Journal of Food Engineering 262 (2019) 170–180

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

High-pressure homogenization treatment to recover bioactive compounds from tomato peels

Slaven Jurić[a,b], Giovanna Ferrari[c,d], Krassimir P. Velikov[e,f,g,**], Francesco Donsì[c,*]

[a] Faculty of Agriculture, University of Zagreb, Department of Chemistry, Svetošimunska Cesta 25, 10000 Zagreb, Croatia
[b] Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia
[c] Department of Industrial Engineering, University of Salerno, via Giovanni Paolo II 132, 84084 Fisciano, Italy
[d] ProdAl Scarl, via Ponte don Melillo, 84084 Fisciano, SA, Italy
[e] Unilever R&D Vlaardingen, Olivier van Noortlaan 120, 3133 AT, Vlaardingen, the Netherlands
[f] Institute of Physics, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, the Netherlands
[g] Soft Condensed Matter, Debye Institute for NanoMaterials Science, Utrecht University, Princetonplein 5, 3584 CC Utrecht, the Netherlands

ARTICLE INFO

Keywords:
High-pressure homogenization
Tomato peels
Lycopene
Bioactive compounds
Agro-food by-products
Natural functional ingredients

ABSTRACT

By-products of tomato processing are rich in bioactive compounds and their recovery might bring significant economic and environmental benefits. High-pressure homogenization (HPH) (1–10 passes at 100 MPa) was used as a disruption method to recover valuable compounds from tomato peels, using solely water as process medium. Micronization of tomato peels suspensions by HPH reduced their size distribution below the visual detection limit, because of the complete disruption of individual plant cells. With respect to high-shear mixing (5 min at 20000 rpm), HPH processing (10 passes) caused an increased release of intracellular compounds, such as proteins (+70.5%), and polyphenols (+32.2%) with a corresponding increase in antioxidant activity (+23.3%) and reduction in oil-water interfacial tension (−15.0%). Remarkably, also the release of water-insoluble lycopene in the aqueous supernatant increased, enabling the recovery of up to 56.1% of the initial peel content, well above what reported in the literature when using organic solvents or supercritical CO_2.

1. Introduction

Tomato processing by-products are generally used as animal feed or compost, despite they are still rich in high value-added compounds, hence projecting significant economic and environmental benefits from their exploitation as functional food ingredients and nutraceuticals (Santini et al., 2013).

On a dry basis, the tomato processing by-products (peels and seeds) are rich in polyphenols (> 1000 mg GAE/kg (Nour et al., 2018)), fibers (about 50 wt % (Nour et al., 2018)), proteins (between 10 (Elbadrawy and Sello, 2016) and 18 wt % (Nour et al., 2018)), and carotenoids, such as β-carotene (about 95 mg/kg (Nour et al., 2018)) and lycopene (about 500–800 mg/kg (Nobre et al., 2009; Nour et al., 2018)).

Lycopene, which is the main component of tomato-residues carotenoids, is found to have significant beneficial effects on human health (Story et al., 2010). It is accumulated in higher concentrations in tomato peels and the water-insoluble fractions of tomatoes (72%–90%) than in the flesh (Sharma and Le Maguer, 1996), which is motivating the interest in the valorization of the tomato processing by-products, which consists mainly of tomato peels (Viuda-Martos et al., 2014). However, it is important to remark that lycopene is found predominantly in the chromoplast of plant tissues. During the ripening process of tomatoes, chloroplasts undergo transformation to chromoplasts and lycopene biosynthesis increases dramatically (Ellis, 1979). Lycopene, as a highly hydrophobic molecule, is located inside the vesicles generated from the inner membrane of the plastid and is arranged exclusively within the inner part of the lipid bilayer (Fiedor and Burda, 2014). In addition, within the vegetable cells, lycopene is present in a complexed form with proteins (Agarwal et al., 2001; Erdman et al., 1988). Because of all these reasons, lycopene recovery from tomato peels requires intensive thermal or mechanical treatments and organic solvents, with negative effects in terms of environmental sustainability, as well as the risk of lycopene thermal degradation (Manzo et al., 2018).

Moreover, tomato lycopene is part of those substances found in edible fruit and vegetables, including also isoflavones, resveratrol, garlic allyl sulfides, onion quercetin, which can be consumed daily, because they have the capability to favorably modulate human

* Corresponding author.
** Corresponding author. Unilever R&D Vlaardingen, Olivier van Noortlaan 120, 3133 AT, Vlaardingen, the Netherlands.
E-mail addresses: Krassimir.Velikov@unilever.com (K.P. Velikov), fdonsi@unisa.it (F. Donsì).

https://doi.org/10.1016/j.jfoodeng.2019.06.011
Received 12 February 2019; Received in revised form 13 June 2019; Accepted 15 June 2019
Available online 17 June 2019
0260-8774/

Abbreviations

AAE	ascorbic acid equivalent
AHC	agglomerative hierarchical clustering
ANOVA	analysis of variance
BHT	butylated hydroxytoluene
BSA	bovine serum albumin
D-Glu	D-glucose
FRAP	ferric reducing antioxidant power
GAE	gallic acid equivalent
HPH	high-pressure homogenization
HPLC	high-pressure liquid chromatography
HSM	high-shear mixing
MeOH	methanol
PEF	pulsed electric fields
SD	standard deviation
TEA	triethylamine
THF	tetrahydrofuran
TPC	total polyphenol content
TPTZ	2,4,6-tripyridyl-S-triazine
US	ultrasounds

metabolism to prevent cancer and other diseases (Santini et al., 2018).

In general, also the other active ingredients of tomato peels are tightly locked inside the plant cells, with consequent significant resistances to mass transfer during conventional extraction processes, such as solvent, enzymatic or thermal extraction (Chan et al., 2014; Franco et al., 2007). Because of that, novel methods are under investigation, for the partial or total disintegration of the vegetable cells. Polysaccharides are predominantly located between the primary and secondary cell walls, which differ in arrangement and structure of cellulose microfibrils, as well as their roles in the life of the plant (Cosgrove and Jarvis, 2012), whereas proteins (with a prevalent amino acid content of glutamic acid, aspartic acid, arginine, leucine, lysine (Elbadrawy and Sello, 2016; Nour et al., 2018)), phenols (in particular caffeic, protocatechuic, vanillic, and gallic acid and catechin (Elbadrawy and Sello, 2016)), and other antioxidants (in particular flavonoids, β-carotene and lycopene (Nour et al., 2018)), along with lipids (in particular, fatty acids (Elbadrawy and Sello, 2016; Nour et al., 2018)), are found in the inner bodies of the cells, i.e. vacuoles and lipid vesicles. Therefore, the permeabilization of the primary cell membranes, such as those induced by Pulsed Electric Fields (PEF) (Pataro et al., 2018), might not be sufficient, and more intensive or selective processes are needed to open up the secondary membranes (Donsì et al., 2013, 2010).

For example, high-shear mixing (HSM), routinely used to prepare foams, emulsions, and suspensions, is able to mill coarse particles suspended in a fluid, under the strong shear forces generated by the high rotation speed of 10,000–20,000 rpm (Chen et al., 2014). However, literature data have shown that this process is able to disaggregate cell lumps, but not to efficiently disrupt vegetable cells (Mustafa et al., 2018). High-pressure homogenization (HPH) has been reported to be a fast and effective method to micronize plant tissue in suspension and to unlock the bioactive compounds entrapped in cells, with high extraction yields (Mustafa et al., 2018; Shouqin et al., 2004). Moreover, HPH is able to produce a homogeneous size distribution of the vegetable particles suspended in a liquid, by forcing the liquid under the effect of pressure through a specifically designed homogenization valve (Patrignani and Lanciotti, 2016). High-pressure homogenization (HPH) is a technique specifically suitable for industrial applications, because of the ease of operation, scalability, reproducibility, and high throughput (Liedtke et al., 2000; Schultz et al., 2004).

The main objective of this work is to investigate the potential of HPH processing of suspensions of tomato peels in water to induce high levels of cell disruption and high yields of recovery of intracellular compounds, such as lycopene, total polyphenols, proteins, and polysaccharides. The final goal of this research is, hence, to investigate the possibility of full exploitation of the by-products of the tomato processing industry, achieving the concept of zero residual waste, and developing a green, sustainable process, which uses water as recovery medium.

2. Materials and methods

HPLC grade methanol, ethanol, acetonitrile, and 2,4,6-tripyridyl-S-triazine (TPTZ) were supplied from Sigma-Aldrich (Steinheim, Germany). Sulphuric acid was purchased from Sigma Aldrich (St. Louis, USA). Analytical grade formic acid was purchased from Riedel-deHaën (Seelze, Germany). The chemicals for total polyphenols (Folin-Ciocalteau reagent), lycopene standard, bovine serum albumin (A7030) standard, and D-Glucose (G8270) standard were purchased from Sigma-Aldrich (Milan, Italy). Peanut oil (Sagra, Italy) was bought from a local supermarket. Piccadilly tomatoes were purchased from a local market and were immediately (fresh) used for this research. Fig. S1 in the Supplementary Material graphically depicts the experimental workflow, including sample preparation, treatments carried out and analysis of samples.

2.1. Pretreatment of the samples

Tomatoes were blanched according to conventional methods adopted in a processing factory (FDP s.r.l., Fisciano, Italy) at 95 °C in a steam oven for 3 min (Pataro et al., 2018). Blanched tomatoes were then immediately ice-cooled and manually peeled with a laboratory blade. The pulp was completely removed and fresh tomato peels were ready for further processing. The moisture content of the tomato peels after preparation was 80 wt %. The tomato peels were mechanically milled in a laboratory blender to the size of 1–2 mm and then distilled water was added to a final concentration of 10 wt % of tomato peels. The suspension was immediately used for the HSM and HPH treatments.

2.2. High-shear mixing and high-pressure homogenization

Tomato peels suspensions (300 mL) were subjected to HSM at 20000 rpm for 5 min with a T-25 Ultra Turrax device (IKA, Germany) equipped with an S25 N18 G rotor. In order to avoid any temperature rises, the treatment was carried out in an ice bath. Additionally, before HPH processing, to prevent the blockage of the homogenization valve, the HSM suspensions were sieved with a mesh size of 600 μm as a precaution. Sieving removed only a small fraction of the solids from the suspension (the final concentration always remained > 9.75 wt %). HPH was carried out using an orifice valve assembly (orifice diameter of 150 μm) at 100 MPa for up to 10 passes. A tube-in-tube heat exchanger was used immediately upstream and downstream of the orifice valve, in order to ensure that the product temperature was always kept below 24 °C. 15 mL of extracts were taken after 1, 3, 5, 7 and 10 passes for further analyses. HSM samples were used as the controls for the corresponding HPH samples. The adopted sample labels are as follows: HSM for high-shear mixing, HPH, followed by a number, for high-pressure homogenization for different passes; for example, HPH 1 indicates one pass, and HPH 10 indicates 10 passes of high-pressure homogenization.

2.3. Macro and microscope imaging and particle size measurement

After HSM and HPH treatments, the suspensions (2 mL) were poured in small Petri dishes to acquire photographs with a Nikon Coolpix S7000 camera. Microscopic images were acquired with an inverted optical microscope (Nikon Eclipse TE2000-S) at 100 × magnification. The particle size distribution of the obtained suspensions was characterized by light diffraction (Mastersizer 2000, Malvern Panalytical, UK), and expressed in terms of the characteristic diameters d(0.1), d (0.5), d(0.9) as well as of the volume weighted mean diameter D[4,3] and surface weighted mean diameter D[3,2], as previously discussed (Mustafa et al., 2018).

2.4. Recovery of aqueous supernatant and pellet fractions from tomato peels suspensions

The tomato peels suspensions, treated by HSM and HPH, were subjected to centrifugation for 10 min at 5 °C and 6500 rpm (PK121R model, ALC International, Cologno Monzese, IT), in order to separate the aqueous supernatant, containing the intracellular compounds released during the treatment, from the cell debris. After centrifugation, the supernatant was filtered through Whatman no. 4 filters under vacuum, to remove residual particles. The obtained aqueous supernatant was then used directly for the analysis of total polyphenols, antioxidant activity, total sugars, total proteins, lycopene and surface activity.

Furthermore, the aqueous supernatant was evaporated in a Büchi Rotavapor R-300 Evaporator System until dry and was resuspended in the same volume of ethyl lactate for spectrophotometric analysis, or in acetone for HPLC analysis.

In contrast, the pellet, recovered from centrifugation, was subjected to solvent (acetone or ethyl lactate) extraction for the quantification of residual lycopene. In particular, 1 g of the pellet was extracted with acetone or ethyl lactate (60 mL) under agitation in a thermostated orbital shaker at 180 rpm and 20 °C in the dark. After 1 h extraction, the pellet extracts were subjected to centrifugation for 10 min at 5 °C and 6500 rpm and then filtered through Whatman no. 4 filter paper. Ethyl lactate extracts were used for UV-Vis analyses. Acetone extracts were used for the determination of lycopene by HPLC.

2.5. Total polyphenols

The total polyphenols content in the aqueous supernatant was determined by adopting a previously proposed method (Slinkard and Singleton, 1977) with slight modifications. The supernatant (1 mL) was added to a test tube along with 5 mL of Folin Ciocalteu reagent (diluted 1:10 with distilled water). 4 mL of 7% Na_2CO_3 was then added, vortexed and left in a dark chamber for 1 h at room temperature. Distilled water was used as a blank. Absorbance was then measured at 765 nm. Gallic acid was used as a calibration standard. Results were expressed as mg Gallic Acid Equivalents (GAE) per volume (L) of the aqueous supernatant.

2.6. Antioxidant activity - FRAP

The antioxidant activity of the aqueous supernatant was evaluated by ferric reducing antioxidant power (FRAP) assay (Benzie and Strain, 1996), modified as described by Bobinaite et al. (Bobinaitė et al., 2015). A standard calibration curve was obtained for ascorbic acid so that the FRAP values were expressed as μmol of ascorbic acid equivalents (μmol AAE) per volume (L) of the aqueous supernatant.

2.7. Total proteins

The total water-soluble protein concentration in the aqueous supernatant was determined using the Lowry method (Lowry et al., 1951) with some changes. Briefly, The Folin-Ciocalteau reagent was initially diluted in distilled water (1:2, v/v) then 0.5 mL of the diluted reagent was added to 1 mL of supernatant. Previously, the supernatant was mixed with 5 mL of the reactive C, made of 50 volumes of reagent A (2% (w/v) Na_2CO_3 + 0.1 mol dm^{-3} NaOH) and of 1 volume of reactive B (½ volume of 0.5% (w/v) $CuSO_4{\cdot}5H_2O$ + ½ volume of 1% KNa-$C_4H_4O_6{\cdot}4H_2O$). 35 min after the start of the chemical reaction, absorbance was measured at 750 nm against a blank (5 mL reactive C + 1 mL of distilled water + 0.5 mL Folin-Ciocalteau reagent) using a V-650 Spectrophotometer (Jasco Inc. Easton, MD, USA). Bovine serum albumin (BSA) standard was used for the calibration curve so that the results were expressed as mg equivalent of BSA per volume (L) of the aqueous supernatant.

2.8. Total sugars

The total sugars concentration in the aqueous supernatants were determined by the DuBois method (Dubois et al., 1956). Briefly, 0.2 mL of 5 wt % phenol and 1 mL of concentrated sulphuric acid was added to 0.2 mL of previously diluted supernatant in the test tube. Samples were incubated at 25 °C for 30 min in the dark before reading the absorbance at 490 nm against a blank (distilled water). D-Glucose was used as a calibration standard, and the results were expressed as mg of equivalent to D-glucose per L of the aqueous supernatant.

2.9. Oil-water interfacial tension measurements

The pendant drop method was used to measure the interfacial tension of the aqueous fraction of the tomato peels suspensions treated by HSM or HPH against peanut oil. The supernatant was recovered from the samples subjected to centrifugation for 10 min at 5 °C and 6500 rpm and then filtered through a Whatman no. 4 filter paper. Details are given elsewhere (Donsì et al., 2012). The interfacial tension was measured in dynamic mode, during 1000 s, over 200 frames, using a CAM200 apparatus (KSV Instruments, Finland) equipped with an image analyzer software (CAM 101, KSV Instruments). The comparison among the different samples was carried through the comparison of the kinetic parameters σ_f, σ_1, τ_1, σ_2 and τ_2 determined by fitting the interfacial tension curves σ as a function of acquisition time t with the following kinetic model (eq. (1)), which had been previously applied to the absorption of macromolecules and different types of emulsifiers onto the water-oil interface (Donsì et al., 2012):

$$\sigma = \sigma_f + (\sigma_1 - \sigma_f)\cdot e^{-\frac{t}{\tau_1}} + (\sigma_2 - \sigma_f)\cdot e^{-\frac{t}{\tau_2}} \quad (1)$$

2.10. UV-vis spectrometry and HPLC lycopene analyses

UV-Vis spectra analysis was performed for a wavelength range between 200 and 700 nm for tomato peel water aqueous supernatant, and the pellet extracts in ethyl lactate, as obtained from the centrifugation of the tomato peels aqueous suspensions treated by HSM (control) and HPH (1, 3, 5, 7 and 10 passes). Lycopene in ethyl lactate was quantified from UV-Vis spectrophotometer (Jasco Inc., Easton, USA) reading at 472 nm, upon obtaining a calibration curve for lycopene standard in ethyl lactate and is expressed as mg of lycopene per L of extract (shown in Fig. S2 of Supplementary Material together with the spectra of pure lycopene in ethyl lactate in Fig. S3). Lycopene in the aqueous supernatant was determined from UV-Vis spectrophotometer (Jasco Inc., Easton, USA) reading at 350 nm, in correspondence of the absorbance maxima observed for complexes of lycopene with bovine serum albumin (Galdón et al., 2013).

The lycopene content in the acetone extracts of the dried aqueous supernatant or of the pellet obtained from the centrifugation of the tomato peel suspensions was measured by reversed-phase high-performance liquid chromatography using isocratic elution and UV detection at 472 nm (Waters, Belgium). A carotenoid C30 reversed-phase column

(250 × 4.6 ID, 3 μm) from YMC Corporation (Waters, Belgium) was used with MeOH/isopropyl alcohol/THF (30:30:35) containing 250 ppm BHT and 0.05% TEA as a mobile phase. The flow rate was 1 mL/min, column temperature was 35 °C and the injection volume of 20 μL, according to a previously described method (Cucu et al., 2012).

2.11. Statistical analysis

All the experiments were carried out in triplicate. The obtained dataset was analyzed with XLSTAT add-on for Microsoft Office 2016. The data are represented as means with standard deviations. One-way analysis of variance (ANOVA) was used for determination of whether the means between samples differ significantly from each other. The significance ($p < 0.05$) was established using the posthoc t-tests with Bonferroni adjustment. All of the data are expressed as mean ± SD of the values. Correlation analysis was also performed using the same statistical package. Percentage of bioactive compounds and antioxidant activity change relative to the control (HSM) was calculated in terms of relative change (%) $\frac{HPHX' - HSM}{HSM} \times 100$, where x' is the number of passes. Agglomerative hierarchical clustering (AHC) with Euclidean Distance Dissimilarity and Agglomeration Ward's method was performed.

3. Results and discussion

3.1. Physical characteristics of tomato peel suspensions

The HSM and HPH treatments induced a measurable disruption of the peels, which became more evident at increasing the number of HPH passes. Preliminary tests, carried out to characterize the particle size distribution of tomato peels suspensions treated at different HPH passes, showed that after 10 passes no significant changes occurred. Therefore, 10 passes were set as the limiting number of passes of HPH treatments.

Visually, as shown in Fig. 1, the tomato peels suspension became progressively more homogeneous in appearance, as the number of passes was increased. These observations can be correlated with the microscopical observations, reported in Fig. 2, which shows that HSM treatment caused only the fragmentation of the peel tissue into smaller cell aggregates, with negligible effects on cell integrity. As HPH treatment was applied, the tomato peels were further fragmented, and, at the same time, the individual cells were progressively disrupted, as suggested by the large fraction of filamentous debris appearing in the suspension, likely as the results of cell wall breakage.

The particle size of the tomato peels suspension is described in Table 1, through the characteristic diameters d(0.1), d(0.5), d(0.9), D[4,3], and D[3,2] as a function of treatment intensity. The results confirm that, when increasing the number of passes, a decrease of the characteristic diameters of the tomato peels suspension was observed.

More specifically, from the variation with the number of passes of the diameters corresponding to the 10th, 50th and 90th percentile of the cumulative distribution (d(0.1), d(0.5), d(0.9), respectively), it can be observed that the size distributions of the tomato peel suspensions became progressively narrower at increasing the number of HPH passes, with a decrease in the distribution width (expressed as d(0.9) - d(0.1)) spanning from about 900 μm for HSM to 20 μm for 10 HPH passes. At the same time, also a progressive reduction of the median value d(0.5) of the distribution was observed, from 331 to 31 μm for HSM and 10 HPH passes, respectively.

When considering the size distribution in terms of volumetric weighted and surface weighted mean diameters (D[4,3] and D[3,2], respectively), although both the mean diameters were reduced by HPH processing, some differences could be observed. For example, D[4,3] was reduced continuously and progressively, as the number of passes is increased, whereas D[3,2], after 5 passes, exhibited only a modest, yet statistically significant, change. This different behavior can be explained by the fact that D[4,3] is greatly influenced by the presence of large particles, whereas D[3,2] depends more on smaller ones, which are more difficult to micronize (Bengtsson and Tornberg, 2011; Mustafa et al., 2018).

Remarkably, the results of Table 1 and Fig. 2 clearly show that HSM treatment is not able to destroy individual plant cells, whereas HPH treatment does. In particular, after 10 passes, the plant cells are completely disrupted, with most of the intracellular content being released in the suspension.

Therefore, a size distribution below the typical plant cell size (~100 μm) provides an indication that cell disruption has occurred successfully, which will promote the recovery with high yields of intracellular compounds. However, a recent study has highlighted that the size distribution of tomato purees, enriched with dietary fibers and polyphenols, has a significant effect also on consumer perception. The

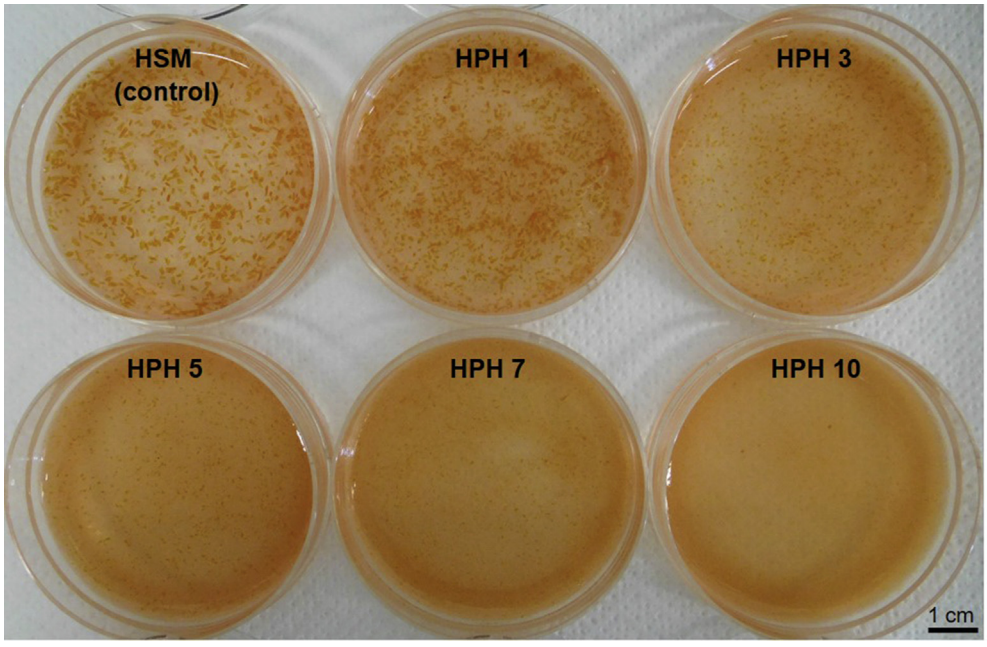

Fig. 1. Images of tomato peel aqueous suspensions after HSM (control) and HPH (1, 3, 5, 7 and 10 passes) treatments.

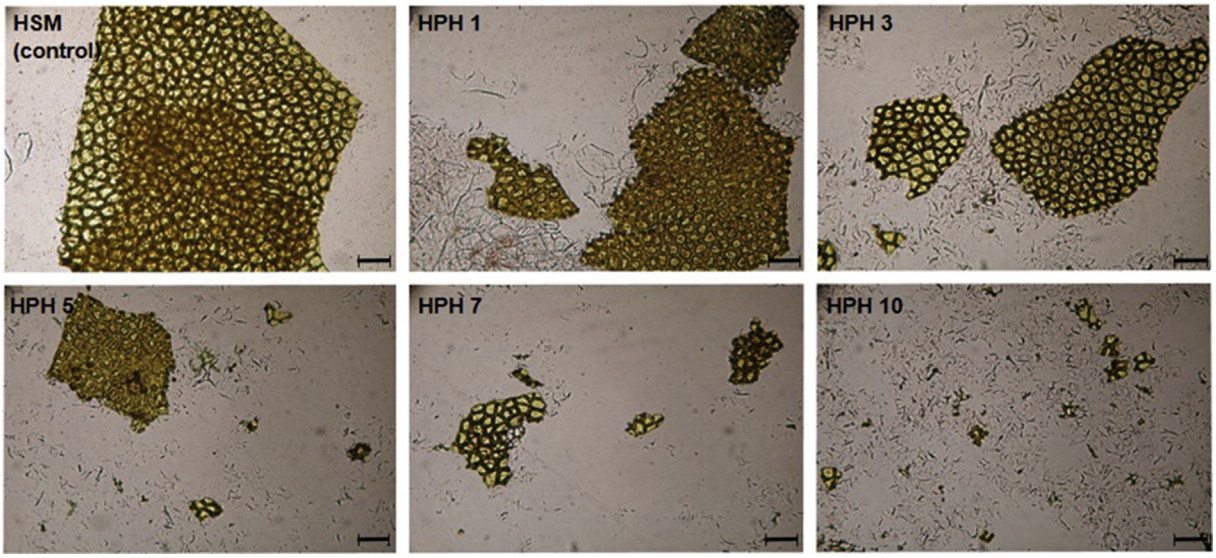

Fig. 2. Micrographs of tomato peel aqueous suspensions after HSM (control) and HPH (1, 3, 5, 7 and 10 passes) treatments. Scale bars correspond to 100 μm.

Table 1
Characteristic diameters (μm) of the particle size distribution of the tomato peels aqueous suspensions treated by HSM (control) and HPH (1, 3, 5, 7 and 10 passes).

HPH passes	d(0.1)	d(0.5)	d(0.9)	D[4,3]	D[3,2]
0 (HSM)	101.2 ± 3.2^{a}	330.9 ± 24.4^{a}	1006.5 ± 42.4^{a}	443.6 ± 11.3^{a}	150.8 ± 11.6^{a}
1	57.4 ± 1.6^{b}	298.1 ± 6.6^{a}	967.3 ± 18.0^{a}	429.9 ± 16.6^{a}	110.0 ± 8.3^{b}
3	19.2 ± 1.8^{c}	165.0 ± 52.2^{b}	679.4 ± 53.1^{b}	272.9 ± 27.2^{b}	38.9 ± 4.3^{c}
5	12.5 ± 0.1^{d}	57.4 ± 0.6^{c}	491.7 ± 6.7^{c}	165.0 ± 1.1^{c}	23.8 ± 0.5^{d}
7	10.5 ± 0.2^{e}	42.1 ± 3.3^{d}	297.6 ± 38.4^{d}	104.1 ± 9.3^{d}	18.8 ± 0.8^{e}
10	9.3 ± 0.6^{f}	30.9 ± 1.8^{e}	111.2 ± 2.4^{e}	49.7 ± 0.8^{e}	16.1 ± 0.8^{f}

Values superscripted with the same letter within a column are not significantly different according to the posthoc *t*-test with Bonferroni adjustment ($p < 0.05$).

study revealed that most of the consumer preferences went to the puree containing particles in the size range 250 μm–500 μm, which was associated to sensations of fresh tomato, as well as crispiness, granularity and vegetable notes (Torri et al., 2015), which are, instead, not perceived in a lower size range. Therefore, in the perspective of using the tomato peels suspension as a food ingredient in juices/sauces/purees, a minimum number of passes of 5 is recommended to obtain a particle distribution within the suggested range (d(0.9) of HPH 5 is 491.7 μm). The presence of larger particles, in addition to providing a grainy texture, can also be detected by the naked eye. More intense conditions (HPH 7 and HPH 10), exhibiting a size distribution below the range 250 μm–500 μm, are suitable for products with a smoother texture. The characteristics of the obtained HPH suspensions make them suitable to be used also in Ready-to Use Therapeutic Food (Santini and Armini, 2013), because of their content in bioactive components, and their oil-structuring ability (Mustafa et al., 2018).

3.2. Total polyphenols and antioxidant activity

After centrifugation, the water supernatant was subjected to further analyses of total polyphenols, antioxidant activity, total proteins, and total sugars. These results are presented in Table 2, where it can be observed that, when the number of HPH passes increased, the concentration of total polyphenols recovered in the supernatant increased. In particular, the suspensions treated by HPH exhibited an increasing antioxidant activity in comparison with HSM suspensions. For example, after 10 HPH passes, the antioxidant activity, as measured by the FRAP method, increased of 23.3% with respect to HSM suspension, from 220.7 ± 0.6 μmol AAE/L to 272.2 ± 0.8 μmol AAE/L, which corresponds to an increase of total polyphenols of 32.2%. Moreover, total

Table 2
The concentration of total polyphenols (TPC), antioxidant activity (FRAP), and concentration of total proteins and sugars in the supernatant obtained from the centrifugation of the tomato peel aqueous suspensions treated by HSM (control) and HPH (1, 3, 5, 7 and 10 passes). In addition, also the percentage variation (%) with respect to the HSM treatment (control) is reported.

HPH passes	TPC (mg GAE/L)		FRAP (μmol AAE/L)		Total proteins (mg BSA/L)		Total sugars (mg D-Glu/L)	
	Absolute value	Relative change[a]	Absolute value	Relative change[a]	Absolute value	Relative change[a]	Absolute value	Relative change[a]
0 (HSM)	38.9 ± 3.1^{a}	–	220.7 ± 0.6^{a}	–	386.4 ± 22.9^{a}	–	2.4 ± 0.1	–
1	44.2 ± 0.5^{ab}	+13.6%	242.3 + 2.0^{b}	+9.8%	548.3 ± 13.6^{b}	+41.9%	2.4 ± 0.3	−0.8%
3	47.7 ± 1.4^{ab}	+22.7%	261.1 ± 4.2^{b}	+18.3%	585.9 ± 07.6^{b}	+51.6%	2.6 ± 0.1	+7.0%
5	50.1 ± 0.5^{c}	+28.7%	267.8 ± 3.5^{c}	+21.4%	643.8 ± 05.5^{c}	+66.6%	2.5 ± 0.2	+4.1%
7	50.8 ± 1.1^{c}	+30.5%	270.1 ± 1.1^{c}	+22.4%	651.7 ± 18.5^{c}	+68.7%	2.5 ± 0.1	+1.2%
10	51.4 ± 1.0^{c}	+32.2%	272.2 ± 0.8^{c}	+23.3%	658.8 ± 31.7^{c}	+70.5%	2.7 ± 0.2	+11.5%

Values superscripted with the same letter within a column are not significantly different according to the posthoc *t*-test with Bonferroni adjustment ($p < 0.05$).
[a] Relative change (%) with respect to HSM treatment (control).

polyphenol concentration could be well correlated with the antioxidant activity in the supernatant (r = 0,997), as determined by FRAP assay. Furthermore, both polyphenol concentration and antioxidant activity could be correlated with the concentration of total proteins in the supernatant (r_{TPC} = 0,993, r_{FRAP} = 0,989), because the HPH technique is non-selective, and the release of intracellular compounds depends mainly on the extent of cell disruption. Previous studies about the microfluidization of aqueous suspensions of corn and wheat bran exhibited similar trends for the antioxidant activity (Wang et al., 2014, 2013). The authors related this observation with the increased release of bioactive compounds in water upon micronization treatment, which also induced an enhanced bioaccessibility of the antioxidant compounds, which are generally contained inside the cells. It is likely that the HPH process substantially loosened the tightly packed architecture of the plant tissue, disrupted and opened the plant cells, thus making the antioxidant compounds, bound to the cell structure, to become accessible to the molecules present in the surrounding liquid phase.

3.3. Proteins and sugars

The release of proteins in the supernatant was found to be in correlation with the total polyphenols content and antioxidant activity, likely due to the ability of polyphenols to associate with proteins (Siebert et al., 1996). The lowest total protein concentration in the HSM suspension (386.4 mg BSA/L) was significantly different from all of the HPH suspensions (1–10 passes). Furthermore, compared to the control, the total released proteins after only 1 pass increased of 41.9% with respect to control, whereas after 10 passes they increased by 70.5%. However, in comparison to the total amount of proteins typically contained in the peels (10–18 wt % of the dry weight (Elbadrawy and Sello, 2016; Nour et al., 2018)), the maximum amount recovered in the supernatant is less than 3 wt % of the dry weight of the used peels.

In the case of total sugars, HPH caused only a moderate, and non-statistically significant, increase (about +11%) with respect to the control (HSM sample), with the highest concentration measured in the supernatant after 10 HPH passes (2.7 mg D-Glu/L).

3.4. Interfacial activity

The release of intracellular compounds, such as proteins and polysaccharides, affected also the interfacial tension of the aqueous phase of tomato peel suspensions, recovered as supernatant after centrifugation. The results of oil-water interfacial tension measurements on the supernatant of suspensions treated by HSM (control) and HPH (1–10 passes), measured by the pendant-drop method, presented in the Supplementary Material (Fig. S4), are summarized in Table 3, in terms of the parameters of Eq. (1), which include the asymptotic interfacial tension σ_f and the dynamic parameters σ_1, σ_2, τ_1, and τ_2 that describe the decay kinetics of the interfacial tension over time until a stationary value is reached (Donsì et al., 2012).

When increasing the number of passes, a reduction in the asymptotic interfacial tension of the supernatant was observed. The HSM suspension exhibited the highest interfacial tension values. However, until after 3 passes, no statistically significant change in σ_f was observed. When the number of HPH passes increased above 3, the asymptotic interfacial tension of the treated suspension significantly decreased, reaching the value of 13.78 mN/m after 10 HPH passes, in comparison with a value of 15.01 mN/m for HSM. The drop in the interfacial tension can be ascribed to the release of surface active molecules, such as proteins, from the intracellular space to the aqueous extract.

At the same time, also a decrease in σ_1, and σ_2 was observed with the number of passes, which also depend on the concentration of surface-active molecules, whereas no clear trend was observed for τ_1, and τ_2, which are related to the characteristic times of absorption and rearrangement of the macromolecules at the oil-water interface (Donsì et al., 2012).

3.5. Lycopene

The release of the intracellular compounds, especially carotenoids, from tomato peel cells in the aqueous phase, by HSM and HPH treatments has been further investigated by UV-Vis spectra analysis of the supernatant, in a wavelength range between 200 and 700 nm. Fig. 3a shows the UV-Vis spectra of the aqueous supernatants obtained from the tomato peel suspensions. The aqueous supernatant spectra clearly reveal that the highest peaks are achieved after 5 to 10 HPH passes, while the lowest peaks are observed for the sample treated only by HSM, suggesting an increased release of intracellular materials, as the treatment intensity is increased. In addition, the UV-Vis spectroscopy analyses in Fig. 3b show the visible absorption spectrum of the ethyl lactate-extracted lycopene from the pellet. Ethyl lactate was used because of its efficiency in solubilizing lycopene (Silva et al., 2018; Strati and Oreopoulou, 2011). The data of Fig. 3b clearly show that a significant fraction of carotenoids (and in particular lycopene) is still trapped inside the tomato peel cells, but this fraction is reduced as the HPH passes are increased, in accordance with what observed from Fig. 4.

The residual content of lycopene in the pellet was quantified by extraction of the pellet with ethyl lactate, using a calibration curve made with different working standard solutions of lycopene (Fig. 4).

Interestingly, the residual content of lycopene in the pellets decreased from an initial value of 4.1 mg/g (wet basis), as characterized for the peels prior to any treatment (balance curve, at 0 HPH passes), to 3.3 mg/g (wet basis) after HSM, and to 1.9 mg/g (wet basis) after 3 passes. Additional processing after 3 passes caused only a marginal additional release of lycopene, as shown by the residual value of 1.6 mg/g (wet basis) in the pellet after 10 passes, which corresponds to a residual content of lycopene in the pellet of 39.2%.

The evaluation of lycopene in the supernatant was more difficult, because lycopene, which is insoluble in the aqueous phase, is likely to be complexed/associated with hydrocolloids present in tomato (e.g.

Table 3
Kinetic parameters (eq. (1)) of the interfacial tension of the supernatant of the suspensions treated by HSM (control) and HPH (1, 3, 5, 7 and 10 passes), as a function of the measurement time.

HPH passes	σ_f (mN/m)	σ_1 (mN/m)	τ_1 (s)	σ_2 (mN/m)	τ_2 (s)
Water[a]	27.45 ± 0.02^{a}	28.52 ± 0.03^{a}	18.32 ± 0.39^{a}	29.24 ± 0.04^{a}	0.86 ± 0.03^{a}
0 (HSM)	15.01 ± 0.36^{b}	19.11 ± 0.42^{b}	51.22 ± 1.50^{b}	17.16 ± 0.66^{b}	3.07 ± 0.88^{b}
1	15.42 ± 0.12^{bc}	20.30 ± 0.21b^{c}	53.77 ± 1.78^{bc}	17.77 ± 0.17^{bc}	5.92 ± 0.80^{c}
3	15.15 ± 0.03^{bd}	19.07 ± 0.46^{bd}	267.23 ± 43.41^{d}	18.20 ± 0.15^{bd}	17.19 ± 1.08^{d}
5	14.33 ± 0.12^{e}	18.27 ± 0.24^{de}	60.21 ± 3.17^{e}	16.73 ± 0.18^{be}	6.35 ± 0.93^{ce}
7	13.19 ± 0.49^{f}	16.75 ± 0.61^{f}	37.85 ± 1.79^{f}	15.88 ± 0.86^{bef}	3.22 ± 1.09^{bf}
10	13.78 ± 0.07^{f}	17.26 ± 0.16^{f}	52.00 ± 2.08^{bcg}	16.20 ± 0.12^{bf}	6.77 ± 0.66^{ceg}

Values superscripted with the same letter within a column are not significantly different according to the posthoc t-test with Bonferroni adjustment ($p < 0.05$).
[a] As reference.

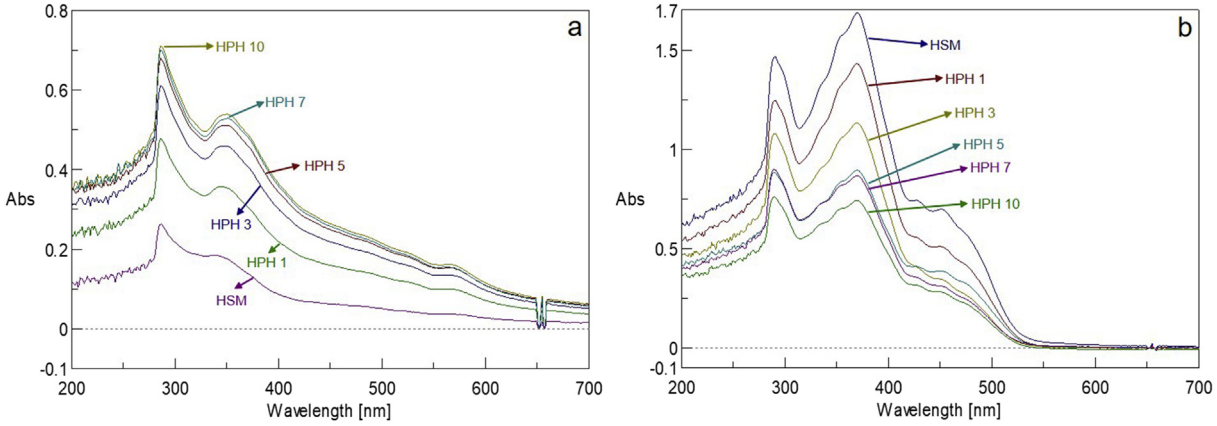

Fig. 3. UV-Vis spectra of (a) the aqueous supernatant, and of (b) ethyl lactate extracts from the pellet, as obtained from the centrifugation of the tomato peels aqueous suspensions treated by HSM and HPH 1–10.

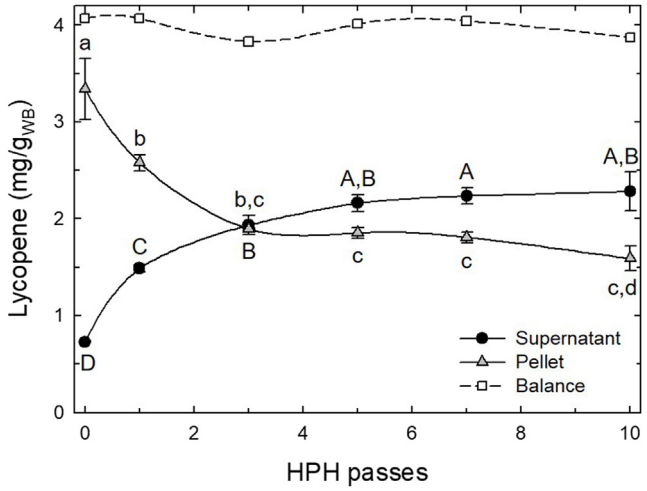

Fig. 4. Lycopene content (reported per wet mass of peels) evaluated by ethyl lactate extraction from the supernatant and the pellet obtained from the centrifugation of the tomato peels aqueous suspensions treated by HSM (control, 0 HPH passes) and HPH (1–10 passes). Values superscripted with the same letter are not significantly different according to the posthoc *t*-test with Bonferroni adjustment ($p < 0.05$).

proteins, pectin) that help to stabilize the lycopene suspension (Jazaeri et al., 2018). The solubility of these stabilizing hydrocolloids, however, is affected by organic solvents and they precipitate in the presence of ethyl lactate, which in turn may significantly decrease the measured concentration of lycopene if strongly trapped in the precipitated hydrocolloid. Previous studies reported similar absorption spectra, with absorbance maxima at 275 nm and 350 nm (this last wavelength was used in the present work) of complexes of lycopene with bovine serum albumin (Galdón et al., 2013). Therefore, the concentration of lycopene in the supernatant was determined directly from the UV-Vis spectra of the aqueous supernatant, calibrating the concentration in the supernatant of the HSH sample with the initial measured content of lycopene in the peels. As shown in Fig. 4, this approach is validated by the closing mass balance on lycopene for all the remaining samples. In addition, the HPLC spectra, reported in section 3.6, qualitatively confirm these results.

Based on this assumption, the maximum amount of lycopene recovered in the supernatant corresponded to 56.1% of total initial lycopene (2.3 mg/g of peels on a wet basis).

This is in agreement with the observation that the size-reduction induced by high-pressure microfluidization of tomato ketchup increased the detectable lycopene levels of the ketchup samples (Mert, 2012).

3.6. Carotenoids in the supernatant

The HPLC analysis of the pellet and of the dried supernatant extracted by acetone, reported in Fig. 5, shows that lycopene was the main carotenoid, both in the supernatant and the pellets after centrifugation of the treated tomato peel suspensions. In addition, Fig. 5 also confirms the results from the UV-Vis analysis: (a) the pellet from HSM suspensions contains significantly higher amounts of lycopene than the pellet from the suspensions treated by 5 HPH passes; coherently, (b) the supernatant from the suspensions treated by 5 HPH passes contains a significantly higher amount of lycopene than the supernatant from the HSM suspensions.

The HPLC analysis also confirmed the quantitative results obtained by UV-Vis analysis. This is particularly relevant, considering that the lycopene content of the analyzed tomato peels (3.86 mg/g on a wet basis, corresponding to 19.3 mg/g on a dry basis) is significantly higher than the values typically reported in literature (on a dry basis, from 0.5 to 0.8 mg/g (Nobre et al., 2009; Nour et al., 2018) to a maximum of 1.5 mg/g (Machmudah et al., 2012)).

When taking into account the dietary factors and food properties, the bioavailability of lycopene is the lowest from raw sources, whereas mild-processed foods show slightly better bioavailability, and thermally processed foods the highest bioavailability (Honest et al., 2011). Therefore, the lycopene uptake in the human body is more favorable when consuming variously processed tomato products (Böhm and Bitsch, 1999; Gärtner et al., 1997; Goñi et al., 2006; Granado-Lorencio et al., 2007; Porrini et al., 1998; Rao and Agarwal, 1998; Richelle et al., 2002). Thermal and mechanical food processing improves lycopene bioavailability by disrupting the cell walls and weakening the chemical bonds between lycopene and the raw tissue matrix, hence making lycopene more accessible (Agarwal et al., 2001; Shi and Le Maguer, 2000). According to these studies, our results show that a significant release of lycopene from the rigid tomato peel structure into the aqueous phase can be achieved by intense high-pressure processing, with a potential increase of its bioavailability.

3.7. Dendrogram of sample groupings

The dendrogram analysis of the influence of the different treatments performed on the dissimilarities between the samples is represented in Fig. 6. The dendrogram analysis is based on the results of particle size distribution d(0.1), d(0.5), d(0.9), D[4,3], D[3,2], total polyphenols, total proteins, total sugars, antioxidant activity and interfacial tension of the supernatant, as well as lycopene content in the pellet and supernatant from tomato peels suspensions treated by HSM and HPH. The

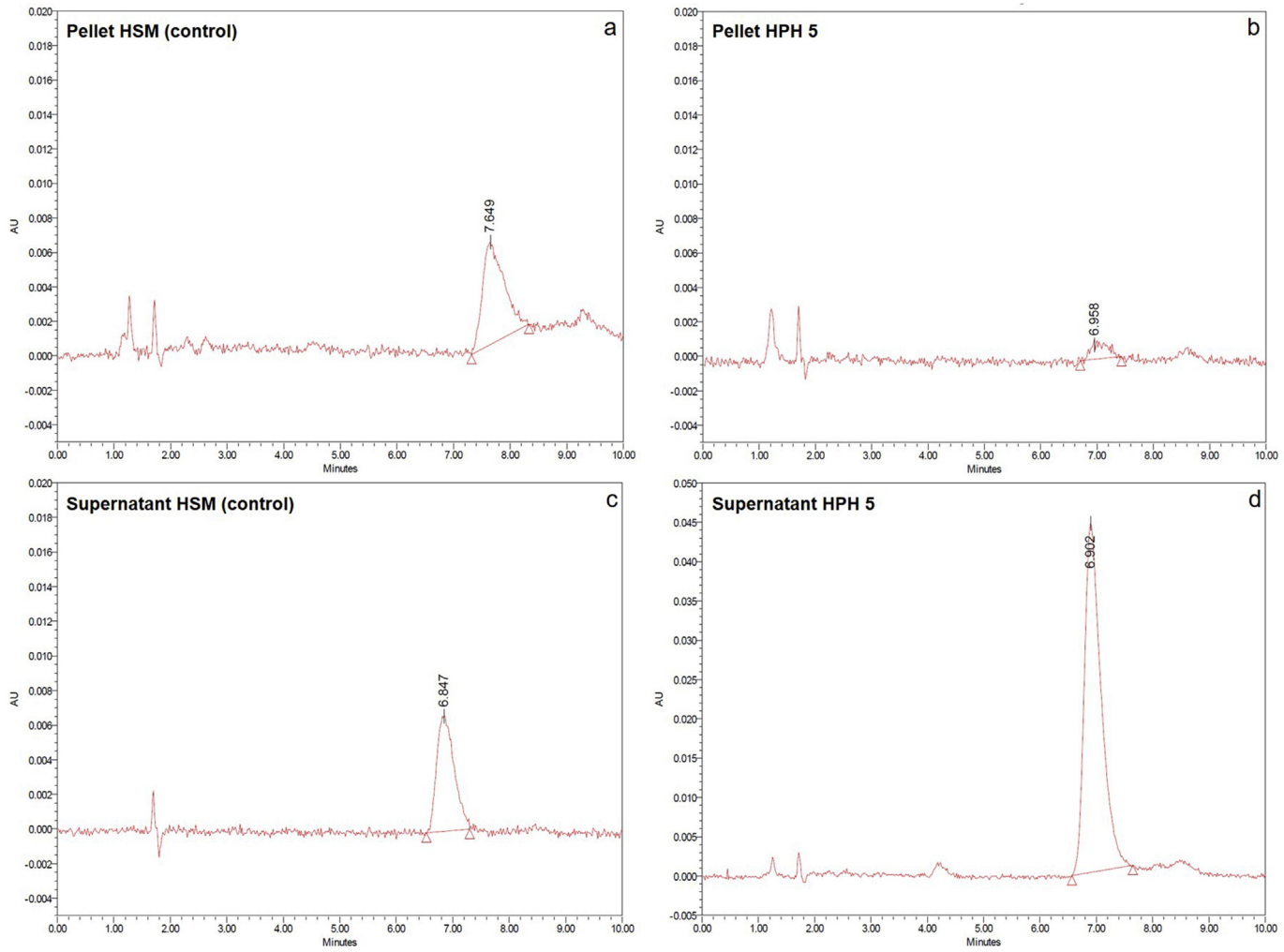

Fig. 5. HPLC spectra of (a, b) the pellet resuspended in acetone and of (c, d) the dried supernatant resuspended in acetone, obtained from the centrifugation of the tomato peels aqueous suspensions treated by HSM (a, c) and 5 HPH passes (b, d).

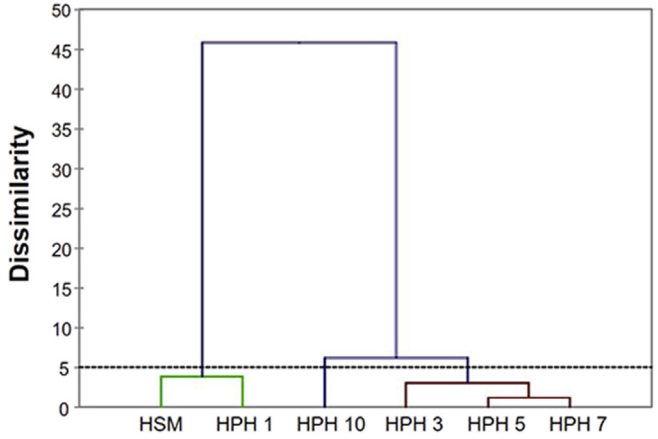

Fig. 6. Dendrogram of treatment influence on dissimilarities between the samples based on obtained results of particle size distribution d(0.1), d(0.5), d (0.9), D[4,3], D[3,2], total polyphenols, total proteins, total sugars, antioxidant activity, interfacial tension of the supernatant and lycopene content in the pellet and supernatant from tomato peels suspensions treated by HSM and HPH.

analysis reveals the formation of two main clusters. In the first cluster, HSM (control) and HPH 1 suspensions are grouped together, because they are more statistically similar than the other treatments. HPH 3 - 10 suspensions were grouped together with significant similarities, despite some sub-groups could also be identified, including HPH 5 and HPH 7, alongside the HPH 3, which is slightly more dissimilar. However, within the HPH 3 - 10 cluster, HPH 10 can be isolated as a separate sub-cluster, at a level of dissimilarity of 5.

4. Discussion

The reported results clearly show that not only water-soluble compounds were released in significant concentrations in the aqueous phase, but also hydrophobic molecules, among which the most abundant in tomato peels is lycopene. In particular, lycopene concentration in the aqueous supernatant reached the value of about 8.5 mg/L, which is remarkable because lycopene is insoluble in water. Therefore, it can be hypothesized that HPH is able to completely open the vegetable cells and release hydrophobic lycopene and stabilizing it in the aqueous phase by complexation with the extracted proteins in colloidal particles. This is clearly visible from Fig. 7, where the different experimental stages followed for the isolation of lycopene are shown. Initially, the aqueous extract is obtained as supernatant after the centrifugation of the HPH-processed peel suspension. At this stage, a fraction of lycopene remains in the pellet, bound to the centrifuged cell debris, while another fraction (up to 56%) is suspended in the aqueous phase. Subsequently, the supernatant is dried in a rotavapor, and the residual solids redispersed in acetone. The addition of acetone causes the precipitation of proteins and polysaccharides, while lycopene is dissolved. At this stage, it can be supposed that the complexes are broken, and,

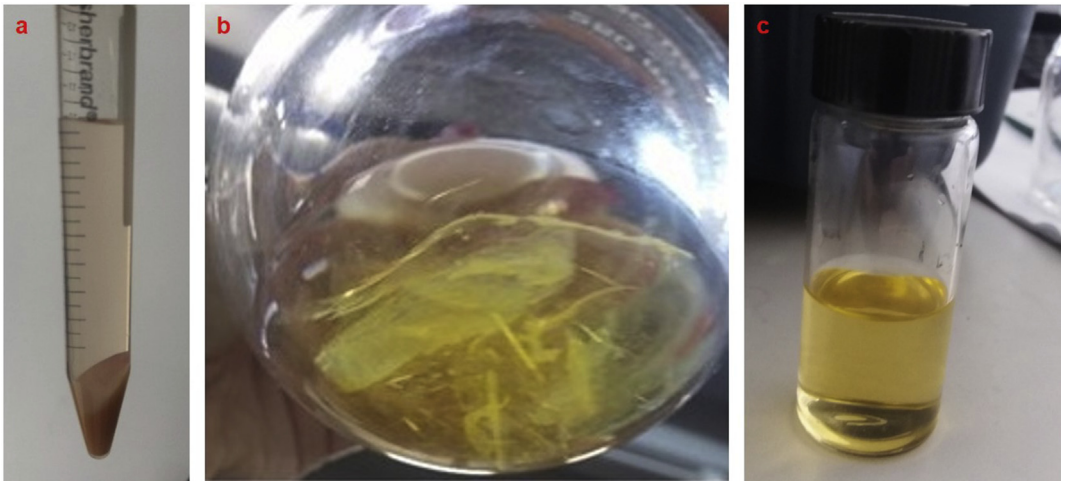

Fig. 7. Pictures of (a) the tomato peel aqueous suspension processed by HPH after centrifugation, and of (b) the supernatant after removal of water and resuspension in the same volume of acetone, and (c) after filtration to remove suspended solids.

consequently, pure lycopene can be recovered upon filtration of the acetone solution. This is confirmed by the typical lycopene color appearing in the acetone solution, as well as by its identification by HPLC (Fig. 5). Ongoing work in our laboratory is addressed to verify this hypothesis, to identify the type of complex and investigate the bioaccessibility of lycopene in complexed form, which could be exploited as an all-natural delivery system in aqueous products for lycopene.

From the processing point of view, it is interesting to compare the yield of extraction of the current work with the literature data, using different solvents and different technologies. Fig. 8 reports, comparatively, the amount (in mg) of lycopene extracted per gram of dry weight of peels, considering a moisture content of 75%, when the value was not explicitly reported.

Interestingly, the data of Fig. 8 show that the yields of extraction of lycopene observed in this work are comparable with the results obtained through solvent extraction assisted by pectinase and cellulase enzymes (Choudhari and Ananthanarayan, 2007) or ultrasounds (US) (Eh and Teoh, 2012; Kumcuoglu et al., 2014; Silva et al., 2018). The

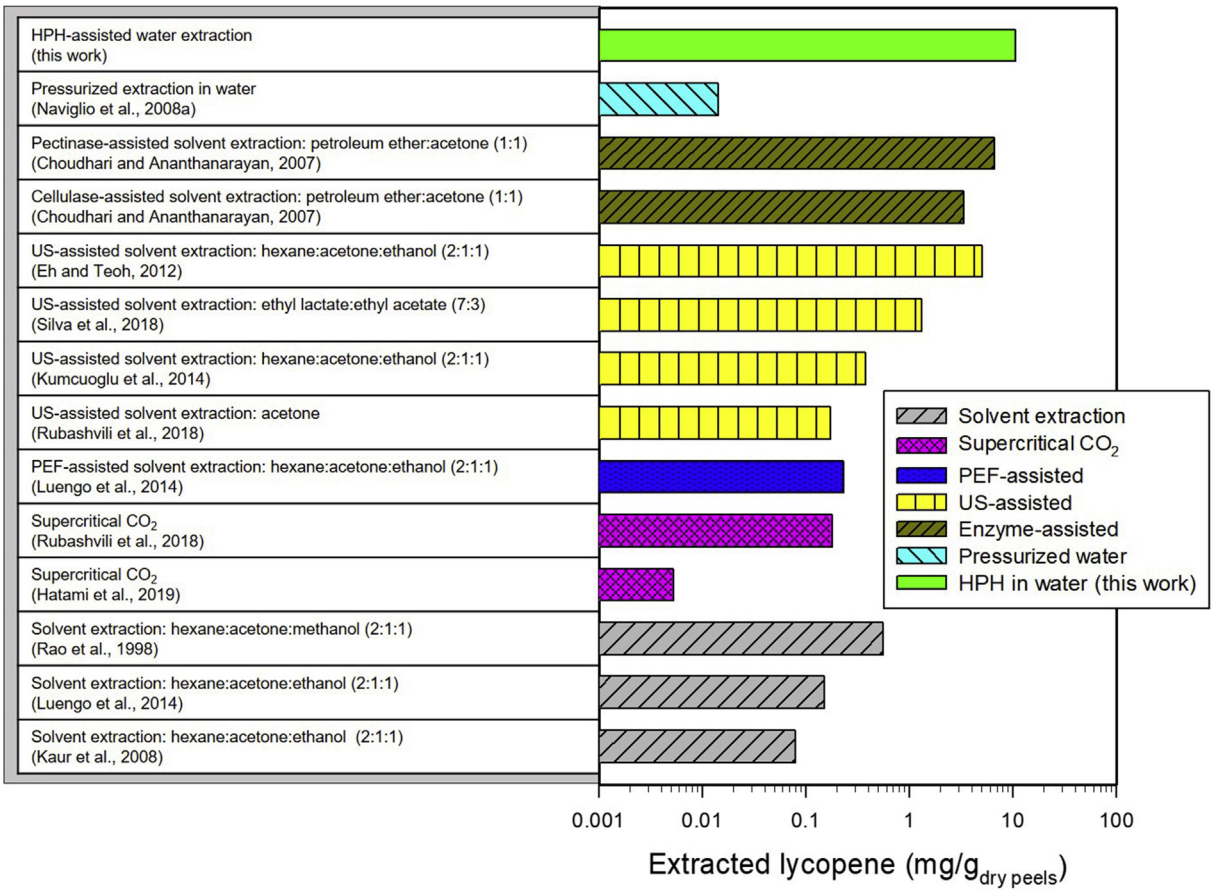

Fig. 8. Comparison of the amount of lycopene recovered from tomato peels by HPH treatment in water (this work) with literature data, where different technologies and solvents were used.

lycopene yields achieved in this work were also significantly higher than what obtained by PEF-assisted solvent extraction (Luengo et al., 2014), supercritical CO_2 extraction (Hatami et al., 2019; Rubashvili et al., 2018), pressurized extraction in water with Naviglio extractor (Naviglio et al., 2008a), as well as conventional solvent extraction from dried peels using different combinations of hexane, acetone and ethanol or methanol (Kaur et al., 2008; Luengo et al., 2014; Rao et al., 1998).

However, it must be highlighted that, as mentioned in section 3.7, the initial content of lycopene in the peels used in this work is significantly higher than the typical value reported in the literature, and differences in lycopene yields of Fig. 8 are also likely to depend on the biological variability of the tomatoes.

In addition to the advantages in terms of lycopene recovery, the use of water as an extraction solvent is intrinsically environmentally benign especially because it prevents the need for organic solvents, which are generally toxic and require their complete removal from the exhaust material before its disposal or further use (i.e. animal feed or compost).

Remarkably, in the case of the proposed technology, it is possible to obtain by means of only physical processing in water a tomato peel suspension, which is very rich in lycopene (up to 56.1% of the initial content of tomato peels). This suspension can be used as it is, as a food ingredient or the aqueous phase can be separated by centrifugation, still carrying a significant concentration of lycopene (up to 39.2% of the initial content, at the optimal processing conditions). The pellet (exhaust material) can be disposed of exactly as the initial residue, as no chemicals were involved in its processing, which adds a significant benefit to the proposed technology (Naviglio et al., 2008b). Therefore, even in the case where pure lycopene is the desired product, rather than a total extract rich in lycopene, the solvent extraction can be carried out directly on the aqueous supernatant, drastically reducing the exhaust material to be disposed of.

5. Conclusions

The use of high-pressure homogenization (HPH) for the treatment of agro-industrial by-products is able to cause the complete disruption of the plant cells, and the release of intracellular material. In this work, we applied the HPH treatment to tomato peels, preliminary dispersed as aqueous suspensions. The HPH suspensions of tomato peels represent a by-product with high added value because the cell aggregates are reduced in size below the perception of the naked eye, with better properties than the simply highly sheared suspensions, because richer in polyphenols, proteins and lycopene. In particular, at increasing the number of HPH passes, a higher amount of total proteins, total polyphenols are released as well as the greater antioxidant power of the suspensions can be observed. In particular, the HPH treatment enables the release of lycopene from the rigid structure of tomato peel cells to the aqueous phase, without the need of any organic solvent, significantly improving its recovery through a green, sustainable and purely physical process, to make a product ready for human consumption. The obtained suspensions could be exploited as functional foods or can be added back to the transformed peeled tomato products, to enrich their bioactive potential.

Declarations of interest

None.

Fundings

This work was supported by the Croatian Science Foundation with the project “High voltage discharges for green solvent extraction of bioactive compounds from Mediterranean herbs” (IP-2016-06-1913), and by the ERA-NET ARIMNet2 Call 2016 with the project “Valorization of Industrial fruits by-products and algae biomass waste: Development of Active Coatings to extend Food shelf life and reduce food losses - VIPACFood (2017–2020)”.

Acknowledgments

The authors wish to thank Luigi Esposito (University of Salerno) for the particle size analysis of the suspensions and Mariangela Falcone for the support with the chemical analysis (ProdAl Scarl).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jfoodeng.2019.06.011.

References

Agarwal, A., Shen, H., Agarwal, S., Rao, A.V., 2001. Lycopene content of tomato products: its stability, bioavailability and *in vivo* antioxidant properties. J. Med. Food 4, 9–15. https://doi.org/10.1089/10966200152053668.

Bengtsson, H., Tornberg, E., 2011. Physicochemical characterization of fruit and vegetable fiber suspensions. I: effect of homogenization. J. Texture Stud. 42, 268–280. https://doi.org/10.1111/j.1745-4603.2010.00275.x.

Benzie, I.F.F., Strain, J.J., 1996. The ferric reducing ability of plasma (FRAP) as a measure of “antioxidant power”: the FRAP assay. Anal. Biochem. 239, 70–76. https://doi.org/10.1006/abio.1996.0292.

Bobinaitė, R., Pataro, G., Lamanauskas, N., Šatkauskas, S., Viškelis, P., Ferrari, G., 2015. Application of pulsed electric field in the production of juice and extraction of bioactive compounds from blueberry fruits and their by-products. J. Food Sci. Technol. 52, 5898–5905. https://doi.org/10.1007/s13197-014-1668-0.

Böhm, V., Bitsch, R., 1999. Intestinal absorption of lycopene from different matrices and interactions to other carotenoids, the lipid status, and the antioxidant capacity of human plasma. Eur. J. Nutr. 38, 118–125.

Chan, C.-H., Yusoff, R., Ngoh, G.-C., 2014. Modeling and kinetics study of conventional and assisted batch solvent extraction. Chem. Eng. Res. Des. 92, 1169–1186. https://doi.org/10.1016/J.CHERD.2013.10.001.

Chen, J., Wu, S.-S., Liang, R.-H., Liu, W., Liu, C.-M., Shuai, X.-X., Wang, Z.-J., 2014. The effect of high speed shearing on disaggregation and degradation of pectin from creeping fig seeds. Food Chem. 165, 1–8. https://doi.org/10.1016/J.FOODCHEM.2014.05.096.

Choudhari, S.M., Ananthanarayan, L., 2007. Enzyme aided extraction of lycopene from tomato tissues. Food Chem. 102, 77–81. https://doi.org/10.1016/J.FOODCHEM.2006.04.031.

Cosgrove, D.J., Jarvis, M.C., 2012. Comparative structure and biomechanics of plant primary and secondary cell walls. Front. Plant Sci. 3, 204. https://doi.org/10.3389/fpls.2012.00204.

Cucu, T., Huvaere, K., Van Den Bergh, M.-A., Vinkx, C., Van Loco, J., 2012. A simple and fast HPLC method to determine lycopene in foods. Food Anal. Methods 5, 1221–1228. https://doi.org/10.1007/s12161-011-9354-6.

Donsì, F., Annunziata, M., Ferrari, G., 2013. Microbial inactivation by high pressure homogenization: effect of the disruption valve geometry. J. Food Eng. 115, 362–370. https://doi.org/10.1016/j.jfoodeng.2012.10.046.

Donsì, F., Ferrari, G., Pataro, G., 2010. Applications of pulsed electric field treatments for the enhancement of mass transfer from vegetable tissue. Food Eng. Rev. 2, 109–130. https://doi.org/10.1007/s12393-010-9015-3.

Donsì, F., Sessa, M., Ferrari, G., 2012. Effect of emulsifier type and disruption chamber geometry on the fabrication of food nanoemulsions by high pressure homogenization. Ind. Eng. Chem. Res. 51, 7606–7618. https://doi.org/10.1021/ie2017898.

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F., 1956. Colorimetric method for determination of sugars and related substances. Anal. Chem. 28, 350–356.

Eh, A.L.-S., Teoh, S.-G., 2012. Novel modified ultrasonication technique for the extraction of lycopene from tomatoes. Ultrason. Sonochem. 19, 151–159. https://doi.org/10.1016/J.ULTSONCH.2011.05.019.

Elbadrawy, E., Sello, A., 2016. Evaluation of nutritional value and antioxidant activity of tomato peel extracts. Arab. J. Chem. 9, S1010–S1018. https://doi.org/10.1016/J.ARABJC.2011.11.011.

Ellis, R.J., 1979. The plastids: their chemistry, structure, growth and inheritance. Trends Biochem. Sci. 4, N305. second ed.. https://doi.org/10.1016/0968-0004(79)90304-9.

Erdman, J.W.J., Poor, C.L., Dietz, J.M., Poor, C.L., Dietz, J.M., 1988. Factors affecting the bioavailability of vitamin A, carotenoids, and vitamin E. Food Technol. 42, 214–221.

Fiedor, J., Burda, K., 2014. Potential role of carotenoids as antioxidants in human health and disease. Nutrients 6, 466–488. https://doi.org/10.3390/nu6020466.

Franco, D., Pinelo, M., Sineiro, J., Núñez, M.J., 2007. Processing of Rosa rubiginosa: extraction of oil and antioxidant substances. Bioresour. Technol. 98, 3506–3512. https://doi.org/10.1016/J.BIORTECH.2006.11.012.

Galdón, B.R., Corraliza, C.P., Carrillo, J.J.C., Laso, P.M., 2013. Spectroscopic study of the interaction between lycopene and bovine serum albumin. Luminescence 28, 765–770. https://doi.org/10.1002/bio.2434.

Gärtner, C., Stahl, W., Sies, H., 1997. Lycopene is more bioavailable from tomato paste than from fresh tomatoes. Am. J. Clin. Nutr. 66, 116–122. https://doi.org/10.1093/ajcn/66.1.116.

Goñi, I., Serrano, J., Saura-Calixto, F., 2006. Bioaccessibility of β-carotene, lutein, and

lycopene from fruits and vegetables. J. Agric. Food Chem. 54, 5382–5387. https://doi.org/10.1021/jf0609835.
Granado-Lorencio, F., Olmedilla-Alonso, B., Herrero-Barbudo, C., Pérez-Sacristán, B., Blanco-Navarro, I., Blázquez-García, S., 2007. Comparative in vitro bioaccessibility of carotenoids from relevant contributors to carotenoid intake. J. Agric. Food Chem. 55, 6387–6394. https://doi.org/10.1021/jf070301t.
Hatami, T., Meireles, M.A.A., Ciftci, O.N., 2019. Supercritical carbon dioxide extraction of lycopene from tomato processing by-products: mathematical modeling and optimization. J. Food Eng. 241, 18–25. https://doi.org/10.1016/J.JFOODENG.2018.07.036.
Honest, K.N., Zhang, H.W., Zhang, L., 2011. Lycopene: isomerization effects on bioavailability and bioactivity properties. Food Rev. Int. 27, 248–258. https://doi.org/10.1080/87559129.2011.563392.
Jazaeri, S., Mohammadi, A., Kermani, A.M.P., Paliyath, G., Kakuda, Y., 2018. Characterization of lycopene hydrocolloidal structure induced by tomato processing. Food Chem. 245, 958–965. https://doi.org/10.1016/J.FOODCHEM.2017.11.077.
Kaur, D., Wani, A.A., Oberoi, D.P.S., Sogi, D.S., 2008. Effect of extraction conditions on lycopene extractions from tomato processing waste skin using response surface methodology. Food Chem. 108, 711–718. https://doi.org/10.1016/J.FOODCHEM.2007.11.002.
Kumcuoglu, S., Yilmaz, T., Tavman, S., 2014. Ultrasound assisted extraction of lycopene from tomato processing wastes. J. Food Sci. Technol. 51, 4102–4107. https://doi.org/10.1007/s13197-013-0926-x.
Liedtke, S., Wissing, S., Müller, R.H., Mäder, K., 2000. Influence of high pressure homogenisation equipment on nanodispersions characteristics. Int. J. Pharm. 196, 183–185.
Lowry, O.H., Rosebrough, N.J., Farr, A.L., Randall, R.J., 1951. Protein measurement with the Folin phenol reagent. J. Biol. Chem. 193, 265–275.
Luengo, E., Álvarez, I., Raso, J., 2014. Improving carotenoid extraction from tomato waste by pulsed electric fields. Front. Nutr. 1, 12. https://doi.org/10.3389/fnut.2014.00012.
Machmudah, S., Zakaria, Winardi, S., Sasaki, M., Goto, M., Kusumoto, N., Hayakawa, K., 2012. Lycopene extraction from tomato peel by-product containing tomato seed using supercritical carbon dioxide. J. Food Eng. 108, 290–296. https://doi.org/10.1016/J.JFOODENG.2011.08.012.
Manzo, N., Santini, A., Pizzolongo, F., Aiello, A., Romano, R., 2018. Degradation kinetic (D_{100}) of lycopene during the thermal treatment of concentrated tomato paste. Nat. Prod. Res. 1–7. https://doi.org/10.1080/14786419.2018.1477147.
Mert, B., 2012. Using high pressure microfluidization to improve physical properties and lycopene content of ketchup type products. J. Food Eng. 109, 579–587. https://doi.org/10.1016/J.JFOODENG.2011.10.021.
Mustafa, W., Pataro, G., Ferrari, G., Donsì, F., 2018. Novel approaches to oil structuring via the addition of high-pressure homogenized agri-food residues and water forming capillary bridges. J. Food Eng. 236, 9–18. https://doi.org/10.1016/J.JFOODENG.2018.05.003.
Naviglio, D., Caruso, T., Iannece, P., Aragòn, A., Santini, A., 2008a. Characterization of high purity lycopene from tomato wastes using a new pressurized extraction approach. J. Agric. Food Chem. 56, 6227–6231. https://doi.org/10.1021/jf703788c.
Naviglio, D., Pizzolongo, F., Ferrara, L., Aragòn, A., Santini, A., 2008b. Extraction of pure lycopene from industrial tomato by-products in water using a new high-pressure process. J. Sci. Food Agric. 88, 2414–2420. https://doi.org/10.1002/jsfa.3334.
Nobre, B.P., Palavra, A.F., Pessoa, F.L.P., Mendes, R.L., 2009. Supercritical CO2 extraction of trans-lycopene from Portuguese tomato industrial waste. Food Chem. 116, 680–685. https://doi.org/10.1016/J.FOODCHEM.2009.03.011.
Nour, V., Panaite, T.D., Ropota, M., Turcu, R., Corbu, A.R., 2018. Nutritional and bioactive compounds in dried tomato processing waste Nutritional and bioactive compounds in dried tomato processing waste. CyTA - J. Food 16, 222–229. https://doi.org/10.1080/19476337.2017.1383514.
Pataro, G., Carullo, D., Bakar Siddique, M.A., Falcone, M., Donsì, F., Ferrari, G., 2018. Improved extractability of carotenoids from tomato peels as side benefits of PEF treatment of tomato fruit for more energy-efficient steam-assisted peeling. J. Food Eng. 233, 65–73. https://doi.org/10.1016/J.JFOODENG.2018.03.029.
Patrignani, F., Lanciotti, R., 2016. Applications of high and Ultra high pressure homogenization for food safety. Front. Microbiol. 7, 1132. https://doi.org/10.3389/fmicb.2016.01132.
Porrini, M., Riso, P., Testolin, G., 1998. Absorption of lycopene from single or daily portions of raw and processed tomato. Br. J. Nutr. 80, 353–361.
Rao, A.V., Waseem, Z., Agarwal, S., 1998. Lycopene content of tomatoes and tomato products and their contribution to dietary lycopene. Food Res. Int. 31, 737–741. https://doi.org/10.1016/S0963-9969(99)00053-8.
Rao, A.V., Agarwal, S., 1998. Bioavailability and *in vivo* antioxidant properties of lycopene from tomato products and their possible role in the prevention of cancer. Nutr. Canc. 31, 199–203. https://doi.org/10.1080/01635589809514703.
Richelle, M., Bortlik, K., Liardet, S., Hager, C., Lambelet, P., Baur, M., Applegate, L.A., Offord, E.A., 2002. A food-based formulation provides lycopene with the same bioavailability to humans as that from tomato paste. J. Nutr. 132, 404–408. https://doi.org/10.1093/jn/132.3.404.
Rubashvili, I., Tsitsagi, M., Ebralidze, K., Tsitsishvili, V., Eprikashvili, L., Chkhaidze, M., Zautashvili, M., 2018. Extraction and analysis of the major carotenoids of agro-industrial waste materials using sequential extraction techniques and high performance liquid chromatography. Eurasian J. Anal. Chem. 13. https://doi.org/10.29333/ejac/82931.
Santini, A., Armini, V., 2013. State of the art of Ready-to-Use Therapeutic Food: a tool for nutraceuticals addition to foodstuff. Food Chem. 140, 843–849. https://doi.org/10.1016/J.FOODCHEM.2012.10.098.
Santini, A., Cammarata, S.M., Capone, G., Ianaro, A., Tenore, G.C., Pani, L., Novellino, E., 2018. Nutraceuticals: opening the debate for a regulatory framework. Br. J. Clin. Pharmacol. 84, 659–672. https://doi.org/10.1111/bcp.13496.
Santini, A., Graziani, G., Ritieni, A., 2013. Nutraceuticals recovery from tomato processing waste and by-products: lycopene. In: Higashide, T. (Ed.), Tomatoes: Cultivation, Varieties and Nutrition. Nova Publishers, Ibaraki (Japan), pp. 313–323.
Schultz, S., Wagner, G., Urban, K., Ulrich, J., 2004. High-pressure homogenization as a process for emulsion formation. Chem. Eng. Technol. 27, 361–368. https://doi.org/10.1002/ceat.200406111.
Sharma, S.K., Le Maguer, M., 1996. Lycopene in tomatoes and tomato pulp fractions. Ital. J. Food Sci. 8, 107–113.
Shi, J., Le Maguer, M., 2000. Lycopene in tomatoes: chemical and physical properties affected by food processing. Crit. Rev. Biotechnol. 20, 293–334. https://doi.org/10.1080/07388550091144212.
Shouqin, Z., Junjie, Z., Changzhen, W., 2004. Novel high pressure extraction technology. Int. J. Pharm. 278, 471–474. https://doi.org/10.1016/J.IJPHARM.2004.02.029.
Siebert, K.J., Troukhanova, N.V., Lynn, P.Y., 1996. Nature of Polyphenol–Protein interactions. J. Agric. Food Chem. 44, 80–85. https://doi.org/10.1021/jf9502459.
Silva, Y.P.A., Ferreira, T.A.P.C., Celli, G.B., Brooks, M.S., 2018. Optimization of lycopene extraction from tomato processing waste using an eco-friendly ethyl lactate–ethyl acetate solvent: a green valorization approach. Waste and Biomass Valorization 1–11. https://doi.org/10.1007/s12649-018-0317-7.
Slinkard, K., Singleton, V.L., 1977. Total phenol analysis: automation and comparison with manual methods. Am. J. Enol. Vitic. 28, 49–55.
Story, E.N., Kopec, R.E., Schwartz, S.J., Harris, G.K., 2010. An update on the health effects of tomato lycopene. Annu. Rev. Food Sci. Technol. 1, 189–210. https://doi.org/10.1146/annurev.food.102308.124120.
Strati, I.F., Oreopoulou, V., 2011. Effect of extraction parameters on the carotenoid recovery from tomato waste. Int. J. Food Sci. Technol. 46, 23–29. https://doi.org/10.1111/j.1365-2621.2010.02496.x.
Torri, L., Piochi, M., Lavelli, V., Monteleone, E., 2015. Descriptive sensory analysis and consumers' preference for dietary fibre- and polyphenol-enriched tomato purees obtained using winery by-products. LWT - Food Sci. Technol. (Lebensmittel-Wissenschaft -Technol.) 62, 294–300. https://doi.org/10.1016/J.LWT.2014.12.059.
Viuda-Martos, M., Sanchez-Zapata, E., Sayas-Barberá, E., Sendra, E., Pérez-Álvarez, J.A., Fernández-López, J., 2014. Tomato and tomato byproducts. Human health benefits of lycopene and its application to meat products: a review. Crit. Rev. Food Sci. Nutr. 54, 1032–1049. https://doi.org/10.1080/10408398.2011.623799.
Wang, T., Raddatz, J., Chen, G., 2013. Effects of microfluidization on antioxidant properties of wheat bran. J. Cereal Sci. 58, 380–386. https://doi.org/10.1016/j.jcs.2013.07.010.
Wang, T., Zhu, Y., Sun, X., Raddatz, J., Zhou, Z., Chen, G., 2014. Effect of microfluidisation on antioxidant properties of corn bran. Food Chem. 152, 37–45. https://doi.org/10.1016/j.foodchem.2013.11.059.