Bidimensional modeling applied to oil extraction kinetics of microwave-pretreated canola seeds

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ABSTRACT

The effect of microwaves on canola oil extraction kinetics and on tocopherol and canolol content in oil was studied. Oil was extracted with hexane at constant temperature (298–333 K) at different times (300 –64800 s). In general, for each temperature and time, a significant yield increase was achieved by effect of the pretreatment. A modified Fick's diffusion model was proposed to explain the extraction process; the parameters were adjusted to obtain washing fractions and the effective diffusion coefficient, which presented an Arrhenius-type temperature-dependence. The analysis of the parameters allowed to develop a modified bidimensional diffusion model (temperature and time-dependent), appropriately correlating the data for pretreated and untreated samples. An increase in the pre-exponential parameter due to pretreatment was observed, evidencing the influence of microwave radiation on the sample structure. The pretreatment did not significantly affect the oil quality indices, but increased the content of canolol and β and δ-tocopherol isomers.

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1. Introduction

Canola oil has a high nutritional value, with high content of linolenic acid (ω-3) and a relatively high level of phytosterols; It is second in total phytosterol content among traditional edible oils, only surpassed by corn oil (McDonald, 2012). Its natural antioxidants include tocopherols (vitamin E), with γ-tocopherol and α-tocopherol being the predominant isomers, and a high content of phenolic compounds, mostly sinapine and sinapic acid (Matthäus, 2012). Canolol (4-ethenyl-2,6-dimethoxyphenol), a potent antioxidant and antimutagenic phenolic compound formed by decarboxylation of sinapic acid, has been found in high concentrations in canola oil subjected to heat treatment (Koski et al., 2003; Wakamatsu et al., 2005; Spielmeyer et al., 2009).

Conventional oil extraction is carried out by pressing and/or solvent extraction. Oil is located within the cells forming fatty substances, so it is necessary to break the structures to facilitate their release. To this end, several pretreatments have been developed (size reduction, grinding, heat treatment, enzymatic hydrolysis, etc.). Among these treatments, one alternative that has gained greater attention in recent years is microwave radiation, offering shorter processing times and energy savings due to its uniform effect throughout the volume of the material by the molecular interactions with the electromagnetic field. Uquiche et al. (2008) observed a change in the structure of Chilean hazelnut caused by the application of microwave pretreatment, increasing the porosity of the sample. The same behavior was observed by Ramos et al. (2014) in canola seeds pretreated by microwave.

The extraction process is affected by many physical and chemical variables that are difficult to assess quantitatively and qualitatively. Several models have been proposed to analyze the extraction kinetics of vegetable oils (Zárate et al., 2015). The most widely used model (a modified Fick's law diffusion model) considers two main mechanisms: a process of washing the oil from the surface of the particles, and a diffusion process that can be carried

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out in one or two stages, depending on the proportion of broken or intact cells resulting from the pretreatment applied (Perez et al., 2011; Fernández et al., 2012; Zárate et al., 2015). This model has been used to analyze the extraction kinetics of canola oil without pretreatment (Fernández et al., 2012) and with hydrothermal pretreatment (Zárate et al., 2015), and in both cases the model was adequate, showing an influence of the hydrothermal pretreatment on the kinetic parameters. Ramos et al. (2014) were able to increase (up to 5.4%) the yield of canola oil extracted by solvent (hexane) by applying a microwave pretreatment without detecting any deterioration in the oil quality, however no study has been conducted on the oil extraction kinetics of microwave-treated canola seeds. The aim of this study was to evaluate the effect of the microwave pretreatment on the extraction kinetics of canola oil, and develop models to explain the various phenomena involved in this process. The influence of the microwave treatment on the antioxidants in the oil was also analyzed.

2. Material and methods

2.1. Sample characterization

A 10 kg bag of canola seeds (winter variety) was supplied by a local company (AL HIGH TECH SRL, Argentina). The seeds were characterized for proximate composition according to standard methods to determine moisture (ASAE S352.2 DEC 97, ASAE, 1999 and AOCS Ba 24-38, AOCS, 1998), oil content (IUPAC 1.122, IUPAC, 1992), proteins (AOCS Ai 4-91, AOCS, 1998) using a BÜCHI distiller (Model 435, Switzerland), crude fiber (AOCS Ba 6-84, AOCS, 1998), ash (AOCS Ba 5a-49, AOCS, 1998), and carbohydrate content as

nitrogen free extract (NFE) calculated by difference using Equation (1):

$$NFE = 100 - (oil + protein + crudefiber + ash) \qquad (1)$$

2.2. Treatment before extraction

Samples were dried to a moisture level of 5.7 ± 0.2% db in a forced convection air oven at 35 °C, so as not to change the oil quality because of the drying process. The moisture level was selected considering the optimum moisture for microwave pretreatment of canola seeds (Ramos et al., 2014).

Samples were divided into two parts. One part was left untreated, and the other one was treated by microwave radiation using the following procedure: an initial sample of 45 g was divided into 5 Pyrex containers and placed inside the microwave (BGH Quick Chef, model 36,960, Argentina). The samples were treated for 5 min at a frequency of 2450 MHz at 100% power (corresponding to 607 W of power absorbed by 1 kg of water, according to the calibration described by Arballo et al., 2010). The procedure was repeated until the amount needed for subsequent tests was obtained, and it was homogenized. Both parts were ground in a coffee grinder (Moulinex, Argentina) and screened to a particle size in the range of 0.420–1.000 mm for the different tests, in accordance with the optimal milling values suggested by the literature consulted (Perez et al., 2011; Fernández et al., 2012; Zárate et al., 2015).

2.3. Kinetic tests

The extraction process was performed in a batch device with a magnetic stirrer (200 rpm) using untreated and microwave-treated seeds. In order to determine the oil extraction kinetics, tests were carried out at different times (from 300 to 64,800 s) and at different temperatures (298, 313, 323 and 333 K). Five grams of ground sample and 85 mL of technical grade hexane (BIOPACK, ≥98.5%) were heated separately to extraction temperature before each test. Then the solvent was transferred into the recipient containing the sample. When the established time elapsed, the miscella was separated from the meal by centrifugation in a Thermo Scientific Sorvall Legend X1 (Germany) equipment at 14,069 G for 5 min. After filtration through Quanty JP40 filter paper, the miscella was collected and the solvent was evaporated in an R-3000 Büchi vacuum rotary evaporator (Switzerland), not exceeding 55 °C. Residual hexane was removed in a DHG-9123 drying oven at 105 °C for 1 h. The amount of oil was measured gravimetrically. The amount of oil obtained at 64,800 s was identified as M_∞ (mass of solute that diffuses at infinite time) because this time was considered long enough to attain the equilibrium state (Perez et al., 2011; Fernández et al., 2012; Zárate et al., 2015).

2.4. Mathematical model

A diffusive model based on a modified Fick's law was used. This model considered a non-stationary state and spherical particles suspended in a medium at a constant concentration without volume restriction (Perez et al., 2011). The solution of Fick's Second Law is given by Equation (2) (Crank, 1975):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6}{n^2\pi^2} e^{-n^2 Bt} \qquad (2)$$

where t (s) is the diffusion time, and M_t and M_∞ represent the mass of the substance (kg solute kg dry defatted meal^{-1}) that diffuses at

time t and infinite time, respectively. B (s^{-1}) is the model fitting parameter.

This model was used with modifications, where a washing stage was included in order to take into account the mass of oil M_0 extracted during the washing time t_0. In that period, rapid non-diffusive phenomenon takes place and the fresh solvent removes the free surface oil of the meal by washing (Perez et al., 2011; Fernández et al., 2012). The proposed model is presented in Equation (3):

$$\frac{M_t}{M_\infty} = 1 - \left(1 - \frac{M_0}{M_\infty}\right) \sum_{n=1}^{\infty} \frac{6}{n^2 \pi^2} e^{-n^2 B(t - t_0)} \tag{3}$$

where $\frac{M_0}{M_\infty}$ represents the mean value of the oil extracted in the washing step, and B is associated with the effective diffusivity (D_{eff}, m^{2}s^{-1}):

$$B = \frac{D_{eff} \cdot \pi^2}{R^2} \tag{4}$$

with R(m) being the average particle radius. It was assumed that particle size and shape remained constant during the extraction process. The same assumption was made in a previous work (Fernández et al., 2012; Zárate et al., 2015), where canola seeds ground with the same grinding method used in the present work.

The experimental data were fitted to the model using the Marquardt-Levenberg algorithm with the SIGMAPLOT software v. 11.0 (Systat Software, USA).

2.5. Statistical analysis

2.5.1. Pretreatment effect

The experimental data were analyzed by means of analysis of variance (ANOVA) using the Infostat software package (Infostat Group, Facultad de Ciencias Agrarias, Universidad Nacional de Córdoba, Argentina, 2004). The effect of the pretreatment for each time and temperature were compared. Differences were considered significant at $p < 0.05$.

2.5.2. Models

A comparison of the non-linear models was carried out by means of the extra sum of squares principle (ESS) in order to determine if coefficients $\frac{M_0}{M_\infty}$ and/or B in Equation (2) were temperature-dependent for the 298–333 K range. The proposed null hypothesis (H$_0$) and alternative hypothesis (H$_1$) are expressed by the following statements:

H$_0$: Coefficients $\frac{M_0}{M_\infty}$ and/or B do not depend on temperature (Global model in the case that neither are temperature-dependent; Common $\frac{M_0}{M_\infty}$ model if only B varies with temperature, and Common B model if only $\frac{M_0}{M_\infty}$ depends on temperature).

H$_1$: Both parameters $\frac{M_0}{M_\infty}$ and B depend on temperature (individual parameters model).

The statistic F_0 was obtained with the ESS of each model, which allowed for a comparison of the models associated with each one of the hypotheses. Lack of fit was tested using a direct comparison method with the help of contrast statistics F_0^{dc} (Fernández et al., 2012).

2.6. Oil characterization

2.6.1. Quality index

The oil obtained from the pretreated and untreated samples was characterized for acid value (IUPAC 2.201, 1992), peroxide (AOCS Cd 8, AOCS, 1998) and fatty acid composition (determined by gas

chromatography, Izquierdo et al., 2002). Determinations were performed in duplicate. The experimental data were analyzed by analysis of variance (ANOVA) using the Infostat software package, followed by Tukey's test (p < 0.05). Differences were considered significant at p < 0.05.

2.6.2. Tocopherol and canolol concentration

2.6.2.1. Synthesis of canolol standard from syringaldehyde (3,5-dimethoxy-4-ydroxybenzaldehyde). The methodology used in this step was based on the procedures described by Zago et al. (2015) and Shrestha et al. (2012). In a 250 mL flask, syringaldehyde (ALFA AESAR, 98%) (10 mmol), malonic acid (ICN, 98%) (40 mmol) and piperidine (Riedel de Haën, 98%) (1.5 mL, 15.2 mmol) were dissolved in toluene (ABERKON QUIMICA, 99.5%; 42 mL). The reaction medium was maintained under magnetic stirring (200 rpm) and heated to reflux (115 °C) for 4 h. Then the medium was cooled to room temperature and the solvent was evaporated under reduced pressure in a rotary evaporator. In order to remove any traces of piperidine, 20 mL of toluene were added to the precipitate and the solvent was evaporated. This step was repeated twice. The resulting precipitate was dissolved in 20 mL ethyl acetate (ANEDRA, 99.5%) and washed three times with a saturated sodium chloride solution in a separatory funnel. The organic phase was dried (sodium sulfate), filtered, concentrated and finally purified on a silica gel column using a mixture of hexane and ethyl acetate (2:1). Crystallization was applied as an additional step to increase the purity. A saturated solution of the synthesized compound in hexane was prepared at ambient temperature, and crystallization was induced by storing it in the freezer (−23 °C). Crystals (white) were separated from the mother liquor and dried under nitrogen. The purity of the compound was confirmed by NMR spectroscopy: Pure canolol (2,6-dimethoxy-4-vinylphenol) was dissolved in CDCl3 and analyzed using a 300 MHz Avance Bruker Digital NMR spectrometer, operating at 300 MHz for ^{1}H and 75.5 MHz for ^{13}C. Assignments of both proton and carbon resonances, identification and structure characterization of products were performed using 2D NMR spectrum analysis, homonuclear ^{1}H and heteronuclear ^{1}H/^{13}C experiments. Chemical shifts were referenced using residual internal CDCl$_3$ signals at 7.26 and 77.0 ppm for ^{1}H and ^{13}C, respectively. ^{1}H NMR (300 MHz, CDCl3) δ (ppm) = 3.91 (s, 6H, Me), 5.15 (d, J = 10.7 Hz, 1H, H7), 5.52 (s, 1H, OH), 5.60 (dd, J = 17.5, 0.5 Hz, 1H, H7), 6.62 (dd, J = 17.5, 10.8 Hz, 1H, H6), 6.65 (s, 2H, H4). ^{13}C NMR (75.5 MHz, CDCl3) δ = 56.27 (Me), 103.05 (2C, C3 and C5), 111.84 (C8), 129.21 (C4), 134.83 (C1), 136.83 (C7), 147.08 (2C, C2 and C6) ppm.

The purity of the compound was also confirmed by GC/MS: Synthetized canolol was analyzed on a Thermo Quest Trace 2000 CG model gas chromatograph (USA) with a 30 m. 0.32 mm i.d., 0.25 μm film thickness, ZB-5HT Inferno capillary column (5% phenyl-95% dimethylpolysiloxane, 30 m, 0.25 mm I.D., 0.25 μm film thickness). Helium was used as carrier gas (1 mL min^{-1}), and the injection port was set at 150 °C in split mode (split ratio: 1:33, split flow: 33 mL min^{-1}). The detection was carried out with a Finnigan Polaris Ion trap mass spectrometer (USA) with transfer line at 210 °C and ion source at 200 °C. The oven temperature was maintained at 60 °C for 2 min, then programmed at 10 °C min^{-1} up to 230 °C for 10 min. The GC/MS spectrum is shown in Fig. 1.

Canolol (m/z 180, parent molecule) fragments at 165, 137, 123 and 94 reported by Morley et al. (2013) are comparable to the values obtained in the present study (Fig. 1).

2.6.2.2. Tocopherol and canolol by HPLC. Tocopherol and canolol concentration in the oil was determined by normal-phase ultra high-performance liquid chromatography (UHPLC) following a modified procedure from Wakamatsu et al. (2005). A Dionex
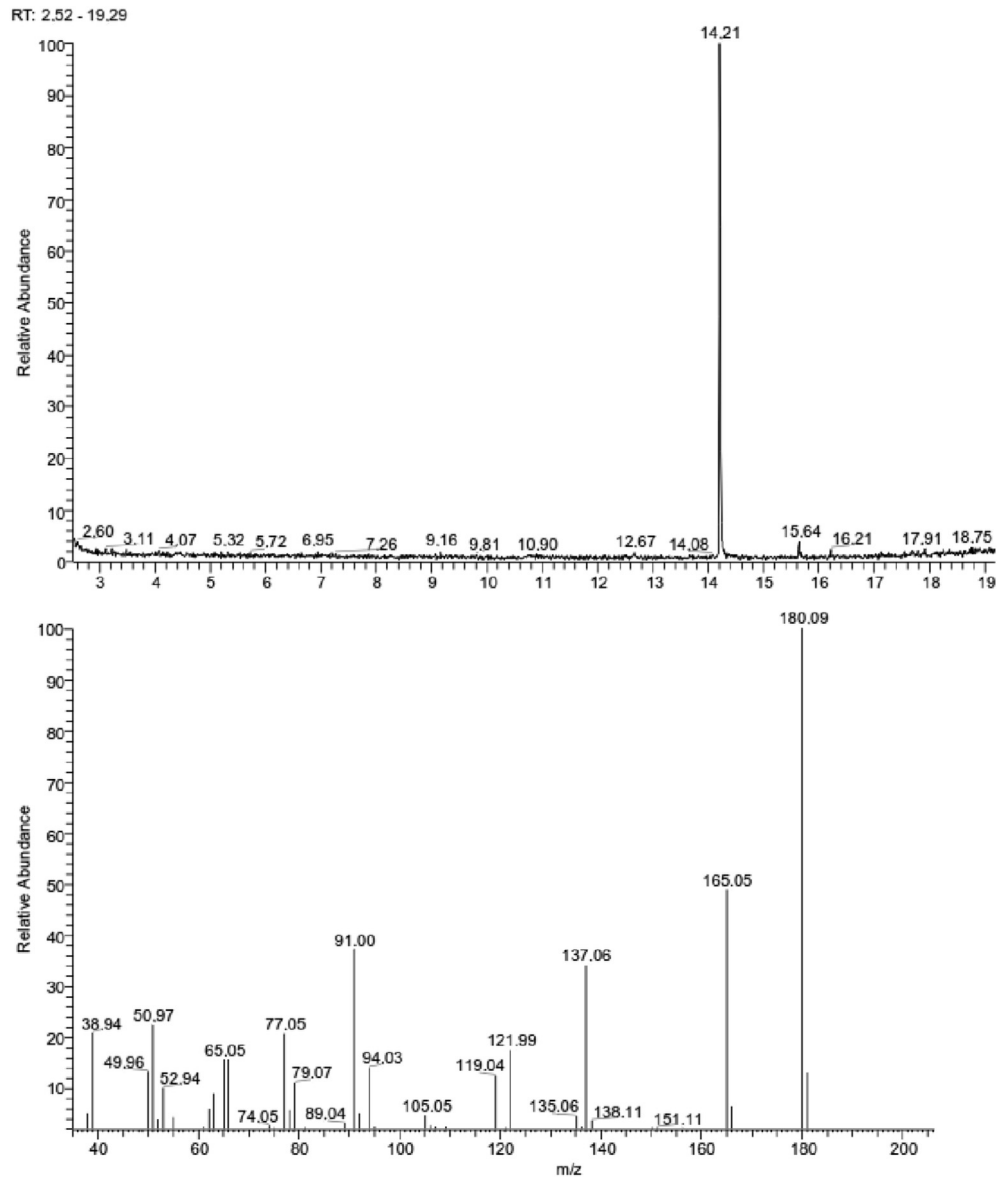
Fig. 1. GC/MS spectrum of synthetized canolol.

Ultimate 3000 chromatograph (Thermo Scientific, Germany) with fluorescence detector (Agilent, 1100 Series Fluorescence Detector G1321A, Palo Alto, CA, USA) with excitation/emission wavelengths of 290/330 nm, equipped with a Luna NH_2 100 column (250 × 4.6 mm i.d., particle size 5 μm; Phenomenex) was used. Hexane:isopropanol (96:4 v/v) was used as mobile phase, with a column flow of 2 mL/min. Levels of α-tocopherol were quantified according to AOCS standard method Ce 8-89 Note 3 (AOCS, 1998), while canolol was quantified on the basis of the calibration curve using the synthesized standard. All determinations were performed in duplicate. Results were analyzed by ANOVA followed by Tukey's test ($p < 0.05$) using the Infostat software.

3. Results and discussion

3.1. Seed characterization

Proximate composition of the canola seeds is shown in Table 1. All the results are expressed on dry basis (d.b.). Oil content was

Table 1
Proximate composition of canola seeds on dry basis (% db).

Proximate composition of canola seeds	
Moisture (% db)	8.5 ± 0.1
Oil (% db)	46.3 ± 0.3
NFE (% db)	24.9.0 ± 0.8
Protein (% db)	20.3 ± 0.1
Crude Fiber (% db)	5.0 ± 0.1
Ash (%db)	3.5 ± 0.1

within the range reported in the literature for this species (33–55%, Windauer and Ploschuk, 2006), while the protein content obtained experimentally (approximately 20% d.b.) corresponded to 37.8% db in the defatted meal, which is similar to the value reported by Downey and Bell (1990) for defatted canola meal (38.7% db). The crude fiber content in the defatted meal (9.3% db) was lower than that observed by Downey and J. M. Bell (11.8% db). In turn, the ash content was similar to that reported by Fernández et al. (2012) for canola seeds of the Barrel variety (3.5% db), and the *NFE* obtained

corresponding to 46.3% of the meal was higher than that reported by Cruz-Suarez et al. (2001) for commercial canola meal (35% db).

3.2. Oil extraction kinetics

Oil yields as a function of time for untreated and pretreated ground canola seeds at 298, 313, 323 and 333 K are shown in Fig. 2A–D.

In general, for each temperature and time, a significant yield increase was achieved by effect of the pretreatment (maximum increase of 41% compared to the untreated sample at 298 K and 7200 s).

3.3. Models

3.3.1. Modified diffusion model

The model was adjusted considering the first eight terms of the series (because when more terms were added to the series, the adjustment parameters remained unchanged) and that the washing process occurs in a short time with t_0 tending to zero (Fernández et al., 2012). In the statistical contrast analysis, F_0 showed a temperature-dependence of parameter B, both for the pretreated and untreated samples ($F_0 = 0.7$ and $F_0 = 0.25$, respectively, both being lower than $F_c = 2.87$), whereas no influence of temperature was detected for M_0/M_∞ for the untreated and pretreated sample ($F_0 = 18.14$ and $F_0 = 3.66$, respectively, both higher

than $F_c = 2.87$). The parameters of the fitted models and R^2_{adj} are shown in Table 2. Since the F_0^{dc} calculated by comparing the experimental data with the data predicted by the common M_0/M_∞ model was 0.017 for the untreated sample and 0.015 for the pretreated sample, being lower than the corresponding critical value at a confidence level of 95% ($F_c^{dc} = 1.88$), lack of fit was not significant, indicating that this model is adequate. Therefore, the model selected to represent oil extraction from ground canola seeds was the common M_0/M_∞ model.

The M_0/M_∞ value calculated by the model indicates that a significant amount of oil is removed during the washing step, for both the pretreated and untreated samples, and the values were similar to those observed by Fernández et al. (2012) for untreated canola seeds of the Barrel variety (0.24) and by Zárate et al. (2015) for untreated canola seeds (0.27). The washing fraction obtained for the sample pretreated by microwave was slightly larger than the value obtained for the untreated sample, with an increase of 8%. This could be associated with a modification in cell structure and a decrease in moisture content (Uquiche et al., 2008; Azadmard-Damirchi et al., 2010). Zárate et al. (2015) reported a 100% increase in the M_0/M_∞ value due to the effect of the hydrothermal pretreatment on canola seeds.

The effective diffusion coefficients (D_{eff}) obtained for the average particle radius of the extreme values ($R = 3.55\ 10{\text -}4$ m) are presented in Table 3.

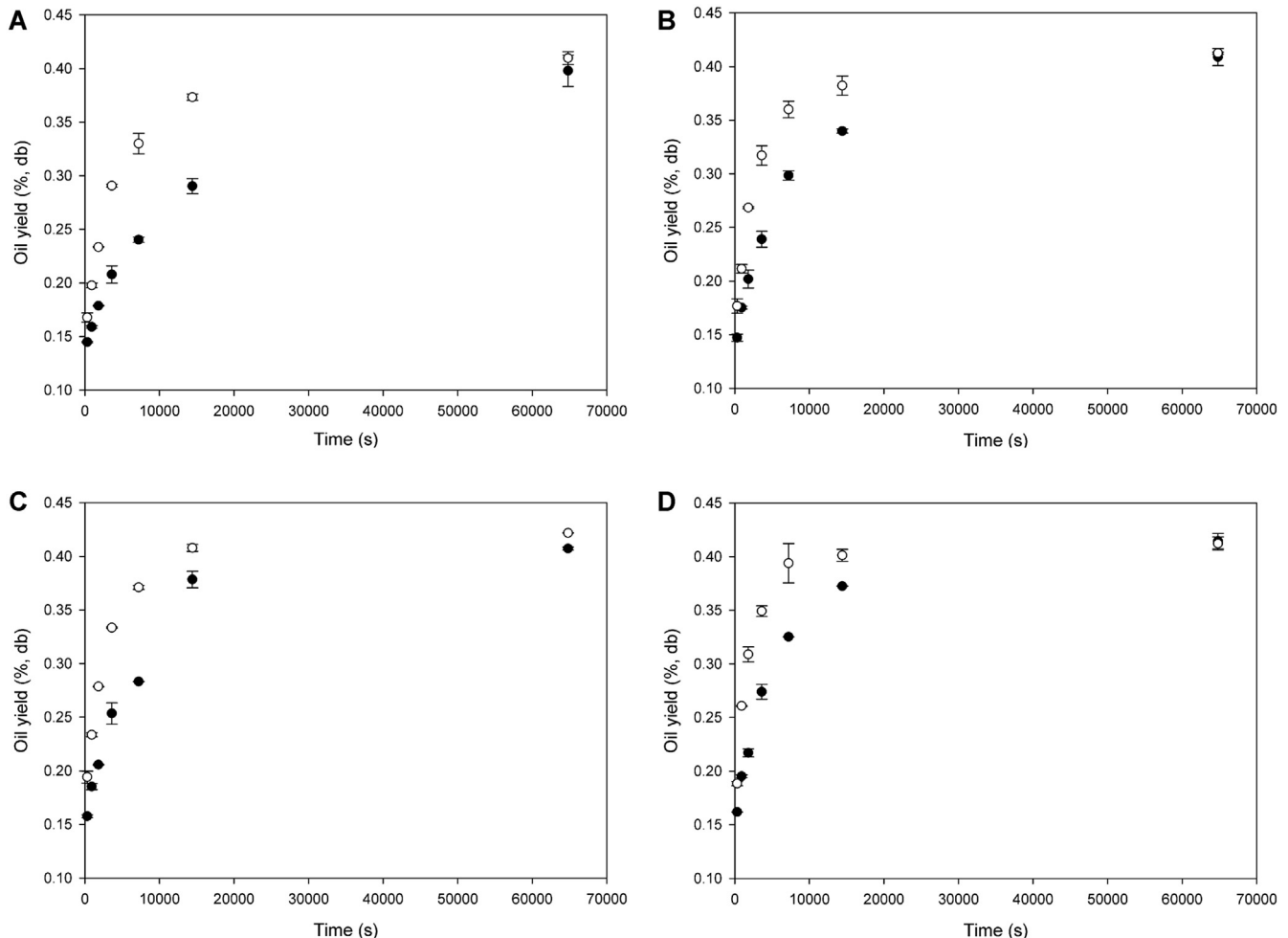D_{eff} values obtained for the untreated sample were lower than

Fig. 2. Oil yield (%w/w db) of pretreated (○) and untreated (●) canola seeds at (A): 298 K; (B): 313 K; (C): 323 K and (D): 313 K extraction temperatures.

Table 2
Coefficients of the models adjusted for untreated and microwave-pretreated samples.

Model	T(K)	Untreated canola			Microwave-pretreated canola		
		M_0/M_∞	$B \times 10^5$	R^2_{adj}	M_0/M_∞	$B \times 10^5$	R^2_{adj}
Global	298–333	0.25 ± 0.02	7.17 ± 0.83	0.952	0.27 ± 0.03	18.50 ± 2.17	0.945
Individual parameters	298	0.26 ± 0.02	4.00 ± 0.02	0.993	0.26 ± 0.02	12.00 ± 0.83	0.996
	313	0.23 ± 0.01	7.33 ± 0.02	0.997	0.25 ± 0.03	17.50 ± 2.00	0.988
	323	0.24 ± 0.04	9.00 ± 1.50	0.977	0.28 ± 0.01	19.50 ± 1.00	0.997
	333	0.24 ± 0.02	10.50 ± 0.67	0.960	0.23 ± 0.03	34.16 ± 3.00	0.993
Common M_0/M_∞	298	0.25	4.00 ± 0.17	0.993	0.27	11.67 ± 0.50	0.996
	313		7.00 ± 0.33	0.997		16.83 ± 1.17	0.990
	323		8.67 ± 0.83	0.981		19.83 ± 0.67	0.997
	333		10.17 ± 0.33	0.997		31.00 ± 1.67	0.992
Common B	298	0.17 ± 0.04	7.17	0.932	0.16 ± 0.04	18.5	0.966
	313	0.24 ± 0.01		0.998	0.24 ± 0.02		0.990
	323	0.27 ± 0.03		0.974	0.29 ± 0.01		0.998
	333	0.31 ± 0.02		0.977	0.38 ± 0.04		0.949

Table 3
Effective diffusion coefficients.

$D_{eff} \times 10^{13}$ (m^{2}s^{-1})				
Temperature (K)	298	313	323	333
Untreated	5.11 ± 0.42	8.94 ± 0.42	11.10 ± 1.91	13.00 ± 0.85
Pretreated	14.90 ± 1,06	21.5 ± 2.55	25.30 ± 1.28	39.60 ± 3.83

those reported by Zárate et al. (2015) $(3.15 \times 10^{-12} -7.44 \times 10^{-12} m^2 s^{-1})$ and Fernández et al. (2012) $(1.3 \times 10^{-12} - 3.0 \times 10^{-12} m^2 s^{-1})$ for canola oil extracted with hexane from untreated seeds, indicating that a variation in the coefficient occurs within the same species. For all the temperatures studied, the diffusion coefficients corresponding to the microwave-pretreated sample were higher than those obtained for the untreated sample in a 2:1 proportion, which is similar to the trend observed by Zárate et al. (2015) for hydrothermal pretreatment.

3.3.2. Temperature dependence

Temperature dependence of D_{eff} is generally described by the Arrhenius equation:

$$D_{eff} = D_0 e^{-\frac{\Delta E}{R_g T}} \tag{5}$$

where D_0 (m^{2}s^{-1}) is the pre-exponential constant, ΔE (kJmol^{-1}) is the activation energy, R_g is the gas constant (kJmol^{-1}·K^{-1}) and T is temperature (K). The linearization of this expression is shown in (6) for the microwave-pretreated sample and (7) for the untreated sample. Graphically in Fig. 3:
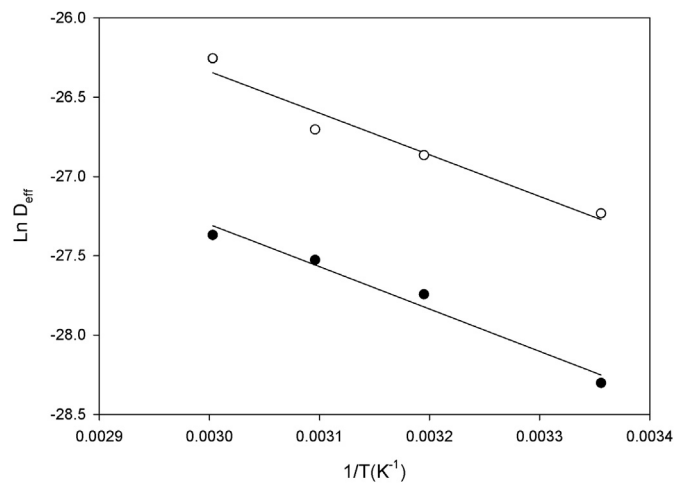

Fig. 3. Linearization of the Arrhenius equation. (○) Pretreated, (●) Untreated sample.

The R^2_{adj} and p values indicate that the Arrhenius equation adequately describes the temperature-dependence of D_{eff}. The parameter values obtained for the untreated sample were $D_0 = 9.6 \times 10^{-9} m^2 s^{-1}$ and $\Delta E = 21.82$ kJ mol^{-1}. These values are similar to those reported by Fernández et al. (2012) but lower than those obtained by Zárate et al. (2015) $(D_0 = 5.25 \times 10^{-6} m^2 s^{-1}$ and $\Delta E = 37.3$ kJ mol$^{-1})$, indicating that both D_0 and ΔE show variability within the species. On the other hand, the parameters obtained for the treated sample were $D_0 = 9.6 \times 10^{-9} m^2 s^{-1}$ and

$$\ln(Deff) = -19.29(\pm 0.99) - \frac{2669(\pm 312)}{T} \quad R^2_{adj} = 0,960 \; p = 0.0026 \tag{6}$$

$$\ln(Deff) = -18.47(\pm 1.29) - \frac{2623(\pm 409)}{T} \quad R^2_{adj} = 0,930 \; p = 0.0235 \tag{7}$$

$\Delta E = 21.82$ kJ mol^{-1}, doubling the value of D_0 with respect to the untreated sample, whereas the ΔE values were similar for both samples. The microwave radiation affects the microstructure of the seeds, increasing the porosity of the sample (Uquiche et al., 2008). The D_0 values obtained are consistent with this effect, since it is dependent on porosity (Fillion et al., 2002).

3.3.3. Temperature and time-dependent model

Considering the Arrhenius equation and combining Equations (3)–(5), we obtain Equation (8):

$$\frac{M_t}{M_\infty}(t,T) = 1 - \left(1 - \frac{M_0}{M_\infty}\right)\sum_{n=1}^{\infty}\frac{6}{n^2\pi^2}e^{-n^2\left[\frac{\left(D_0 e^{-\frac{\Delta E}{R_g T}}\right)\cdot\pi^2}{R^2}\right](t-t_0)} \quad (8)$$

For the application of this model, it was assumed that M_0/M_∞ is independent of temperature, and Equation (8) was used considering the first 8 terms (since when more terms were added to the series, the adjustment parameters remained unchanged) to fit the experimental data. The adjustment results are presented in Fig. 4 and Table 4:

The R^2_{adj} and p values indicate the high correspondence between the experimental data and the model selected. The parameters obtained are also consistent with those reported in Sections 3.3.1 And 3.3.2.
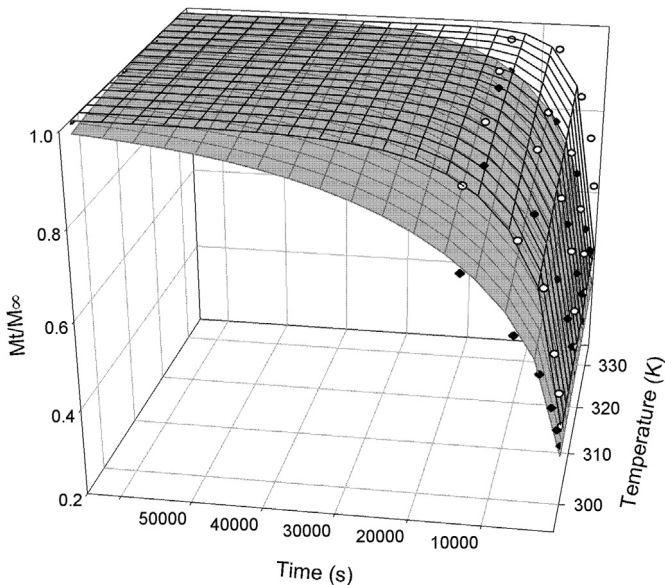
Fig. 4. Relative oil yields for pretreated (○) and untreated (●) samples at different temperatures and adjusted surfaces according to Equation (8) (R^2_{adj} = 0.992; p =<0.0001 and R^2_{adj} = 0.990; p°=°<0.0001, respectively).

Table 4
Adjusted model coefficients, R^2_{adj} and p values for untreated and pretreated samples.

	Untreated	Pretreated
M_0/M_∞	0.24 ± 0.01	0.26 ± 0.01
$D_0 \times 10^9$	3.10 ± 2.57	9.41 ± 6.36
ΔE	21.37 ± 2.20	21.70 ± 1.78
R^2_{adj}	0.990	0.992
p	<0.0001	<0.0001

Table 5
Quality indices, acid composition, tocopherol content and canolol content for untreated and microwave-pretreated canola samples.

Determination	Untreated	Pretreated
C16:0 (%)	4.34[a] ± 0.39	4.25[a] ± 0.38
C18:0 (%)	1.80[a] ± 0.13	1.82[a] ± 0.13
C18:1 (%)	62.27[a] ± 5.70	62.59[a] ± 5.73
C18:2 (%)	18.94[a] ± 0.36	18.70[a] ± 0.35
C18:3 (%)	8.00[a] ± 0.56	7.98[a] ± 0.56
Free acidity (% oleic)	0.89[a] ± 0.04	0.75[a] ± 0.01
P.V (meq kg^{-1})	1.20[a] ± 0.10	0.97[a] ± 0.01
TTC (µg g oil^{-1})	952.6[a] ± 9.1	965.4[a] ± 14.9
α-TC (µg g oil^{-1})	330.1[a] ± 3.8	327.9[a] ± 5.4
β-TC (µg g oil^{-1})	33.2[a] ± 0.9	42.7[b] ± 0.9
γ-TC (µg g oil^{-1})	580.3[a] ± 5.5	563.1[a] ± 4.9
δ-TC (µg g oil^{-1})	9.0[a] ± 1.1	31.7[b] ± 3.0
Canolol (µg g oil^{-1})	27.2[a] ± 1.1	167.9[b] ± 6.2

Means followed by the same letter in the same line are not significantly different (Tukey's test, p > 0.05). db, dry basis; C16:0, palmitic acid; C18:0, stearic acid; C18:1, oleic acid; C18:2, linoleic acid; C18:3, linolenic acid; AV, acidity value in % oleic; PV, peroxide value in meq peroxides kg oil^{-1}; TTC, total tocopherol; α-TC, α-tocopherols; β-TC, β-tocopherols; γ-TC, γ-tocopherols, δ-TC, δ-tocopherols. All tocopherols content in µg tocopherols g oil^{-1}.

3.4. Analysis of the oil obtained

The quality indices, free acidity, peroxide index, fatty acid profile, tocopherol content and canolol content for the pretreated and untreated canola samples are shown in Table 5.

When comparing the oil extracted from the pretreated sample (Table 5) with the oil from the untreated sample, it can be observed that there were no significant differences in the quality indices evaluated and fatty acid composition, with an acid and peroxide values lower than the maximum limit for refined oils (0.6 mg KOH/g of oil and 10 meO2/kg oil, respectively; CODEX STAN 210-1999, 2015). These results are consistent with those reported by Ramos et al. (2014), who detected no significant differences in the acid value and fatty acid composition of canola oil by the effect of the microwave pretreatment. No significant effect of microwave radiation was observed on total tocopherol content, which was above the range established by the Codex Alimentarium (2015) for crude low erucic acid rapeseed oil (240−670 mg/kg of oil; CODEX STAN 210-1999, 2015), whereas significant increases were observed in the content of β- and δ-tocopherols, which could indicate a greater extraction of these isomers as a result of the microwave pretreatment. In turn, the canolol content in oil increased 517% due to the pretreatment. It has been suggested that canolol is formed by decarboxylation of the sinapic acid during heating of canola seeds (Koski et al., 2003; Wakamatsu et al., 2005; Spielmeyer et al., 2009). The exposure of canola seeds to microwave radiation, which entails a raise in temperature, led to a significant increase in the content of this compound in the oil. The formation of canolol (586 mg/g) in rapeseed by effect of microwave treatment was also reported by Spielmeyer et al. (2009), who roasted the samples for 6 min at 70% power in a domestic microwave oven (800 W).

4. Conclusions

Microwave pretreatment affected the canola oil extraction with hexane, leading to significant yield increases. The modified Fick's diffusion model considered (first eight terms in the series) was suitable for both extraction processes and all the temperatures tested with R^2_{adj}>0.98. At the same time, both for the pretreated and untreated samples, the model allowed calculating the effective diffusion coefficients (D_{eff}), which showed an Arrhenius-type temperature dependence ($R^2 > 0.95$), whereas no temperature

dependence was detected for the parameter M_0/M_∞. The analysis of the model parameters allowed for the development of a modified diffusion model dependent on temperature and time, which could correlate all the data obtained (300–64800 s and 298–333 K) for both pretreated and untreated samples with high correlation coefficients ($R^2_{adj} \geq 0.99$). The model also exhibited an increase in the pre-exponential parameter (D_0) due to the pretreatment, which could show the effect of microwave radiation on the structure of the sample, facilitating the process of oil extraction by solvent, therefore the value of D_{eff} increased because of the pretreatment applied. No significant differences were detected in the quality indexes due to microwave radiation, while the treated samples showed an increase in the content of β- and δ-tocopherols, and of canolol by 517%, yielding an oil of higher quality given the antioxidant and nutritional properties of these compounds.

Acknowledgments

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