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Estimation of mass transfer terms in the lycopene recovery employing *Moringa oleifera* Lam oil as solvent

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SUMMARY: The aim of this work was to assess the terms associated with mass transfer in the lycopene recovery from the waste of a tomato canning plant. *Moringa oleifera* Lam oil was employed as solvent. An ultrasonic extraction was carried out on skin and seeds. The operational variables were temperature (skin: 45, 60, 75, 90 ºC; seed: 45, 60, 75 ºC), matrix/solvent ratio (m/v) (1:20, 1:25, 1:30), particle size (skin: < 1, 1-2, > 3.15 mm; seed: < 1, 1-2, > 2 mm) and extract separation method (filtration and centrifugation). Kinetic constant, lycopene concentration on the solid surface, volumetric coefficient of mass transfer and effective diffusivity were determined. The more the kinetic constant increased, the higher the volumetric coefficient of mass transfer was. Effective diffusivity increased with temperature. Activation energy values suggest a possible deterioration of lycopene at temperatures higher than the optimum. The use of *M. oleifera* oil as solvent should increase the biological value of the lycopene extracts.

KEYWORDS: *Effective diffusivity; Kinetic constant; Lycopene recovery; Mass transfer coefficient;* Moringa oleifera *seed oil.*

RESUMEN: ***Estimación de los términos de transferencia de masa en la recuperación de licopeno empleando aceite de* Moringa oleifera *Lam como solvente.*** El objetivo del presente trabajo fue evaluar los términos asociados a la transferencia de masa en la extracción de licopeno a partir del residuo de la industria de conservas de tomate. Como solvente se utilizó aceite de *Moringa oleífera* Lam. Se realizó una extracción ultrasónica sobre piel y semillas. Las variables operacionales investigadas fueron, temperatura (piel: 45, 60, 75, 90 ºC; semillas: 45, 60, 75 ºC), relación soluto/solvente (m/v) (1:20, 1:25, 1:30), tamaño de partícula (piel: <1, 1-2, >3.15 mm; semilla: <1, 1-2, >2 mm) y métodos de separación del extracto (filtración y centrifugación). Se determinaron la constante cinética, la concentración de licopeno en la superficie del sólido, el coeficiente volumétrico de transferencia de masa y la difusividad efectiva. A mayor contante cinética, mayor coeficiente volumétrico de transferencia de masa. La difusividad efectiva aumentó con la temperatura. Los valores de energía de activación sugieren un posible deterioro del licopeno a temperaturas superiores a las óptimas. El uso del aceite de *M. oleífera* como solvente debe incrementar el valor biológico de los extractos de licopeno.

PALABRAS CLAVE: *Aceite de semilla de* Moringa oleífera; *Coeficiente de transferencia de masa; Constante cinética; Difusividad efectiva; Extracción de licopeno.*

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1. INTRODUCTION

The consumption of fruits and vegetables has beneficial effects on health due to the presence of compounds with biological properties. Bioactive compounds, obtained from vegetable by-products, have a considerable interest as dietary supplements or food preservatives (Oreopoulou and Strati, 2011; Nour *et al.*, 2018). The development of functional foods has been explored recently in order to obtain favorable effects on health which go beyond their nutritional value (Waliszewski and Blasco, 2010). Carotenoid pigments are a group of nearly 600 fat-soluble pigments which are responsible for the yellow, orange and red colors in fruits and vegetables (Baranska and Kaczor, 2016). These tonalities are derived from lycopene, which is the main pigment responsible for the red color of tomatoes. It represents approximately, 80 – 90% of the total pigment content (Dolatabadi *et al.*, 2016). In addition to the coloring effect, its antioxidant capacity represents other outstanding property (Waliszewski and Blasco, 2010; Cruz *et al.*, 2013). Lycopene, by acting as a powerful antioxidant, reduces the risk of cardiovascular, inflammatory, neurodegenerative diseases and cancer or mitigates their damages (Waliszewski and Blasco, 2010; Dolatabadi *et al.*, 2016; Rodríguez, 2016). Its absorption depends on food intake and only 10 to 30% is absorbed, resulting in a limited contribution through the diet (Cruz *et al.*, 2013). Its use as a food additive could be a solution for increasing its consumption.

The tomato processing industry generates a large amount of waste (Poojary and Passamonti, 2015; Galanakis, 2015; Nour *et al.*, 2018). A satisfactory solution to this environmental and economic problem would be waste recovery and reuse (Cruz *et al.*, 2016). This means the waste would be converted into the raw matter for the lycopene extraction process with a potential environmental, social and economic impact (Galanakis, 2015; Cruz *et al.*, 2016). However, for its recovery, efficient isolation and protection technologies are required. These technologies should not affect the structure or physiological properties of lycopene and must take into account its sensitivity to oxygen, extreme pH, light and high temperatures (Choksi and Vishal, 2007; Bailey, 2015).

Extraction is a very important stage in the recovery of lycopene (Lianfu and Zelong, 2008; Nour *et al.*, 2018). Bearing in mind the high solubility of lycopene in lipids, an oily solvent should be employed. The extracts obtained can be incorporated tino foods where an oily ingredient is required (Cruz, 2013; Gámez *et al.*, 2016). The recovery of lycopene by employing *M. oleifera* oil as solvent may be a favorable option. The oil obtained from its seeds is composed of a wide variety of unsaturated fatty acids. Among them oleic acid is the predominant one. Values have been reported to range from 65.14 - 73.36%. (Ferrer *et al.*, 2020; Gharsallah *et al.*, 2021). The high resistance of *M. oleífera* oil to oxidation can be attributed to its high level of unsaturated fatty acids (Ferrer *et. al.*, 2020; Özcan, 2020). *M. oleifera* oil also has antioxidant properties due to its phytochemical content. A wide range of total phenolic compound, 48 – 400,17 mg GAE/kg oil, has been reported (Özcan, 2020; Gharsallah *et al.*, 2021). Both unsaturated acids and polyphenols content provide nutritional and antioxidant effects from *M. oleífera* (Ferrer *et al.*, 2020). Moreover, an additive which is free of organic solvent will contribute to obtaining more healthy foods. These aspects will give an additional value to lycopene extracts.

The industrial method most commonly used to obtain this pigment is based on conventional solid–liquid extraction (Rodríguez, 2016; Yilmaz *et al.*, 2017; Hoyos *et al.*, 2022). The simultaneous application of ultrasound as an intensification technology has been studied (Rodríguez, *et al.*, 2014; Yilmaz *et al.*, 2017). A 50% decrease in extraction time (Kumcuoglu *et al.*, 2014) and a yield of up to 87.25% (Rahimi and Mikani, 2019) have been reported with respect to conventional extraction.

The knowledge of the terms associated with mass transfer, such as effective diffusivity, mass transfer coefficient and kinetic constant are required for modelling and process assessment. Although the literature includes papers where those terms are reported, those corresponding to lycopene extraction from *M. oleifera* oil have not been published before. The aim of this work was to assess the terms associated with mass transfer in the lycopene recovery from the waste of tomato canning by employing *M. oleifera* oil as solvent.

2. MATERIALS AND METHODS

2.1. Tomato waste

Tomato waste (*Lycopersicum esculentum* Mill. var. *Amalia*) was obtained from a tomato canning

plant. Samples were taken during the tomato harvest season, January to March of 2019 in the western region of Cuba. Waste, composed of skins and seeds, was protected from light and stored at 2 ± 0.5 ºC until the experiments were conducted.

2.2. *Moringa oleifera* seed oil

The oil obtained from *Moringa oleifera* Lam var. *Supergenius*, was the extraction solvent to be employed. It was produced by milling the seeds harvested in the same region and period.

2.3. Procedure for obtaining lycopene

The separation of skins and seeds by means of a flotation-sedimentation process in water was the primary treatment for the industrial waste (Devinder, 2008). Afterwards, the skins and seeds were dried. In order to avoid a possible degradation of lycopene, the experimental material was dried at 55 ºC for 1.5 h in an oven (Incubator, model P/G 2007, R. P. China). The degradation of bioactive compounds has been linked to the drying temperature-time combination (Cruz *et al.*, 2016). The moisture contents of both experimental materials were determined and expressed as percentage (AOAC, 2000).

Ultrasonically-assisted extraction was carried out in a bath with a temperature control (SB-120DT, R. P. China). The equipment was operated at a frequency of 40 kHz and 120 W. These values are within the recommended ranges according the literature (20 – 100 kHz and 100 – 800 W, respectively) (Rodríguez *et al.*, 2014). To avoid an increase in temperature as a consequence of the ultrasonic effect, a cryostat (Ningbo Scientz Biotechnology Co, LTDDC-3006, R. P. China) was included in the system. Prior to the experiments, the operational temperature of the cryostat was defined according to the reactor temperature. In this way, the cryostat operation guaranteed the bath temperature to be ± 1 ºC. A diagram of the experimental system is shown in Figure 1. In all cases the extraction process was carried out in 1 h.

The extracts obtained were centrifuged (Hitachi, SCT15B, Japan) at 3800 g for 10 min. or filtered through a gauze piece. Their absorbance were measured in a AUV-visible spectrophotometer (Rayleigh, model Vis-723G, R. P. China).

2.4. Lycopene quantification

A methodology without organic volatile solvents was employed. Lycopene was extracted and quantified in the oil. Lycopene concentration was measured from a calibration curve ($R^2 = 0{,}998$) of pure lycopene standard (Sigma- Aldrich, USA). The specific extinction coefficient ($A^{1\%} = 3\,465$) was estimated from the curve. Absorbance was measured in an AUV-visible spectrophotometer (Rayleigh, model Vis-723G, R. P. China) with *M. oleifera* oil as blank. Lycopene concentration was measured at the maximal wavelength identified (483 nm) to minimize interference from other carotenoids (Poojary and Passamonti, 2015). Figure 2 shows the UV-vis spectra of lycopene stand-

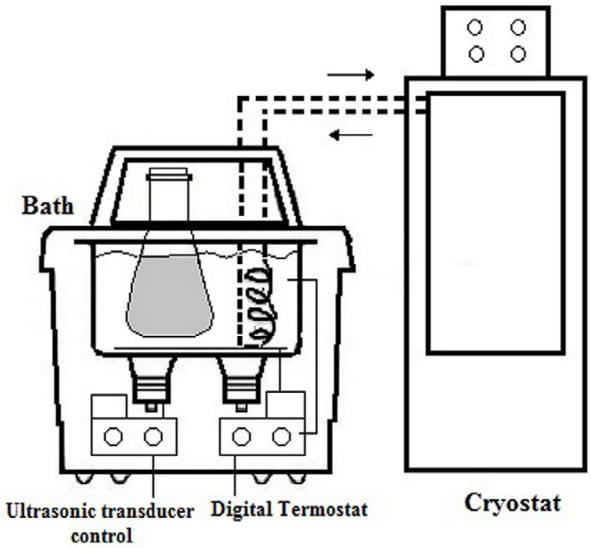

Figure 1. Experimental system.

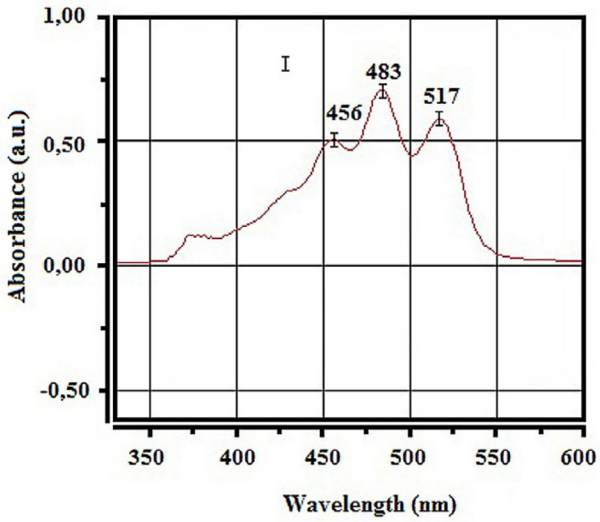

Figure 2. UV-vis spectra of lycopene standard in *M. oleifera* oil.

ard in *M. oleifera* oil. The upper wavelength is explained from the redshift phenomena as a result of the interaction between lycopene and the solvent (Hoyos *et al.*, 2022). Lycopene concentration was expressed as μg/mL (or μg/g dry matter).

2.5. Experimental design

The operational parameters should be previously defined to determine the terms associated with mass transfer. The combining effect of temperature (T) and matrix/solvent ratio (MSR) on the extraction assisted by ultrasound was considered in a first experimental design (skin: $4^1 \cdot 3^1$; seed: 3^2). The levels of the operational parameters for both materials are shown in Table 1.

In the case of skin, for a better detection of the effect of temperature, the design was made at 90 º C. The particle size ranging 1 – 2 mm was used for both experimental materials.

A second experimental design to assess the influence of particle size (PS) and separation method (SM) was developed at the optimum temperature corresponding to the first design and MSR at 1:25. To guarantee the total imbibition of the experimental materials, the MSR value was selected. Table 1 shows the operational parameter levels for both materials (skin and seed: $2^1 \cdot 3^1$). Filtration, through a gauze piece, and centrifugation were the SM applied to both experimental materials.

The mid-range and the largest PS for both skin and seed corresponded to the waste received. The experimental material was ground in a domestic blade mill (Oster, BVSTBMH23-053, U.K.). The material obtained was sieved for selecting the sizes required.

In all experiments a mass of 0.4 g of skin or seed was weighed (Sartorius, model BS124S, Germany). The experimental designs were carried out for both skin and seed, separately.

2.6. Extraction stages

An exhaustive extraction was developed in irder to determine the extraction stages for each experimental material. It was performed in four stages, on the same sample, at the optimum T, PS of 1-2 mm each , and MSR of 1/25 (m/v). To make the absorbance measurement procedure easier, the last condition was selected. Each extraction stage lasted 80 min. The total extracted lycopene mass was determined from the sum of the extracted masses in each of the successive stages. The yield was obtained from equation 1 (Rodríguez, 2016).

$$Y = \frac{\text{m (extracted mass)}}{\text{M (total mass)}} \cdot 100 \qquad (1)$$

where: Y is the extracted lycopene yield (%); m is the extracted lycopene mass in each stage (μg/g dry matter); M corresponds to the total mass of lycopene extracted (μg/g dry matter).

2.7. Extraction kinetics

Ultrasonic-assisted extractions were developed at different T (45, 50, 55, 60, 70, 75, 80 and 90 °C) for

Table 1. Experimental designs (n =3)

First experimental design			
Skin		Seed	
Temperature (ºC)	Matrix/solvent ratio (m/v)	Temperature (ºC)	Matrix/solvent ratio (m/v)
45	1:20	45	1:20
60	1:25	60	1:25
75	1:30	75	1:30
90			
Second experimental design			
Skin		Seed	
Particle size (mm)	Separation method	Particle size (mm)	Separation method
< 1 1 - 2 > 3.15	Filtration Centrifugation	< 1 1 – 2 > 2	Filtration Centrifugation

80 min. They were developed under the corresponding conditions previously decided by the study about extraction stages. Samples were taken and their absorbance measured every 10 min. The results were fitted to the fundamental leaching equation (equation 2), which corresponds to a first-order kinetic model (Treybal, 1997; Poojary and Passamonti, 2015).

$$C = C_s\left(1 - e^{-k \cdot t}\right) \quad (2)$$

where: k is the kinetic constant (min^{-1}); Cs is the lycopene concentration on the solid surface (µg/mL); Cis the lycopene concentration(µg/mL); t refers to time (min).

Upon this base, the leaching equation can be expressed as shown in equation 3 (Turhan *et al.*, 2006).

$$C = C_s\left(1 - e^{-\frac{k_L \cdot A}{V} \cdot t}\right) \quad (3)$$

where: volumetric mass transfer coefficient, $k_L \cdot A$ (m^3/s) can be calculated using this equation. The activation energies were evaluated from the kinetic constants, after being fitted to the Arrhenius model (equation 4).

$$k = k_o \cdot e^{\frac{Ea}{RT}} \quad (4)$$

where: k is the kinetic constant (min^{-1}); k_o is the frequency factor (min^{-1}), Ea corresponds to activation energy (J/mol); R is the universal constant of gases (8.31 J/mol·K); Tis temperature (K).

Lycopene diffusivity on *M. oleifera* oil was estimated by applying Ficks' second law and considering diffusion as the controlling mechanism. Due to the irregular shapes of the skin particles, they were assumed to be solids of infinite slab geometry (thickness: 0.091 mm, according to preliminary studies); while seed particles were taken as spheres (diameter: 0.1915 mm, related to a granulometric analysis). In both cases a uniform lycopene content was considered. Equations 5 and 6 show the solutions of the diffusion model for skin and seed, respectively. These equations are simplifications of the differential equation solutions based on a series with an infinite number of terms (Varzakas *et al.*, 2005).

$$\frac{C}{C_0} = \frac{8}{\pi^2} \cdot e^{\left[-\pi^2 \frac{D_e}{4L^2} t\right]} \quad (5)$$

$$\frac{C}{C_0} = \frac{6}{\pi^2} \cdot e^{\left[-\pi^2 \frac{D_e}{r^2} t\right]} \quad (6)$$

where: Cis the lycopene concentration (µg/mL); C_0 is the initial lycopene concentration; D_e refers to effective diffusivity, m^2/s; L is half-thickness of the skin particle, m; r, is the radius of the seed particle, m; tis time, min.

2.8. Statistical analysis

All experiments were carried out in triplicate. The response surface method to establish the optimal operational conditions in the experimental designs was applied. The statistical analysis was performed using Statgraphics Centurion XVII (Statistical Graphics, Rockville, MD, USA).

3. RESULTS AND DISCUSSION

3.1. Lycopene extraction

The experimental results showed good agreement with the models (Table 2). Both parameters, T and MSR, were linked to the lycopene extraction. The effect of these variables on the extraction from skin and seed is shown in Figures 3 A and C, respectively.. An increase in the lycopene concentration was achieved when MSR decreased. The influence of this variable on the extraction from skin was greater than the extraction from seeds due to the higher lycopene content of the skin.

As expected, the extraction depended on T as stated in the literature (Meireles *et al.*, 2012; Rodríguez, 2016). The same temperature-related behavior was detected in the skin and seed experiments. This behavior depended on the value of this variable (quadratic term in the models). The higher the temperature, the higher the extraction, until an inflection point was reached. A later increase in T brought about the opposite effect. The increase in T increased the solubility of the lycopene and decreased the dissolvent viscosity (Devinder, 2008; Rodríguez, 2016). Both effects favor the mass transfer from the solid matrix to solvent. However, the subsequent decrease might be associated with the degradation (oxidation) and/or isomerization reactions of lycopene when the extraction was carried out at temperatures higher than the aforementioned inflection point (Devinder, 2008; Poojary and Passamonti, 2015). It has been reported that lycopene isomerization causes a decrease in the visible-band absorption in UV-Vis spectrophotometric analysis (Poojary and Passamonti, 2015; Rodríguez, 2016). These two effects, to all appear-

Table 2. Statistical models for significant parameters of both experimental designs (p value < 0.05)

	First experimental design			Second experimental design	
Terms	Skin	Seed	Terms	Skin	Seeds
Independent term	6.6190	2.2347	Independent term	2.1019	0.6984
T: Temperature		0.0621	PS: particle size	-0.2638	-0.6214
MSR: matrix/ solvent ratio	-2.2768	-0.3580	SM: separation method	-0.1002	- 0.1285
T^2	-3.2822	-0.2771	PS^2	0.2219	0.5940
SSR^2			PS·SM	0.0680	0.0678
T· SSR	0.8797				
R^2 (%)	91.07	91.95	R^2 (%)	92.86	99.06
Mean absolute error	0.3166	0.0758	Mean absolute error	0.0629	0.0462
Durbin-Watson value	2.2371	2.1605	Durbin-Watson value	3.2354	2.1938
T optimum (ºC)	67 (-0.103)[a]	63(0.112)[a]			
SSR optimum (m/v)	1/20 (-1)[a]	1/20 (-1)[a]			
Optimum concentration (µg//mL)	7.57	2.59			

a: coded variable levels

ances, were less pronounced in seeds as a result of their lower lycopene content Lycopene content in tomato seed is approximately half that of the skin (Bailey, 2015; Baranska and Kaczor, 2016; Yilmaz *et al.*, 2017).

The optimum values for lycopene concentration (Table 2) were 7.57 µg/mL (18.9 mg/kg dry matter) and 2.59 µg/mL (6.5 mg/kg dry matter) for skin and seed, respectively. These were achieved for MSR, 1/20 (m/v) and 67 °C for skin, and 63 °C for seed.

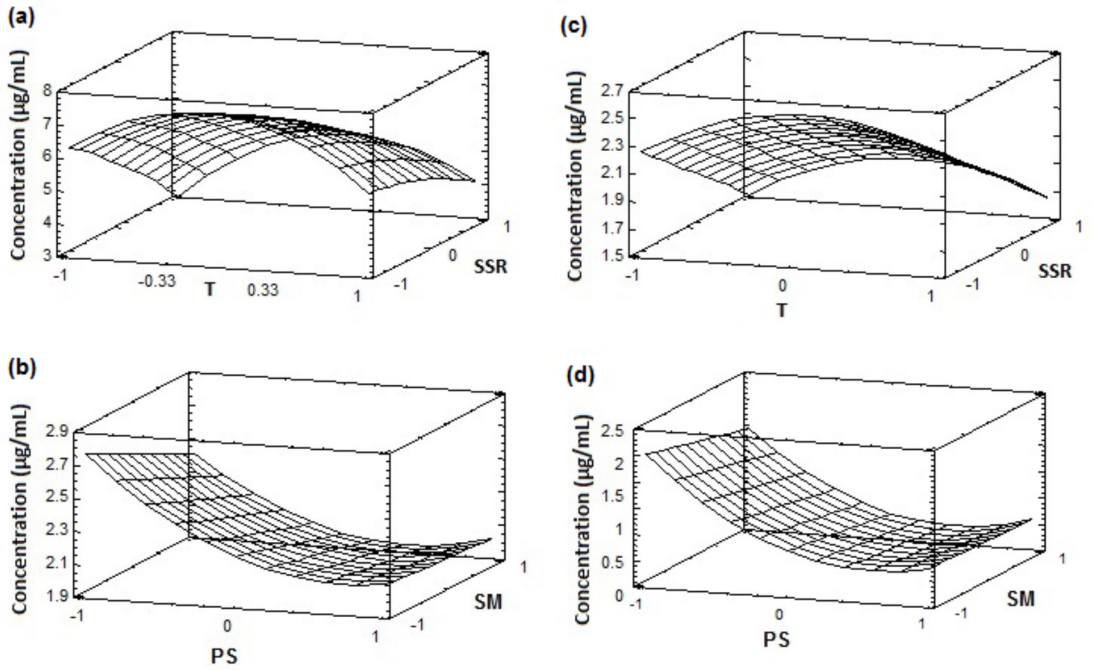

Figure 3. Surface graphics. First experimental design: a) skin; c) seed. Second experimental design: b) skin; d) seed.

The employment of *M. oleifera* oil as solvent in the lycopene extraction shows, in general terms, a similar behavior to the organic solvents described in the literature (Gámez *et al.*, 2016). The ease for lycopene to be dissolved in an oil phase was enhanced with the employment of ultrasound because of its effects up the viscosity values of the oil (Rodríguez, *et al.*, 2014; Yilmaz *et al.*, 2017; Rahimi and Mikani, 2019).

3.2. Extract separation

Table 2 (second experimental design) shows the fitted models. They describe the effect of the researched variables satisfactorily. The effects of PS and SM are shown in Figures 3 B and D for skin and seed, respectively. The lycopene concentration increased when PS decreased. Therefore, the highest concentration was achieved for the smallest size for both experimental materials. The lycopene concentration in the skin extracts, Figure 3 B, did not show an appreciable increasing trend with PS because the difference between their levels at the experimental design was lower than 1 μg/mL. The thinness of the skin could be the cause of these slight differences.

The highest lycopene concentration in both MS was reached for the smallest PS (Figures 3 B and D). This result is due to an apparent higher concentration when filtration was employed. However, errors in the absorbance measurement were detected for the smallest PS when filtration was applied. Very small particles can pass through the gauze leading to distortion in the extract absorbance. Therefore, centrifugation as SM should be used when the smallest PS is employed. At the other PS there were no differences between the SM employed, so filtration could be considered sufficient to separate the solid residues in the extracts obtained. Nevertheless, the decision to use a PS of less than 1 mm will depend on a balance between the higher lycopene recovered and the acquisition and operation costs of the centrifugal equipment. Extraction from the seed would be more complex and expensive compared to the skin, due to the milling and centrifugation to be added as additional steps in the extraction process.

The concentrations obtained in extract separation were smaller than in the extraction stage. A MSR equal to 1/25 (m/v) was applied in the extract separation.

The employment of organic solvents for the conventional extraction (CE) of lycopene was used. A mixture of hexane, acetone and ethanol in different proportions at 50 – 60 ºC has been reported. Contents of 90 and 20 mg/kg dry matter for skin and seed have been considered (Devinder, 2008). However, other authors obtained values close to 20 mg/kg dry matter. A maximum lycopene yield of 20 mg/kg dry matter in the ultrasound-assisted extraction (UAE) from skin and seed with acetone has been reported (Oreopoulou and Strati, 2011). Maximum contents of 90.1 mg/kg dry matter and 79.4 mg/kg dry matter for UAE and CE, respectively, were reported by Kumcuoglu (2014). Concentrations of 76.87 mg/kg dry matter and 57.19 mg/kg dry matter for UAE and CE, respectively, were reported by Yilmaz *et al*. (2017). The lycopene concentration ranged from 34.7 – 40.3 mg/kg dry matter (Poojary and Passamonti, 2015) using a mixture of hexane:acetone, with a lower polarity than ethanol. A comparative study of the CE from tomato waste processing using ethanol and edible soybean oil as solvents has been reported by Gámez *et al.* (2016), with recovery of 86.1 mg/kg dry matter and 25.40 mg/kg dry matter, respectively. The lower lycopene recovery when soybean oil was used can be attributed to its low polarity and consequently it is more selective (Gámez *et al.*, 2016). Nonetheless, the value reported is close to the one obtained in the extraction with *M. oleifera* oil because of the similar polarity of both oils (Gámez *et al.*, 2016; Ferrer *et al.*, 2020; Hoyos *et al.*, 2022). In spite of a smaller lycopene concentration when *M. oleifera* oil was used, its employment can contribute to keeping the pigment stability over time, besides the added value that this solvent represents (Gámez *et al.*, 2016).

It should be taken into account that lycopene content is dependent on genetic, agronomic, climatic factors and the extraction and processing conditions. These factors are present in the different results reported in the literature.

3.3. Extraction stages

Figures 4 A and B show the lycopene extraction yield for skin and seed, respectively. Extraction yields of 54, 28, 12 and 6% in the first, second, third and fourth stages, respectively, were reached from skin. In the extraction from seed, a yield of 78% was obtained in the first stage but 16, 6 and 0% in the second, third and fourth stages, respectively. This behaviour is due to the higher original lycopene con-

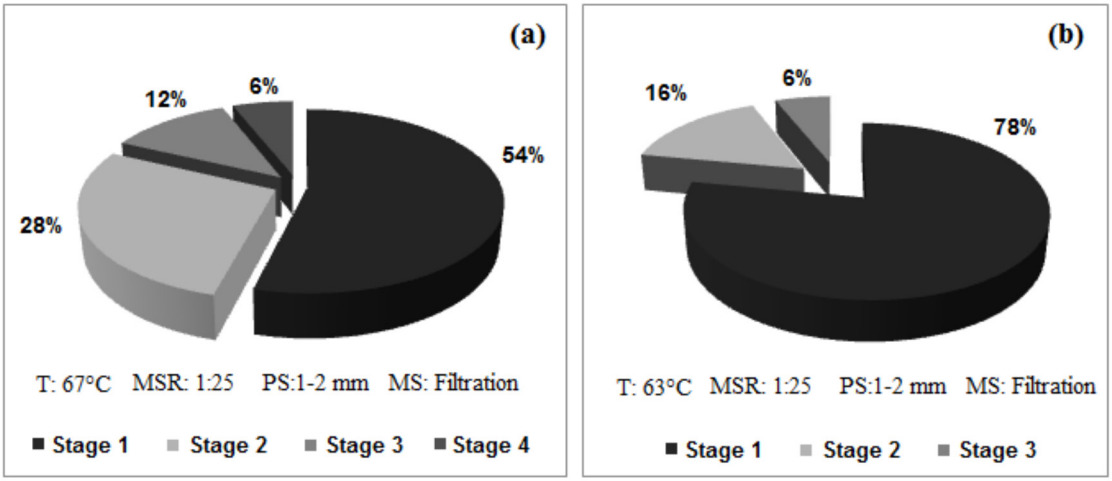

Figure 4. Lycopene yield obtained in each extraction stage for skin (a) and seed (b) (n = 3)

tent in the skin (74.32 µg/g dry matter) than the seed (35.35 µg/g dry matter). It has been proven that the lycopene content in tomato seeds is approximately half of the lycopene content in the skin (Bailey, 2015; Baranska and Kaczor, 2016; Yilmaz *et al.*, 2017). This agrees with previously reported values. The total lycopene masses obtained for both skin and seed are inside the interval for common varieties of red and yellow tomatoes (25 – 150 µg/g dry matter) (Choksi and Vishal, 2007; Bailey, 2015; Rodríguez, 2016; Yilmaz *et al.*, 2017).

3.4. Extraction kinetic

Figures 5 A and D show the behavior of lycopene concentration with extraction time at 45, 70 and 90 ºC for skin and seed, respectively. These temperatures were selected taking into account the lowest temperature (45 ºC), the highest temperature (90 ºC) and a temperature close to the optimum temperature (70 ºC). The profiles show, at first, that lycopene concentration rises rapidly because of the solvent penetration into the solid. A high concentration gradient and a quick mass transfer towards the liquid phase are caused. This increase was gradually diminished with time and the solute transfer from the solid phase was developed more slowly due to the decrease in the concentration gradient among phases (Poojary and Passamonti, 2015; Dolatabadi *et al.*, 2016). A maximum value was obtained at 60 min. and 30 min. for skin and seed (Figures 5 A and D), respectively. These times are similar to those recommended by other authors (Lianfu and Zelong, 2008; Yilmaz *et al.*, 2017). Both times contrast with the CE time of 6 – 6.5 h (data unpublished). As expected, and as stated in the literature (Kumcuoglu, 2014; Rodríguez *et al.*, 2014; Yilmaz *et al.*, 2017) ultrasound application accelerated the extraction process.

Parameters Cs and k, obtained from the fitting of the experimental data to equation 1 are shown in Table 3 for both experimental materials at the studied temperatures. The result demonstrates that the basic leaching equation describes the lycopene extraction from *M. oleifera* oil. A similar fact was reported by Poojary and Passamonti (2015) and Turhan *et al.* (2006). Valdés *et al.* (2015) also reported the satisfactory application of this model to the extraction kinetics of polyphenols from *M. oleifera* leaves. Similar results of the application of this equation for other natural products have been reported in the literature (Pineilo and Sineiro, 2006; Thurhan *et al.*, 2006).

The mass transfer coefficients obtained in this study are similar to ones reported by other authors (Varzakas *et al.*, 2005; Turhan *et al.*, 2006) and they are in correspondence with the behavior of the kinetic constant. In the interval 45 – 70 °C, Cs and k increased with the temperature increment. However, within the range 70 – 90 °C, both parameters decreased although temperature was increased. This behavior of the lycopene concentration (quadratic effect of temperature) in both materials shows what was explained in the first experimental design.

Parameters k, $k_L \cdot A$ and Cs showed a dependence with temperature, although the highest was the last one (Table 3). Firstly, all skin and seed parameters

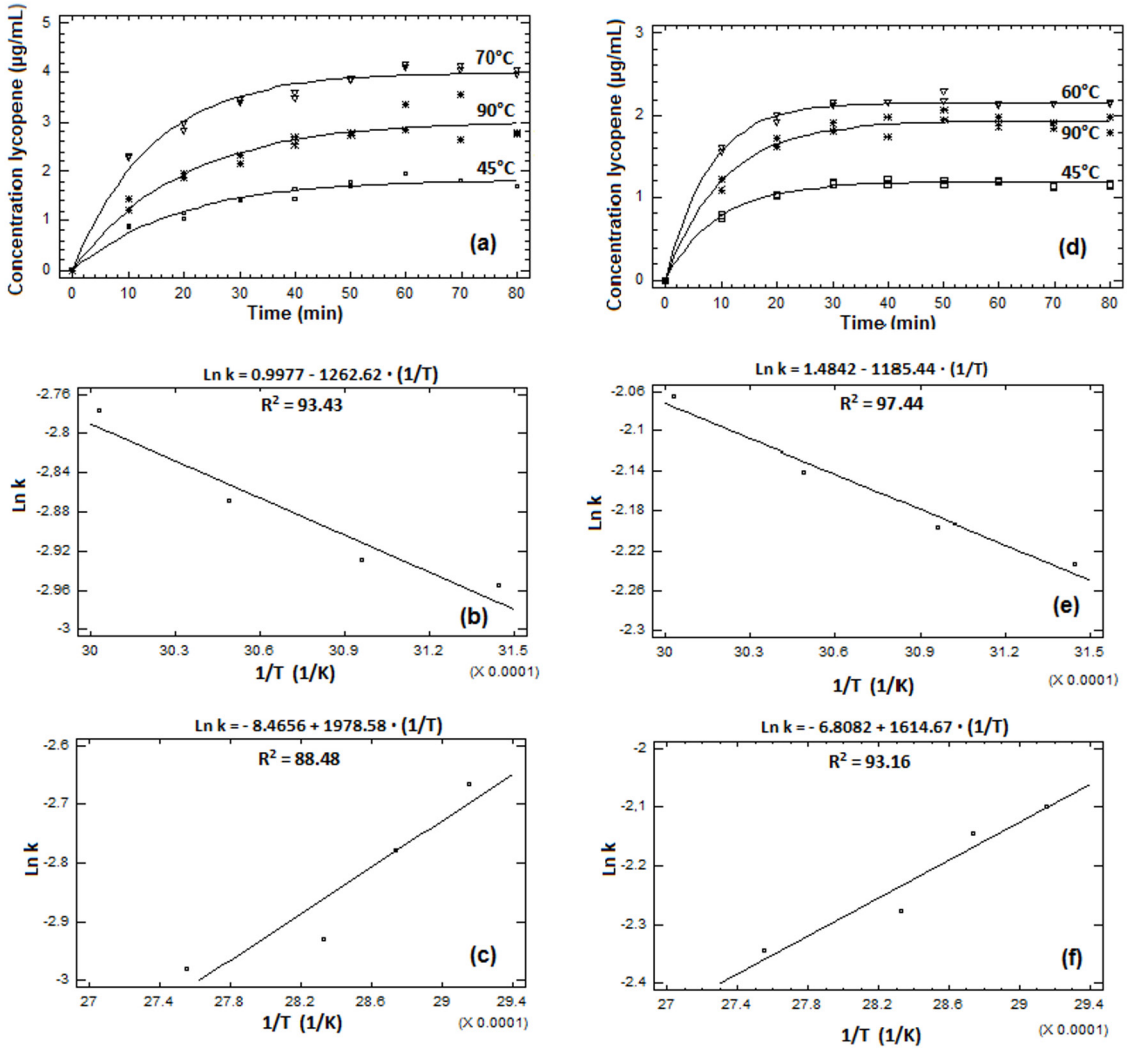

Figure 5. Extraction kinetics of lycopene at different temperatures for skin (a) and seed (d). Relationship among the kinetic constant and temperature: below the optimum temperature: (b) skin, (e) seed, and above the optimum temperature: (c) skin, (f) seed.

increased up to 70 °C. This value is close to the optimum extraction temperature (skin: 67 °C; seed: 63 °C). After these temperatures, a decrease in the parameters was obtained. The solubility and diffusivity of the compounds to be extracted were enhanced when temperature was increased. Moreover, the decrease in viscosity with temperature is another aspect that favored extraction. A small increase in the speed and mass transfer coefficient with temperature as a consequence of the resistance among phases has been reported by other authors (Treybal, 1997; Meireles *et al.*, 2012; Valdés *et al.*, 2015). An opposite behavior was seen after 70 ºC. The deterioration of the lycopene with temperature might be related to the decrease in such parameters (Meireles *et al.*, 2012; Rodríguez, 2016).

Although the temperature increased up to 70 ºC, it caused the increase in Cs and k and $k_L \cdot A$ (Table 3), and the highest increase was seen in the last one. As a consequence of the temperature increase, the lycopene leaching speed was increased. Nevertheless, the convective mass transfer showed a lower increase,

After 70 ºC, this behavior changed and it might be associated with lycopene degradation. As expected, and as stated in the literature (Varzakas *et al.*, 2005), the higher the temperature, the higher D_e (Table 3). The De value for the skin was higher than the one presented for the seeds. This could be explained by the structural differences between them. To all appearances, the lycopene transfer through the solid material predominated regarding the behavior

Table 3. Parameters of the kinetic model, volumetric coefficient of mass transfer and effective diffusivity at different extraction temperatures (n = 3)

Temperature (°C)	45	50	55	60	70	75	80	90
				Skin				
Cs (μg/mL)	1.8607	1.9820	2.9920	3.9758	4.0042	3.3263	3.1142	3.0297
k (min^{-1})	0.0520	0.0534	0.0567	0.0622	0.0696	0.0621	0.0533	0.0508
R^2 (%)	95.45	96.08	97.22	96.77	97.51	88.49	94.86	92.29
Mean absolute error	0.0856	0.0803	0.1046	0.1605	0.1304	0.2427	0.1723	0.1561
$k_L \cdot A$ (m^3/s)	0.0399	0.0414	0.0423	0.0433	0.0584	0.0359	0.0338	0.0276
$D_e.10^{-11}$ (m^2/s)	3.6619	3.8299	4.8714	4.9050	4.9722	5.0394	5.1401	5.5097
Ea (kJ/mol)			10.49			16.44		
				Seed				
Cs (μg/mL)	1.1842	1.3618	1.7832	2.1613	2.1692	2.1717	2.0062	1.9286
k (min^{-1})	0.1067	0.1113	0.1176	0.1268	0.1227	0.1172	0.1026	0.0959
R^2 (%)	98.98	98.43	98.96	99.38	98.87	97.76	98.87	97.29
Mean absolute error	0.0234	0.0320	0.0356	0.0278	0.0493	0.0631	0.0428	0.0663
$k_L \cdot A$ (m^3/s)	0.0399	0.0421	0.0467	0.0499	0.0428	0.0385	0.0351	0.0347
$D_e.10^{-11}$ (m^2/s)	0.9671	1.0971	1.1160	1.1301	1.1810	1.2500	1.3483	1.4600
Ea (kJ/mol)			9.85			13.42		

of Cs. In general terms, D_e values were in the range reported for other agro-food products (Varzakas *et al.*, 2005; Pineilo and Sineiro, 2006).

Although the same behavior with respect to temperature was seen in both skin and seed, a higher increment was obtained in the skin. It might be related to the structural characteristics of these materials. In leaching operations, the leachable solids are contained in a framework of insoluble solids. This restricts the diffusion process and affects the rate of diffusion. This barrier associated with the solid structure provides the dominant resistance (Varzakas *et al.*, 2005). Therefore, the structure of the skin would favor higher lycopene mobility than the seed structure.

Figures 5 B and E show the relation of k with temperature when it was increased up to the optimum value, for skin and seed, respectively. Figures 5 C and F correspond to the temperature variation from the optimum value up to 90 ºC for skin and seed, respectively. In both intervals a good adjustment to the Arrhenius equation (equation 4) was provided.

The knowledge of k, $k_L \cdot A$ and D_e and their relation is very useful information for designing and assessing leaching processes.

The Ea was 10.49 kJ/mol and 9.85 kJ/mol at 45 – 60 °C, for skin and seed, respectively. In the interval 70 – 90 °C, its value was 16.44 kJ/mol and 13.42 kJ/mol for skin and seed, respectively. These values indicate that the lycopene extraction from skin was more dependent on temperature than from seed. The relatively high values for Ea imply that a small temperature change was sufficient to affect the kinetic constant and therefore the speed of the extraction process (Turhan *et al.*, 2006). In both cases, the process was controlled by the diffusion mechanism in the interval of 45 – 70 °C because the activation energy was smaller than 12 kJ/mol. However, in the interval 70 – 90 °C the activation energy was higher than 12 kJ/mol and this is an indicator of chemical processes such as degradation or isomerization (Pineilo and Sineiro, 2006; Turhan *et al.*, 2006; Valdés *et al.*, 2015; Cruz, 2016). This result supports the behavior of Cs, k and $k_L \cdot A$ with temperature taking into account the effect of this parameter on the lycopene concentration.

4. CONCLUSIONS

The experimental values showed good agreement with the basic leaching equation. The optimal

T and MSR (skin: 67 ºC and 1:20; seed: 63 ºC and 1:20) were determined. Moreover, from an operational point of view, PS and SM (skin: 1–2 mm and filtration; seed: < 1 mm and centrifugation) are recommended. The greater the kinetic constant the higher the volumetric coefficient of mass transfer will be. They increased up to the optimum temperature of extraction. A decrease in these parameters with a subsequent increase in temperature was observed. This behavior may be linked to lycopene degradation, which is, in all appearances, the predominant effect of the highest temperatures. The activation energy values support this statement. On the other hand, the effective diffusivity of lycopene in all range of temperature was increased in both materials. The seed showed lower values than the skin taking into account its structural characteristics. The major lycopene concentration was obtained to the optimum values of the investigated variables. The terms associated with mass transfer can be employed for designing and evaluation the lycopene recovery process by employing *M. oleifera* oil as solvent.

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