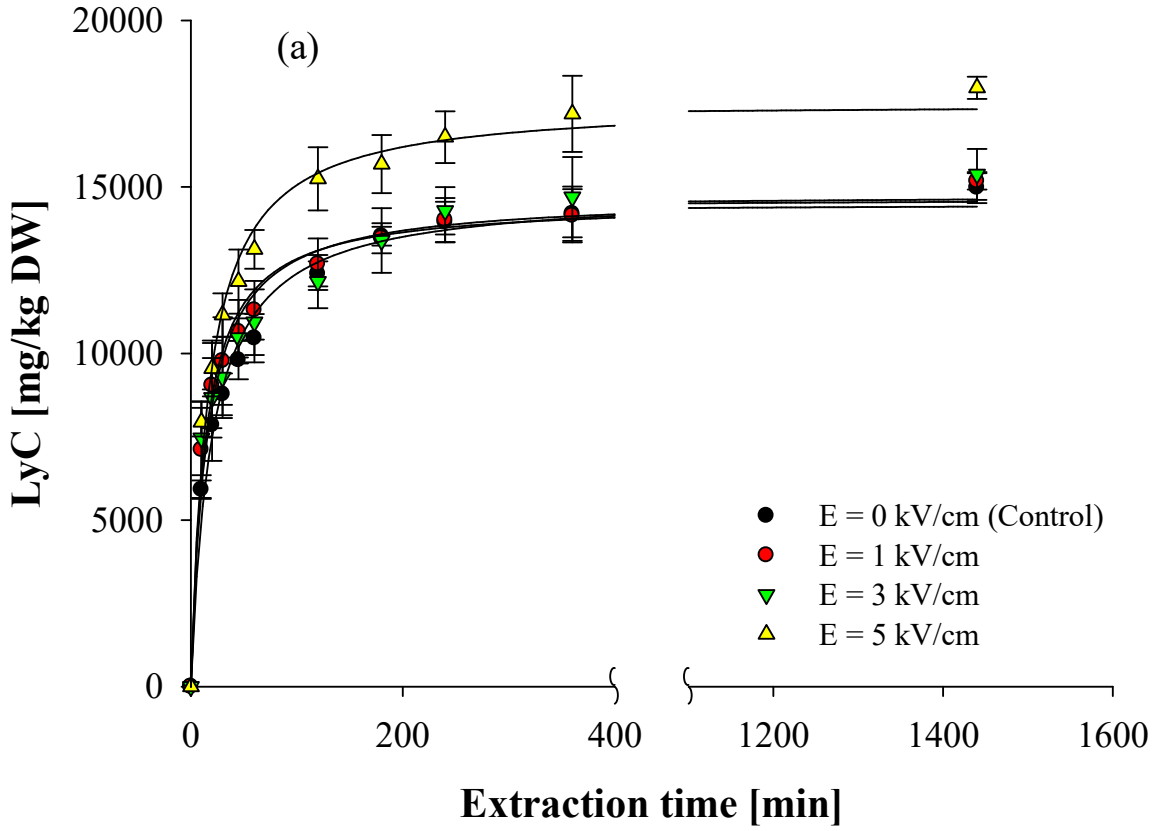
Figure 2 Extraction kinetics of lycopene in ethyl lactate solvent from untreated (E = 0 kV/cm) and PEF treated tomato peel samples at variable field strength (E) and for two different total specific energy input (W_T): (a) 5 kJ/kg and (b) 10 kJ/kg. Extraction temperature was set at 25°C.

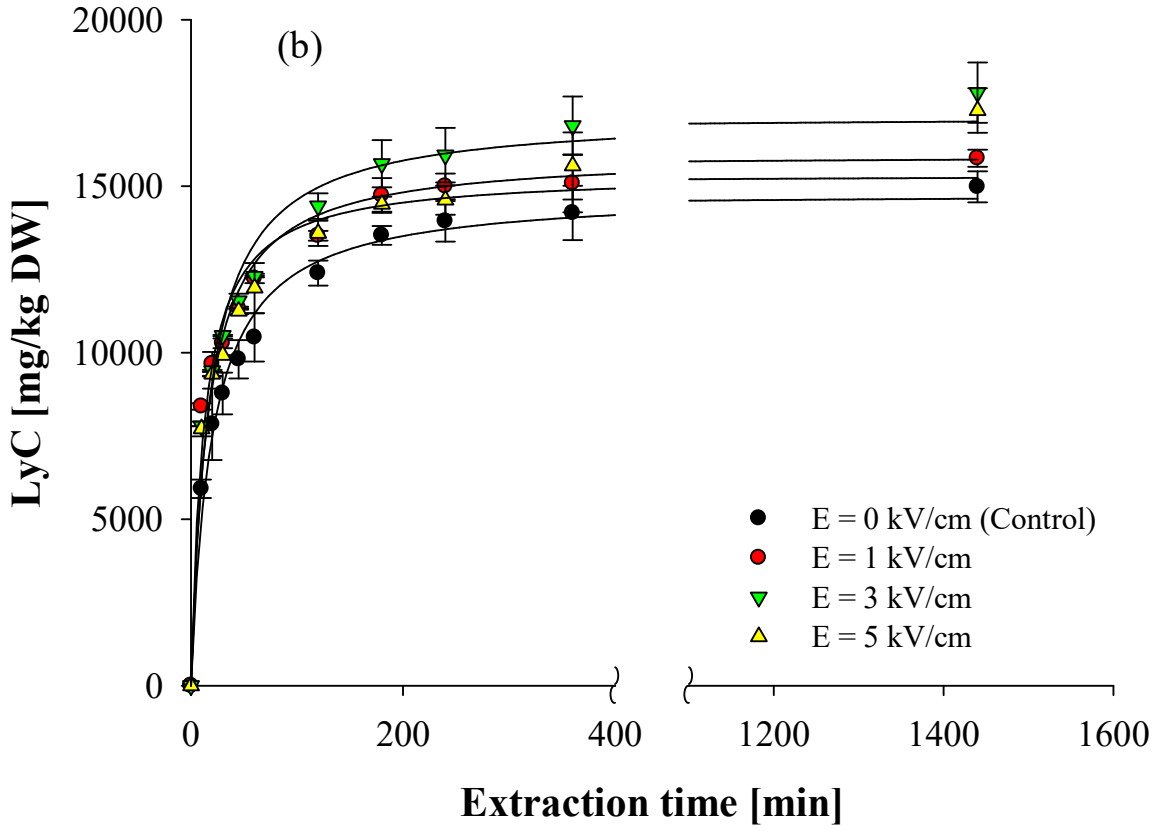
Figure 3 Micrographs (20x magnification) of tomato peels after (a) hand peeling of fresh fruits, (b) industrial steam peeling, and (c) industrial steam peeling followed by PEF treatment (E = 5 kV/cm; W_T = 5 kJ/kg).

Figure 4 HPLC chromatograms (λ = 473 nm) of acetone extracts obtained after 240 min extraction at 25°C from (a) untreated (Control) and (b) PEF treated (5 kV/cm, 5 kJ/kg) industrially derived tomato peels. Peak identification: (1) all-trans lycopene ($t_{elution}$: 8.3 min), (2) undefined carotenoid compounds ($t_{elution}$: 9.9 min).

Figure 5 HPLC chromatograms (λ = 478 nm) of ethyl lactate extracts obtained after 240 min extraction at 25°C from (a) untreated (Control) and (b) PEF treated (5 kV/cm, 5 kJ/kg) industrially derived tomato peels. Peak identification: (1) all-trans lycopene ($t_{elution}$: 9.5 min), (2) undefined carotenoid compounds ($t_{elution}$: 11.2 min).

Figure 1


(a)
LyC [mg/kg DW]
20000
15000
10000
5000
0
0
200
400
1200
1400
1600
Extraction time [min]
E = 0 kV/cm (Control)
E = 1 kV/cm
E = 3 kV/cm
E = 5 kV/cm


(b)
LyC [mg/kg DW]
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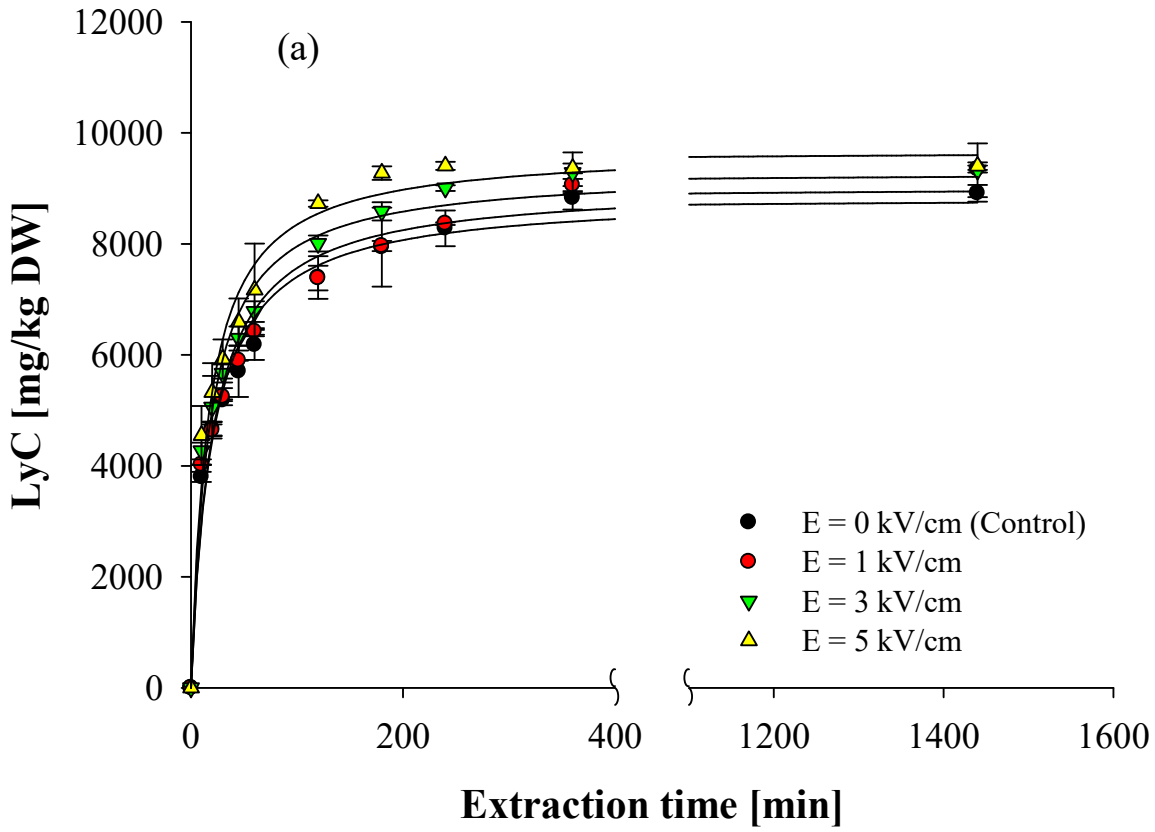
15000
10000
5000
0
0
200
400
1200
1400
1600
Extraction time [min]
E = 0 kV/cm (Control)
E = 1 kV/cm
E = 3 kV/cm
E = 5 kV/cm

Figure 2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LyC [mg/kg DW]
Extraction time [min]
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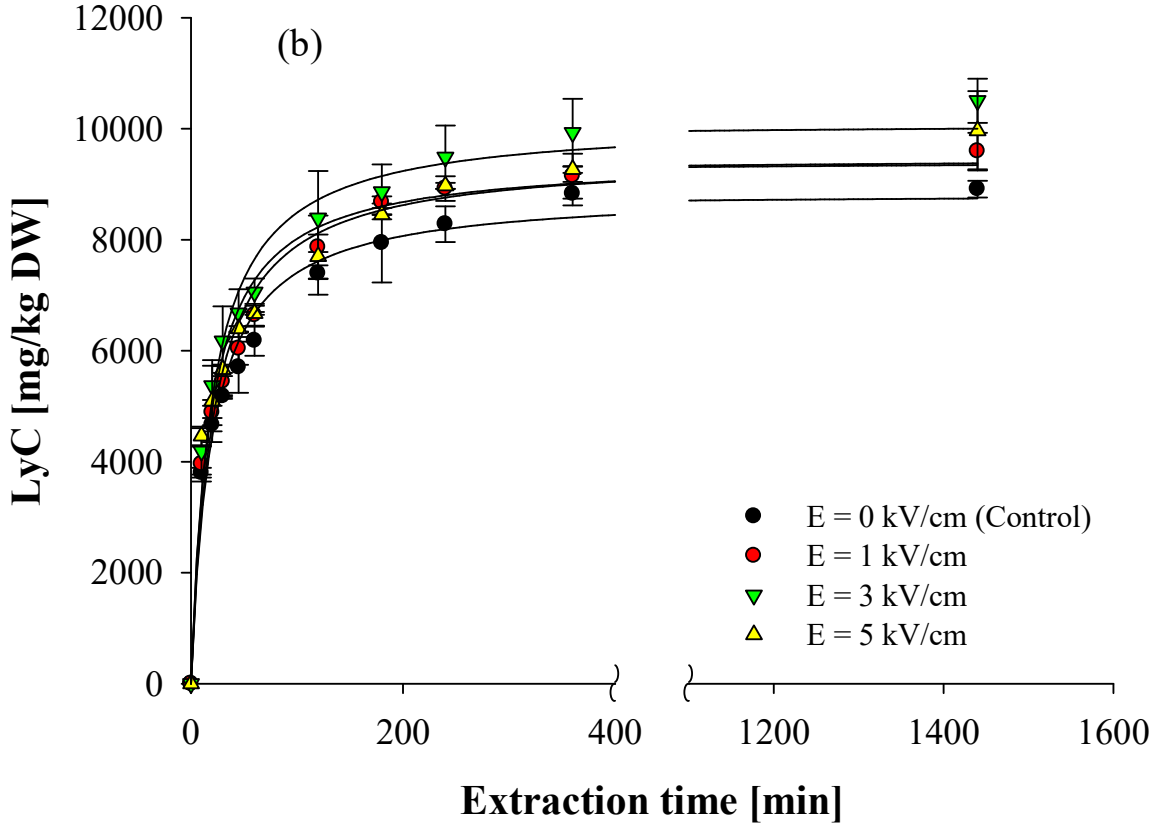
E = 1 kV/cm
E = 3 kV/cm
E = 5 kV/cm


(b)
LyC [mg/kg DW]
Extraction time [min]
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E = 1 kV/cm
E = 3 kV/cm
E = 5 kV/cm

Figure 3

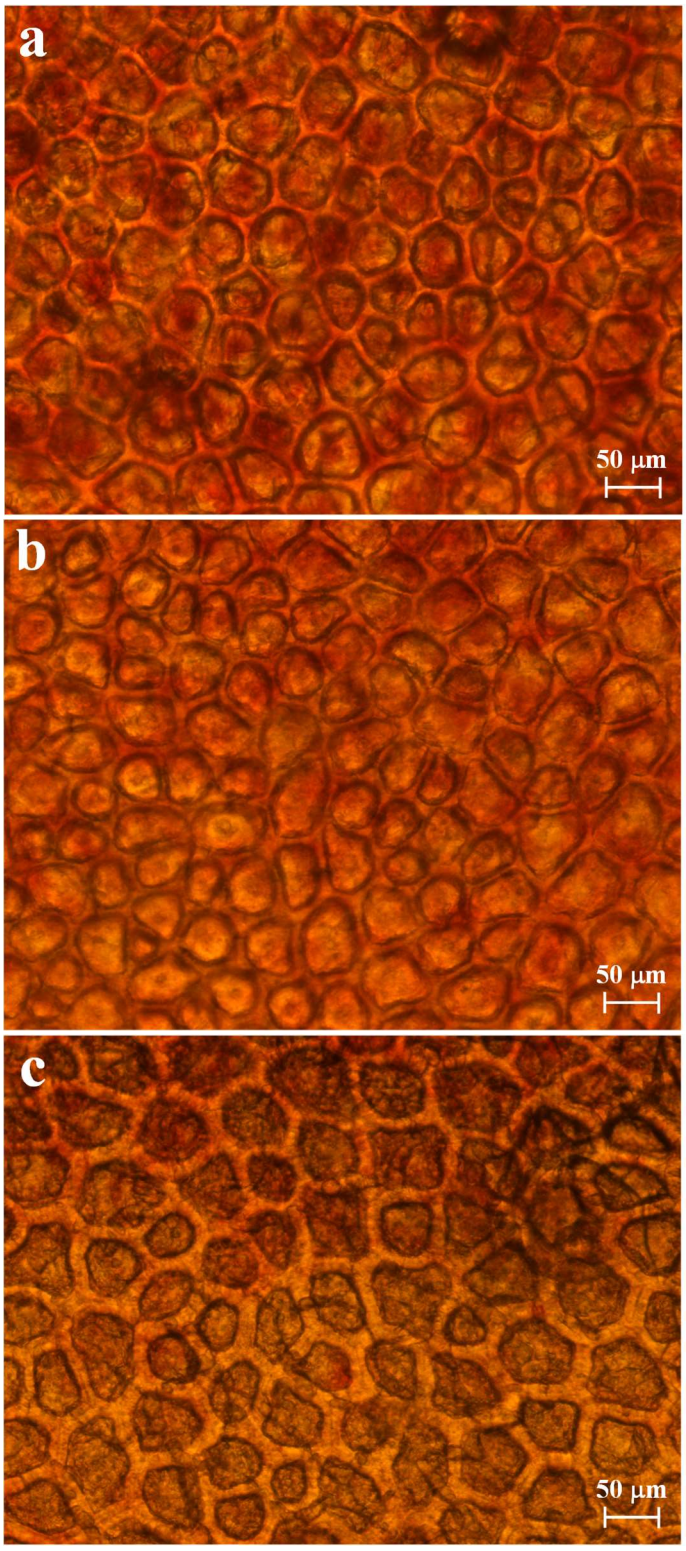
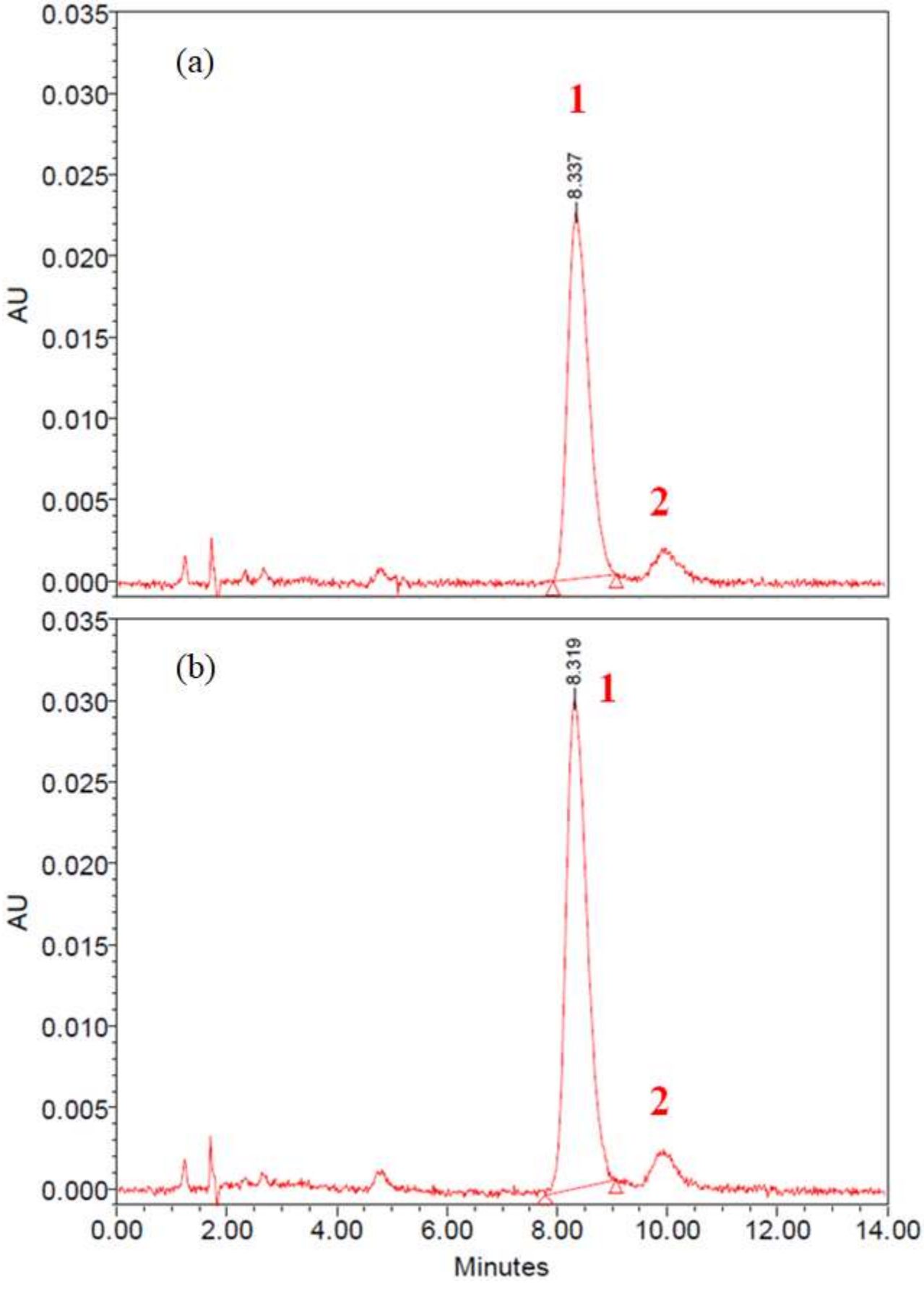


Figure 4


(a)
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(b)
8.319
1
2
AU
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0.015
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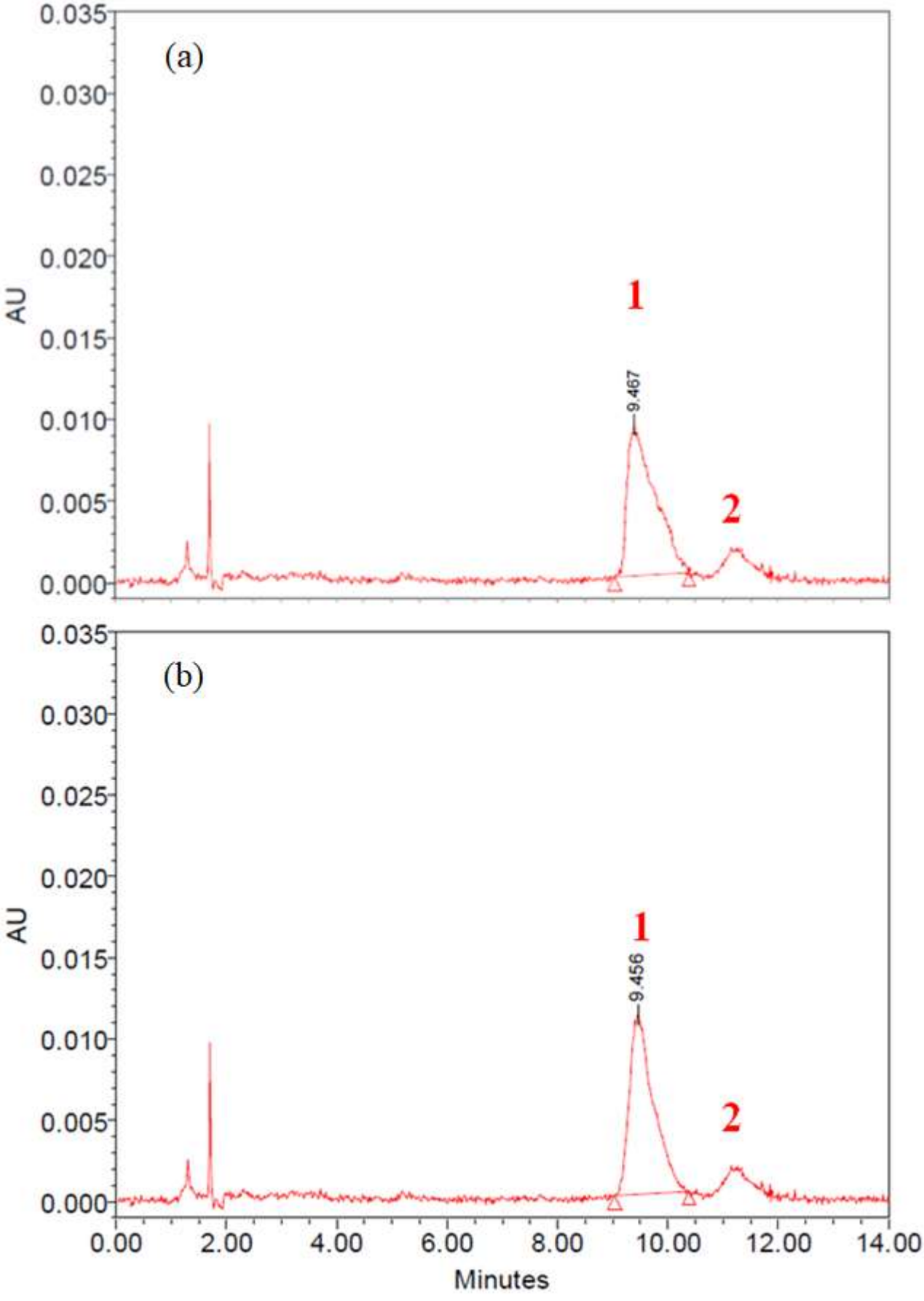
12.00
14.00
Minutes

Figure 5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0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
AU
1
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2
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
Minutes

Table 1. Initial extraction rate (v_0) and maximum lycopene content (LyC_∞) of acetone extracts from untreated (Control) and PEF treated (E = 1 – 5 kV/cm; W_T = 5 – 10 kJ/kg) industrially derived tomato peels, obtained by fitting the experimental data of lycopene extraction kinetics (Figure 1) with Peleg's model (Eq. 1).

Sample	**E (kV/cm)**	**W_T (kJ/kg)**	**v_0 (mg/kg DW min)**	**LyC_∞ (mg/kg DW)**	**R^2**
Control	0	0	756.8	14823	0.989
PEF	1	5	1097.1	14541	0.988
	1	10	1284.6	15375	0.972
	3	5	993.7	14702	0.969
	3	10	979.8	17147	0.979
	5	5	1032.9	17532	0.987
	5	10	1025.7	15968	0.979

Table 2. Initial extraction rate (v_0) and maximum lycopene content (LyC_∞) of ethyl lactate extracts from untreated (Control) and PEF treated (E = 1 – 5 kV/cm; W_T = 5 – 10 kJ/kg) industrially derived tomato peels, obtained by fitting the experimental data of lycopene extraction kinetics (Figure 2) with Peleg's model (Eq. 1).

Sample	**E (kV/cm)**	**W_T (kJ/kg)**	**v_0 (mg/kg DW min)**	**LyC_∞ (mg/kg DW)**	**R^2**
Control	0	0	450.2	8861	0.979
PEF	1	5	455.7	9068	0.974
	1	10	462.5	9509	0.983
	3	5	524.3	9778	0.976
	3	10	491.5	10140	0.968
	5	5	569.8	9930	0.973
	5	10	524.3	9461	0.982

Table 3. Ferric reducing antioxidant power (FRAP) of acetone and ethyl lactate extracts obtained from untreated (Control) and PEF treated (5 kV/cm, 5 kJ/kg) industrially derived tomato peels. Extraction temperature and time were set at 25°C and 240 min, respectively. Data are expressed as means ± Standard deviation. Values with different lowercase letters within the same row are significantly different ($p<0.05$), while values with different uppercase letters within the same column are significantly different ($p<0.05$).

Sample	**Solvent**	
	Acetone	**Ethyl Lactate**
Control	13.68 ± 0.18^{aA}	8.24 ± 0.12^{bA}
PEF (5 kV/cm – 5 kJ/kg)	16.11 ± 0.22^{aB}	9.74 ± 0.51^{bB}

Supplementary material

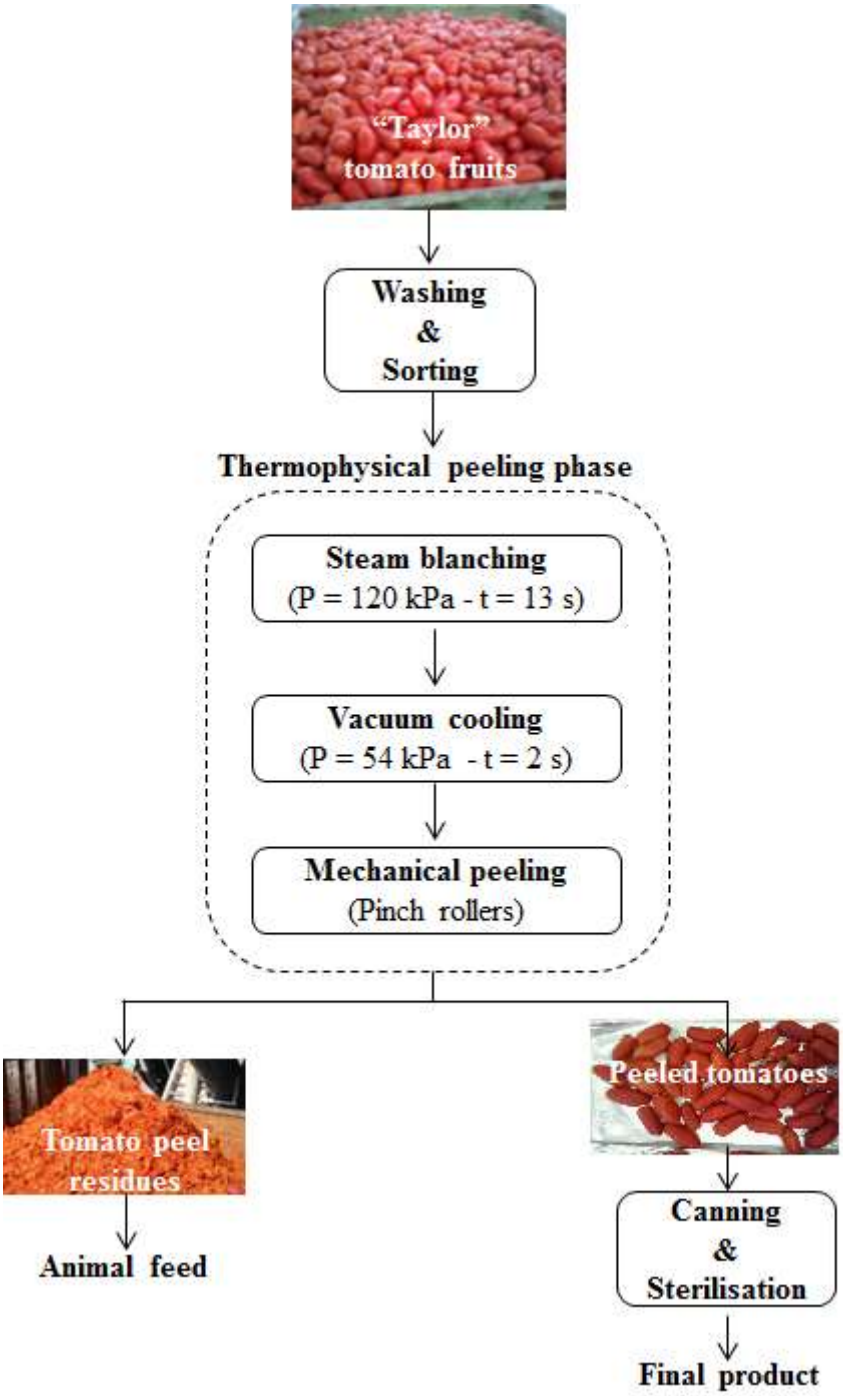

Figure S1. Flow diagram of industrial production line of peeled tomatoes.