Journal of Food Engineering 194 (2017) 1–8

Contents lists available at ScienceDirect

Journal of Food Engineering

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

Diffusion of tocopherols, phospholipids and sugars during oil extraction from sunflower collets using ethanol as solvent

Erica R. Baümler*, María E. Carrín, Amalia A. Carelli

Planta Piloto de Ingeniería Química (PLAPIQUI), Universidad Nacional del Sur-Consejo Nacional de Investigaciones Científicas y Técnicas, 8000 Bahía Blanca, Argentina

ARTICLE INFO

Article history:
Received 17 February 2016
Received in revised form
31 August 2016
Accepted 3 September 2016
Available online 5 September 2016

Keywords:
Ethanol
Sunflower oil
Solvent extraction
Minor compounds
Sugars

ABSTRACT

The ethanolic extraction of minor compounds (phospholipids, tocopherols and sugars) present in sunflower collets was studied at 50 and 60 °C in a batch reactor. The extracted material consisted of two phases: a hexane-soluble fraction, comparable to degummed sunflower oils, and a hexane-insoluble fraction high in phospholipids and sugars. Sugars were extracted in large proportion, especially the indigestible raffinose, increasing the nutritional value of the meal. The sugar reduction percentage in the sunflower collets increased over extraction time to up to 60 and 80% at 50 and 60 °C. The effective diffusion coefficient (D_e) for tocopherols was higher than that for phospholipids ($3.950\ 10^{-9}$ and $2.596\ 10^{-9}$ m^2/s, respectively), both being temperature-independent in the analyzed range. D_e of sugars was $6.50\ 10^{-10}$ and $1.51\ 10^{-9}$ m^2/s for 50 and 60 °C, respectively. Using ethanol as extraction solvent could improve the oil and meal quality, and help obtain a third phospholipid-rich phase after fractionation.

1. Introduction

There is nowadays a strong consumer demand for natural products. Beneficial substances can be extracted from many seeds and vegetables, for example oils for food and cosmetic applications. The solvent usually used when the raw materials are oilseeds is hexane, but due to its toxicity and flammability (Johnson and Lusas, 1983) alcoholic extraction can be used as an alternative, as demonstrated in our previous work (Baümler et al., 2016). In addition, safety, health and environmental concerns have increased the interest in alternatives to hexane to reduce the emissions of volatile organic compounds to the atmosphere as well as potential traces of hexane in edible oils after refining. As a result of this new trend towards greater environmental protection and the development of a green chemistry, hexane should be gradually substituted by alternative solvents that are recognized as economically viable and environmentally safer (Li et al., 2014). Ethanol has been widely investigated as extraction solvent (Rao and Arnold, 1956, 1957; Rittner, 1992; Ferreira-Dias et al., 2003; Baümler et al., 2016), being recognized as non-toxic and with less handling risks than hexane. The use of this alcohol as extraction solvent also avoids eventual toxicity problems of meals for animal feedstuff (Ferreira-Dias et al., 2003). On the other hand, it has been reported that the solubility of lipids in ethanol is drastically affected by the extraction temperature (Rao and Arnold, 1956, 1957).

Due to the lower selectivity of ethanol towards triglycerides, other compounds such as phosphatides, polyphenols, pigments and soluble sugars are extracted jointly during the extraction process (Hron et al., 1982, 1994; Sineiro et al., 1996; Baümler et al., 2016). This extraction of compounds different from triglycerides could lead to complications in the refining processes, due to the presence of larger amounts of these compounds than that obtained with the conventional extraction process using hexane as solvent. Knowledge about the extraction of these compounds is a very important point to be taken into account to determine the quality of the extracted oil and the requirements of the subsequents purification steps. In the literature there are reports that analyze the extraction of minor compounds when n-hexane is used as solvent (Baümler et al., 2010, 2011); however, little is known about the extraction of these compounds when ethanol is used instead of hexane.

Minor oil components as well as sugars are extracted when ethanol is used (Baümler et al., 2016). The aim of this work was to complete our study about the use of ethanol as solvent in the oil extraction from sunflower collets, considering the extraction kinetics of phospholipids, tocopherols and sugars. Model equations

* Corresponding author. PLAPIQUI (UNS-CONICET), Camino La Carrindanga km. 7, CC 717, 8000 Bahía Blanca, Argentina.
E-mail address: ebaumler@plapiqui.edu.ar (E.R. Baümler).

http://dx.doi.org/10.1016/j.jfoodeng.2016.09.003
0260-8774/

Abbreviations

d.b.	dry basis
D_e	effective diffusion (m^2/s)
e.m.	extracted material
M_t/M_{inf}	ratio of mass extracted at time t to mass extracted at infinite time
PA	phosphatidic acid
PC	phosphatidylcholine
PE	phosphatidylethanolamine
PI	phosphatidylinositol
t	time (s)
Λ_n	roots of $J_0(R\,\Lambda_n) = 0$
J_0	Bessel function of the first kind of order zero
ESS	Extra sum of squares

were proposed to explain the behavior of these compounds during oil extraction, and effective diffusion coefficients are reported.

Sunflower waxes are other minor components that are extracted with sunflower oil and have to be removed during the refining processes. However, since the wax composition of the material extracted with ethanol was much smaller than that obtained with hexane (Baümler et al., 2016), it was not considered necessary to study the wax extraction kinetics.

2. Materials and methods

2.1. Raw material

Experimental determinations were conducted with sunflower expanded material (known as collets), kindly provided by a local factory. The sample characterization was performed in a previous work (Baümler et al., 2016) giving the following results: collets dimension: length = 49.17 ± 7.57 mm; radius = 9.56 ± 0.34 mm; initial moisture content = 6.00± 0.59% d.b.; oil content = 22.84± 0.55% d.b.; maximal ethanolic extraction = 32.2 ± 1.3% d.b.; total sugar content = 44.56 ± 4.60 mg/g d.b.. The sugar profile exhibited a high relative percentage of sucrose (51.1± 1.8%) and raffinose (35.7 ± 0.9), and smaller amounts of glucose (4.1± 0.7%), rhamnose (3.2± 0.5%), galactose (2.1± 0.7%), fructose (2.1± 0.5%) and arabinose (1.7± 0.4%) (Baümler et al., 2016).

2.2. Solvent extraction experiments

The minor components were determined in samples of extracted material obtained from ethanolic solvent extraction experiments carried out in a previous work (Baümler et al., 2016). These extraction experiments were performed in a similar way to that described in Baümler et al. (2010), working in a batch system at 50 and 60 °C with extraction times from 0 to 960 min (considered as infinite time). All the extractions were carried out in triplicate.

2.3. Analyses of minor components

The extracted material was fractionated into hexane-soluble material and other compounds (hexane-insoluble fraction) by phase separation with n-hexane. Tocopherol content was determined in the hexane-soluble fraction while phospholipids were quantified in both fractions. The total extracted amount was considered for obtaining the phospholipid extraction kinetic curves.

Tocopherol content was determined using AOCS method Ce 8-89 (AOCS, 2009) with a Waters e2695 HPLC (Waters Associates, Milford, MA, USA) equipped with a Nucleosil Si-100A column (250 mm length, 4.6 mm i.d., 5 μm particle size, Phenomenex, USA). Determinations were performed in triplicate.

Quantitative determination of phospholipids in the hexane-soluble fraction was carried out by SPE-HPLC-UV following the method proposed by Carelli et al. (1997). A Waters 600E HPLC system (Waters Associates, Milford, MA, USA) and a Lichrosorb SI-60 column (250 × 4 mm, 5 μm particle size, Merck, Darmstadt, Germany) were used. The phospholipid determination in the hexane-insoluble fraction was carried out following AOCS method Ja-4-46 for lecithin analysis (AOCS, 2009). Determinations were performed in duplicate.

Sugar content of sunflower collets after solvent extraction was determined by an exhaustive extraction followed by HPLC-IR according to the method described in a previous work (Baümler et al., 2016). A Waters e2695 HPLC (Waters Associates, Milford, MA, USA) equipped with a Rezex ROA organic acid column (300 × 7.8 mm, 8 μm particle size, Phenomenex, USA) and a refraction index detector was used. Determinations were performed in quadruplicate.

2.4. Mathematical modeling

Modeling of the extraction kinetics of minor components was performed following the theory used in our previous work to determine the oil extraction kinetics using ethanol as solvent (Baümler et al., 2016), a theory that was proposed by various authors (Meziane et al., 2006; Carrín and Crapiste, 2008; Meziane and Kadi, 2008; Baümler et al., 2010; Pérez et al., 2011; Saxena et al., 2011). The dissolution rate of the extractable material into the extraction solution for long times was described by the following equation (Pérez et al., 2011):

$$M_t \Big/ M_{inf} = 1 - A\,\exp(-B\,t) \tag{1}$$

where M_t and M_{inf} represent the mass of extracted material (phospholipids, tocopherols, sugar) that diffuses at time t and infinite. The exponential coefficient is given by $B = D_e\lambda_1^2$, (λ_1 is the first root of the Bessel function of the first kind of order zero, $J_0(R\lambda_1) = 0$, and R is the average radius (m) (Crank, 1975)). The pre-exponential A is associated with the average value of the material extracted in the washing step (M_0, kg solute/kg dry defatted meal) and it is given by the following equation:

$$A = \left(1 - \frac{M_0}{M_{inf}}\right) A_1\,\exp(B\,t_0) \tag{2}$$

where M_0 represents the mass of extractable material that is extracted in the washing step at time t_0, and A_1 is the model-fitting parameter (Crank, 1975). In cylindrical particle geometry its expression is:

$$A_1 = \frac{4}{R^2\lambda_1^2} \tag{3}$$

The mathematical model represented by Eq. (1) was applied to fit the experimental extraction data of phospholipids, tocopherols and sugar from sunflower collets at different temperatures using nonlinear regression (Systat Software, 2008).

2.5. Statistical analysis

The statistical analysis was carried out by analysis of variance

using the Infostat software (Di Rienzo et al., 2011). Fisher's LSD method was used to compare pairs of treatment means with a significance level of $p \leq 0.05$. The number of replicates performed (n) was stated above.

Fitting regression models for different solvents and temperatures were compared through their parameters using a procedure based on the principle of "Extra Sum of Squares" (ESS) and "conditional error", with a significance level of 95%, a method that was described in a previous work (Baümler et al., 2016). The null hypothesis (H_0) and the alternative hypothesis (H_1) proposed were: H_0, the model parameters A and/or B do not depend on temperature or solvent (*Global model* if both are consistent with temperature or solvent -considers all the temperature or solvent experimental data, respectively-, *common A model* when only B varies with temperature or solvent, and *common B model* when only A depends on temperature or solvent), and H_1: model parameters A and B depend on temperature or solvent (individual parameter model). In order to test the null and alternative hypotheses by parameter comparison, contrast statistics (F_o) was compared with the corresponding critical value (F_c).

3. Results and discussion

The experimental data of tocopherol and phospholipid extraction and the fitting model selected for both components are shown in Fig. 1. To achieve 80% of tocopherol extraction about 90 min were sufficient, whereas virtually double that time was needed to reach the same level of phospholipid extraction. When analyzing the solvent extraction of major and minor compounds of sunflower collets using n-hexane, Baümler et al. (2010), determined that the percentages of phospholipid extraction at 150 min were 70.4% at 50 °C and 96.2% at 60 °C, and tocopherols were almost completely extracted after 60 and 30 min at 50 °C and 60 °C, respectively. It was also determined that the rate of mass transfer increased with temperature, being phospholipids more difficult to extract than tocopherols.

The comparison of the different A and B model with the common A, common B and global models was carried out for each compound (tocopherols and phospholipids). The coefficients obtained from the models and the results of the comparison of the non-linear models carried out by means of ESS are shown in Table 1. In the phospholipid analysis, no significant differences were found ($F_o < F_c$), demonstrating that both parameters A and B do not depend on temperature. Thus, the global model was selected to represent the kinetics of phospholipid extraction. As the temperature increase did not produce significant differences in the extraction rate, a single diffusion coefficient was determined from the model. The effective diffusion value, calculated from Eq. (1), was $2.596\ 10^{-9}$ m^2/s.

When tocopherols were analyzed, the comparison of the different A and B model with the global and common B models did not show significant differences ($F_o < F_c$). On the other hand, the comparison of the different A and B model with the common A model did show significant differences ($F_o > F_c$), demonstrating the existence of an interaction between the variables involved (temperature and time), whose effect is not represented by the global model. As increasing temperature did not cause significant differences in parameter B and the interaction between temperature and time cannot be omitted, the model selected to represent tocopherol extraction was the common B model. Thus, a single diffusion coefficient was obtained, with a value of $3.950\ 10^{-9}$ m^2/s. Parameter A involves the amount of tocopherols extracted in the washing step (M_0), and it turned out to be temperature-dependent. Similar results were reported by Fernández et al. (2012), who analyzed the kinetic extraction of canola oil using technical grade hexane at 25, 40, 50 and 60 °C. The tocopherol yield at infinite time was not appreciably affected by extraction temperature ($6.29\ 10^{-2} \pm 4.73\ 10^{-3}$ and $6.46\ 10^{-2} \pm 4.79\ 10^{-3}$ g tocopherols/kg dry defatted meal at 50 and 60 °C, respectively, $p = 0.9276$).

Phospholipids were mainly concentrated in the hexane-insoluble fraction, with the partition coefficients (defined as the mass ratio of the compound in the hexane-insoluble fraction to that in the hexane-soluble fraction) being above 2 near the beginning of extraction and reaching values of up to 20 at infinite time. The total mass extracted at infinite time was larger at a higher temperature (7.74 ± 0.73 and 17.15 ± 1.50 g phospholipids/kg dry defatted meal at 50 and 60 °C, respectively, $p = 0.0154$), showing that the final yield was affected by the operating conditions. The material obtained by exhaustive extraction using ethanol as solvent (Baümler et al., 2016) showed a higher phospholipid content ($0.93 \pm 0.32\ 10^{-2}$ g phospholipids/kg dry defatted meal) compared with the material extracted using n-hexane ($0.58 \pm 6.68\ 10^{-2}$ g phospholipids/kg dry defatted meal), and the phospholipids were more concentrated in phosphatidylcholine (PC).

Kinetic results were compared with published data for the extraction of phospholipids and tocopherols from sunflower collets using n-hexane (Fig. 2) (Baümler et al., 2010). As it can be observed in the figure, phospholipid extraction at 60 °C and tocopherol extraction at 50 and 60 °C using n-hexane as solvent occurred faster. Non-linear regression results were compared by means of ESS (Tables 2 and 3) to confirm this observation statistically. Taking into account the phospholipid extraction at 50 °C, the comparison of the different A and B model with the global and common B models did not show significant differences ($F_o < F_c$). On the other

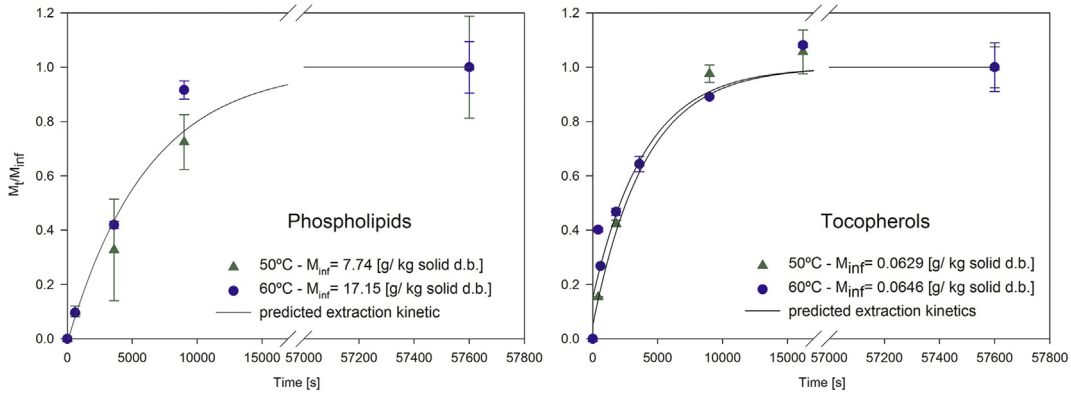

Fig. 1. Experimental (bullets) and predicted (lines) extraction kinetics of phospholipids and tocopherols at 50 °C and 60 °C using ethanol as solvent.

Table 1
Coefficients obtained from the different models proposed for the extraction kinetics of phospholipids, tocopherols and sugars using ethanol as solvent.

Fitting description	Coefficients	Temperature (°C)		F_o	F_c
		50	60		
Phospholipids					
Different A and B	$A \times 10^1$	10.530 ± 1.063	9.947 ± 0.515	–	–
	$B \times 10^4$	2.048 ± 0.447	1.293 ± 0.165		
	R^2	0.975	0.992		
Common A	$A \times 10^1$	10.220	10.220	0.269	7.709
	$B \times 10^4$	1.973 ± 0.281	1.349 ± 0.109		
	R^2	0.974	0.991		
Common B	$A \times 10^1$	9.833 ± 0.775	10.600 ± 0.591	3.653	7.709
	$B \times 10^4$	1.643	1.643		
	R^2	0.961	0.974		
Global (Common A and B)	$A \times 10^1$	10.220 ± 0.675		2.223	6.944
	$B \times 10^4$	1.643 ± 0.247			
	R^2	0.964			
Tocopherols					
Different A and B	$A \times 10^1$	9.729 ± 0.516	7.518 ± 0.621	–	–
	$B \times 10^4$	3.001 ± 0.334	2.160 ± 0.489		
	R^2	0.990	0.959		
Common A	$A \times 10^1$	8.326	8.326	6.563	5.117
	$B \times 10^4$	2.439 ± 0.351	2.571 ± 0.415		
	R^2	0.969	0.945		
Common B	$A \times 10^1$	9.144 ± 0.405	7.793 ± 0.459	2.178	5.117
	$B \times 10^4$	2.500	2.500		
	R^2	0.983	0.955		
Global (Common A and B)	$A \times 10^1$	8.326 ± 0.516		3.327	4.256
	$B \times 10^4$	2.500 ± 0.379			
	R^2	0.958			
Sugar					
Different A and B	$A \times 10^1$	8.725 ± 0.2796	8.644 ± 0.6817	–	–
	$B \times 10^5$	4.283 ± 0.5840	9.859 ± 2.798		
	R^2	0.984	0.937		
Common A	$A \times 10^1$	8.533	8.533	0.217	5.318
	$B \times 10^5$	4.112 ± 0.4711	9.553 ± 2.085		
	R^2	0.982	0.936		
Common B	$A \times 10^1$	9.054 ± 0.3700	8.012 ± 0.5978	6.044	5.318
	$B \times 10^5$	5.908	5.908		
	R^2	0.958	0.902		
Global (Common A and B)	$A \times 10^1$	8.533 ± 0.4536		4.564	4.459
	$B \times 10^5$	5.908 ± 1.258			
	R^2	0.914			

hand, the comparison of the different A and B model with the common A model showed significant differences ($F_o > F_c$), demonstrating the existence of an interaction between the variables involved, whose effect is not represented by the global model (Table 2). Thus it was confirmed that A, and therefore M_0, depend on the solvent used for the selected operating conditions.

For the extraction of phospholipids at 60 °C and of tocopherols at 50 and 60 °C, the comparison of the different A and B model with the common A, common B and global models did not show significant differences ($F_o > F_c$) (Tables 2 and 3), demonstrating that in such cases both parameters A and B depend on the solvent used, as it was possible to observe in the experimental results (Fig. 2).

Phospholipids are the major non-neutral component in sunflower oil, being the most abundant class of lipids found in cell membranes. Phospholipids are well known messengers involved in developmental and stress responses mediating intracellular signaling (Regente et al., 2008). Cytosolic, mitochondrial and vacuolar membranes are composed of phospholipids, among which phosphatidylcholine (PC), phosphatidylethanolamine (PE), phosphatidic acid (PA) and phosphatidylinositol (PI) are the most prominent species (Salas et al., 2006; Regente et al., 2008). Most of them are hydratable and can be removed from the crude oil during the degumming process (Carelli et al., 1997). The experimental extraction results for each molecular species of phospholipids (PE, PA, PI and PC) are shown in Fig. 3. At both analyzed temperatures, PC (main component of the phospholipids in the extracted material (Baümler et al., 2016)) and PE presented the highest extraction rate, with PC being the one that produced the greatest impact on the total extraction of phospholipids. At infinite time the phospholipid content in the hexane-soluble fraction was 2.30 ± 0.04 and 8.42 ± 0.13 g phospholipids/kg hexane-soluble fraction at 50 and 60 °C, respectively ($p = 0.0002$). As only the kinetic data (M_t/M_{inf}) are reported in the work by Baümler et al. (2010), the mass of phospholipids extracted from sunflower collets in a batch system using n-hexane as solvent at infinite time was determined using the original data of the hexane extraction. When hexane was used, the phospholipid content was 6.41 ± 0.55 and 8.79 ± 0.17 g phospholipids/kg oil at 50 and 60 °C, respectively. This allowed us to confirm that the phospholipid content obtained at 50 °C in ethanolic extraction for the hexane-soluble fraction was lower than that obtained by hexane extraction, and similar to that of a degummed sunflower oil (Brevedan et al., 2000), which might reduce refining costs.

As stated above, phospholipids were mainly concentrated in the hexane-insoluble fraction, with the mass extracted at infinite time being 75.32 ± 7.59 and 94.02 ± 12.74 g phospholipids/kg hexane-insoluble fraction at 50 and 60 °C, respectively ($p = 0.2173$). This fact offers the possibility of obtaining, by simple fractionation, sunflower oil and a solid (from the hexane-insoluble phase obtained after fractionation of the extracted material) in which phospholipids are concentrated. This shows an interesting advantage of ethanol over hexane, because the traditional extraction with

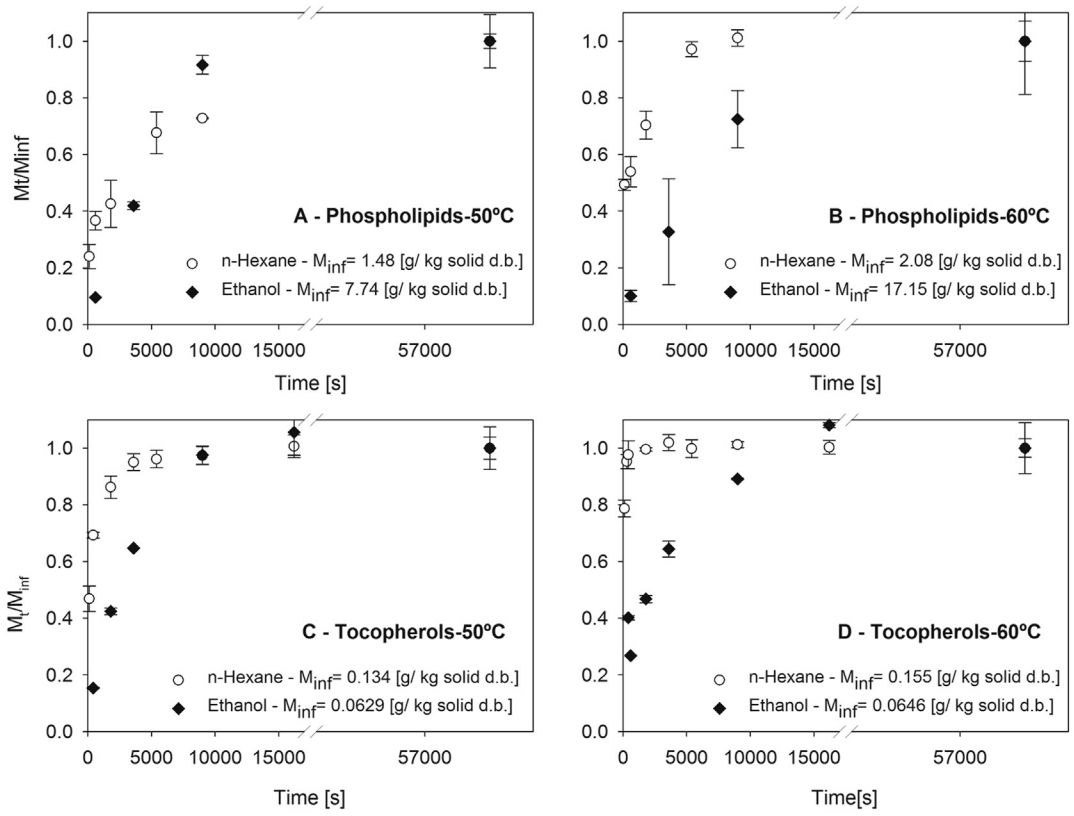

Fig. 2. Comparison of the extraction kinetics of phospholipids at 50 °C (A) and 60 °C (B) and of tocopherols at 50 °C (C) and 60 °C (D) using ethanol (this work) with the reported data for phospholipid and tocopherol extraction using n-hexane (Baümler et al., 2010).

Table 2
Comparison of the coefficients obtained from the different models proposed for the fitting of phospholipid extraction kinetics when ethanol and n-hexane were used as solvents. Results of the ESS.

Fitting description	Coefficients	Solvent		F_o	F_c
		Ethanol	n-hexane		
50 °C					
Different A and B	$A \times 10^1$	10.220 ± 0.675	7.267 ± 0.304	–	–
	$B \times 10^4$	1.643 ± 0.247	1.289 ± 0.167		
	R^2	0.964	0.982		
Common A	$A \times 10^1$	8.193	8.193	8.753	5.987
	$B \times 10^4$	1.499 ± 0.501	1.604 ± 0.238		
	R^2	0.906	0.943		
Common B	$A \times 10^1$	9.650 ± 0.837	7.512 ± 0.284	1.236	5.987
	$B \times 10^4$	1.549	1.549		
	R^2	0.953	0.973		
Global (Common A and B)	$A \times 10^1$	8.193 ± 0.609		4.419	5.143
	$B \times 10^4$	1.549 ± 0.310			
	R^2	0.921			
60 °C					
Different A and B	$A \times 10^1$	10.220 ± 0.675	5.583 ± 0.288	–	–
	$B \times 10^4$	1.643 ± 0.247	3.996 ± 0.571		
	R^2	0.964	0.987		
Common A	$A \times 10^1$	6.499	6.499	88.009	5.987
	$B \times 10^4$	0.596 ± 0.461	5.081 ± 0.849		
	R^2	0.778	0.954		
Common B	$A \times 10^1$	10.770 ± 0.716	4.552 ± 0.571	13.714	5.987
	$B \times 10^4$	1.748	1.748		
	R^2	0.964	0.857		
Global (Common A and B)	$A \times 10^1$	6.499 ± 1.375		137.612	5.143
	$B \times 10^4$	1.748 ± 0.967			
	R^2	0.606			

hexane leaves about 50% of total phospholipids in the spent seed matrix, while the other 50% are extracted jointly to oil (Montanari et al., 1999; Baümler et al., 2016). Hence, only this latter portion of phospholipids is recovered from the extraction process using hexane to extract the raw oil. Thus the use of ethanol as extraction solvent could allow for a higher recovery of phospholipids, which

Table 3
Comparison of the coefficients obtained from the different models proposed for the fitting of tocopherol extraction kinetics when ethanol and n-hexane were used as solvents. Results of the ESS.

Fitting description	Coefficients	Solvent		F_o	F_c
		Ethanol	n-hexane		
50 °C					
Different A and B	$A \times 10^1$	8.326 ± 0.516	5.396 ± 0.456	–	–
	$B \times 10^4$	2.500 ± 0.379	8.642 ± 1.884		
	R^2	0.958	0.962		
Common A	$A \times 10^1$	6.260	6.260	1133.896	4.965
	$B \times 10^4$	1.737 ± 0.728	12.690 ± 2.123		
	R^2	0.844	0.948		
Common B	$A \times 10^1$	10.080 ± 0.377	4.170 ± 0.490	1299.588	4.965
	$B \times 10^4$	3.330	3.330		
	R^2	0.988	0.866		
Global (Common A and B)	$A \times 10^1$	6.260 ± 1.119		66.418	4.103
	$B \times 10^4$	3.330 ± 1.338			
	R^2	0.699			
60 °C					
Different A and B	$A \times 10^1$	8.326 ± 0.516	5.588 ± 0.693	–	–
	$B \times 10^4$	2.500 ± 0.379	80.450 ± 8.863		
	R^2	0.958	0.986		
Common A	$A \times 10^1$	3.464	3.464	326.770	4.747
	$B \times 10^4$	0.829 ± 0.993	53.480 ± 4.869		
	R^2	0.454	0.947		
Common B	$A \times 10^1$	7.510 ± 0.420	0.769 ± 0.320	694.672	4.747
	$B \times 10^4$	2.150	2.150		
	R^2	0.959	0.319		
Global (Common A and B)	$A \times 10^1$	3.464 ± 1.140		142.147	3.885
	$B \times 10^4$	2.150 ± 1.982			
	R^2	0.306			

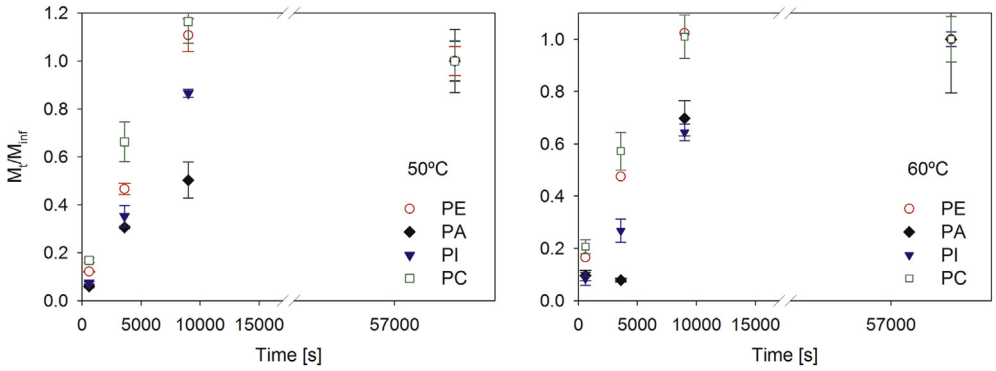

Fig. 3. Experimental extraction kinetics of each molecular species of phospholipids using ethanol as solvent.

could be refined and used as sunflower lecithin.

The use of this alcohol as extraction solvent also avoids eventual toxicity problems of meals for animal feedstuff (Ferreira-Dias et al., 2003), but due to the lower selectivity of ethanol towards triglycerides, other compounds are extracted jointly to the oil. Some of these compounds are sugars, and as it was demonstrated in our previous work (Baümler et al., 2016), they are extracted in a large proportion, making it important to analyze their extraction kinetics. The extraction kinetics of sugars was determined by measuring the residual amount of these compounds in the dry defatted meal obtained after carrying out the corresponding solvent extraction. The increase in total sugar mass in the extracted material over extraction time is shown in Fig. 4. It is possible to observe that not only did the rate of sugar mass transfer increase, but also that the extraction yield increased with temperature, being the yield at infinite time 31.97 ± 1.09 and 39.72 ± 0.43 g sugar/kg dry defatted meal at 50 and 60 °C, respectively ($p < 0.0001$). The mathematical model (Eq. (1)) was applied to fit the experimental

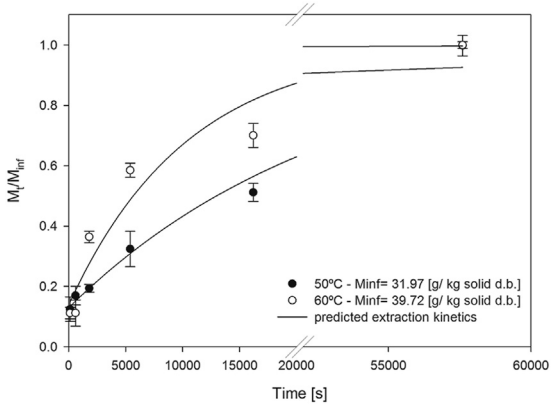

Fig. 4. Experimental (bullets) and predicted (lines) sugar extraction kinetics at 50 °C and 60 °C using ethanol as solvent.

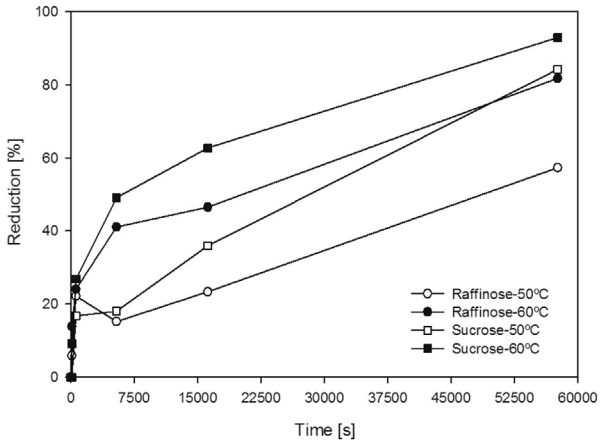

Fig. 5. Reduction percentage of the main sugar components in the solid matrix on dry and defatted basis during the extraction process.

sugar extraction data, and the fitting coefficients of the non-linear models were compared by means of ESS methodology (Table 1). The data obtained from the comparison of the different A and B model with the global model using contrast analysis F_o, shows that significant differences exist between them ($F_o > F_c$), and thus a dependence of one or both coefficients on temperature becomes evident. On the other hand, the comparison between the different A and B model and the common A model showed no significant differences ($F_o < F_c$), demonstrating that parameter A does not depend on temperature. Therefore, it could be concluded that parameter B depends on the temperature used during extraction. Thus the common A model was selected to represent the sugar extraction kinetics. The temperature increase produced significant differences in the extraction rate of these compounds, but only parameter B of the fitting model was affected. Parameter B involves the diffusion coefficient, so one diffusion coefficient was obtained for each analyzed temperature. The effective diffusion values for sugar, calculated from Eq. (1), were 6.50 10^{-10} and 1.51 10^{-9} m^2/s for 50 and 60 °C, respectively.

As stated above, sugars were composed mainly of sucrose and raffinose (51.1 and 35.7%), with raffinose being indigestible and associated with flatulence and abdominal discomfort (Rackis, 1975). The reduction of this minor component could increase the nutritional value of the meal. The reduction percentage of the main sugar components (sucrose and raffinose) in the solid matrix on dry and defatted basis during the extraction process are shown in Fig. 5. The reduction percentage of these sugars increased over extraction time, reaching values of over 50% and 80% at 50 and 60 °C, respectively.

4. Conclusions

The extraction of tocopherols, phospholipids and sugars was studied experimentally in a batch system using ethanol as solvent at 50 and 60 °C. Their extraction kinetics were described by modified nonlinear diffusion models derived from Fick's second law, involving two parameters: A, associated with the portion extracted during the washing stage, and B, proportional to the effective diffusion coefficient. A statistical comparison was carried out in order to evaluate the temperature dependence of model parameters A and B. In the comparison, differences between the models could be detected. When the sugar extraction rate was analyzed, only parameter B depended on temperature, and the model selected was that which contemplated a temperature-dependent diffusion coefficient (common A model). On the other hand, when phospholipid extraction was analyzed, it was found that coefficients A and B did not vary significantly over the temperature range, and therefore the global model was selected. In the case of tocopherols, it was found that coefficient B did not vary significantly over the analyzed temperature range, and therefore the common B model was selected.

The same analysis described above was performed to evaluate the solvent dependence of model parameters A and B. For tocopherol extraction, as expected, results showed that both parameters depended on the solvent used over the temperature range. On the other hand, for phospholipid extraction the results were different for both temperatures: at 60 °C both parameters depended on the solvent used, but for the temperature fixed at 50 °C only parameter A did, and therefore the amount of phospholipids extracted in the washing step depended on the solvent used, for the selected operating conditions.

The extracted material obtained using ethanol was fractionated using n-hexane into two phases: a hexane-soluble fraction that consisted of sunflower oil, and a hexane-insoluble fraction that was a solid composed of oil, phospholipids, pigments and sugars. Thus it was possible and easy to obtain a crude sunflower oil with low phospholipid and wax content on the one side, and also a higher recovery of phospholipids in the hexane-insoluble fraction. The hexane-insoluble fraction could be refined and used as sunflower lecithin, conferring an interesting advantage to ethanol as extraction solvent. It was also demonstrated that sugars are extracted in a large proportion when ethanol is used as solvent. Thus the sugar content in the obtained residual solid material is reduced, especially the indigestible raffinose, increasing its nutritional value.

Conflict of interest statement

The authors have declared no conflict of interest.

Acknowledgments

The authors acknowledge the financial support from CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), ANPCyT (Agencia Nacional de Promoción Científica y Tecnológica), and Universidad Nacional del Sur, Argentina.

References

AOCS, (2009). In D. Firestone (Eds.). 6th. Champaign, Illinois, USA, AOCS Press.
Baümler, E.R., Carelli, A.A., Crapiste, G.H., Carrín, M.E., 2011. Solvent extraction modeling of vegetable oil and its minor compounds. J. Food Eng. 107 (2), 186–194.
Baümler, E.R., Carrín, M.E., Carelli, A.A., 2016. Extraction of sunflower oil using ethanol as solvent. J. Food Eng. 178, 190–197. http://dx.doi.org/10.1016/j.jfoodeng.2016.01.020.
Baümler, E.R., Crapiste, G.H., Carelli, A.A., 2010. Solvent extraction: kinetic study of major and minor compounds. J. Am. Oil Chemists' Soc. 87 (12), 1489–1495.
Brevedan, M., Carelli, A.A., Crapiste, G.H., 2000. Changes in composition and quality of sunflower oils during extraction and degumming. Grasas aceites 51 (6), 417–423.
Carelli, A.A., Brevedan, M.V., Crapiste, G.H., 1997. Quantitative determination of phospholipids in sunflower oil. J. Am. Oil Chemists' Soc. 74 (5), 511–514.
Carrín, M.E., Crapiste, G.H., 2008. Mathematical modeling of vegetable oil–solvent extraction in a multistage horizontal extractor. J. Food Eng. 85 (3), 418–425.
Crank, J., 1975. Diffusion in a Cylinder. The Mathematics of Diffusion. Oxford University Press, pp. 69–88.
Di Rienzo, J.A., Casanoves, F., Balzarini, M.G., Gonzalez, L., Tablada, M., Robledo, C.W., 2011. InfoStat Versión 2011. U. N. D. Córdoba, Grupo InfoStat.
Fernández, M.B., Pérez, E.E., Crapiste, G.H., Nolasco, S.M., 2012. Kinetic study of canola oil and tocopherol extraction: parameter comparison of nonlinear models. J. Food Eng. 111 (4), 682–689.
Ferreira-Dias, S., Valente, D.G., Abreu, J.M., 2003. Comparison between ethanol and hexane for oil extraction from Quercus suber L. fruits. Grasas Aceites 54 (4), 378–383.
Hron, R.J., Koltun, S.P., Graci, A.V., 1982. Biorenewable solvents for vegetable oil extraction. J. Am. Oil Chem. Soc. 59 (9), 674A–684A.

Hron, R.J., Kuk, M.S., Abraham, G., Wan, P.J., 1994. Ethanol extraction of oil, gossypol and aflatoxin from cottonseed. J. Am. Oil Chemists' Soc. 71 (4), 417–421.
Johnson, L.A., Lusas, E., 1983. Comparison of alternative solvents for oils extraction. J. Am. Oil Chemists' Soc. 60 (2), 229–242.
Li, Y., Fine, F., Fabiano-Tixier, A.S., Abert-Vian, M., Carre, P., Pages, X., Chemat, F., 2014. Evaluation of alternative solvents for improvement of oil extraction from rapeseeds. Comptes Rendus Chim. 17 (3), 242–251.
Meziane, S., Kadi, H., 2008. Kinetics and thermodynamics of oil extraction from olive cake. J. Am. Oil Chemists' Soc. 85 (4), 391–396.
Meziane, S., Kadi, H., Lamrous, O., 2006. Kinetic study of oil extraction from olive foot cake. Grasas Aceites 57 (2), 175–179.
Montanari, L., Fantozzi, P., Snyder, J.M., King, J.W., 1999. Selective extraction of phospholipids from soybeans with supercritical carbon dioxide and ethanol. J. Supercrit. Fluids 14 (2), 87–93.
Pérez, E.E., Carelli, A.A., Crapiste, G.H., 2011. Temperature-dependent diffusion coefficient of oil from different sunflower seeds during extraction with hexane. J. Food Eng. 105 (1), 180–185.
Rackis, J.J., 1975. Oligosaccharides of food legumes: alpha-galactosidase activity and the flatus problem. Physiological effects of food carbohydrates. A. Jeanes and J. Hodge. Washington, D.C. Am. Chem. Soc. 207, 207–222.
Rao, R.K., Arnold, L.K., 1956. Alcoholic extraction of vegetable oils. II. Solubilities of corn, linseed, and tung oils in aqueous ethanol. J. Am. Oil Chemists' Soc. 33 (2), 82–84.
Rao, R.K., Arnold, L.K., 1957. Alcoholic extraction of vegetable oils. Part IV. Solubilities of vegetable oils in aqueous 2-propanol. J. Am. Oil Chem. Soc. 34 (8), 401–404.
Regente, M., Monzon, G.C., de la Canal, L., 2008. Phospholipids are present in extracellular fluids of imbibing sunflower seeds and are modulated by hormonal treatments. J. Exp. Bot. 59 (3), 553–562.
Rittner, H., 1992. Extraction of vegetable oils with ethyl alcohol. Oléagineux 47 (1), 29–42.
Salas, J.J., Martínez-Force, E., Garcés, R., 2006. Phospholipid molecular profiles in the seed kernel from different sunflower (Helianthus annuus) mutants. Lipids 41 (8), 805–811.
Saxena, D.K., Sharma, S.K., Sambi, S.S., 2011. Kinetics and thermodynamics of cottonseed oil extraction. Grasas Aceites 62 (2), 198–205.
Sineiro, J., Domínguez, H., Núñez, M.J., Lema, J.M., 1996. Ethanol extraction of polyphenols in an immersion extractor. Effect of pulsing flow. J. Am. Oil Chemists' Soc. 73 (9), 1121–1125.
Systat Software, I., 2008. SigmaPlot for Windows, Version 11.0. Systat Software, Inc San Jose, California.