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Extraction of sunflower oil using ethanol as solvent

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ABSTRACT

The ethanolic extraction of oil from sunflower collets was studied and compared with previous data where hexane was used as extraction solvent. First, the extractive power of ethanol was determined by Soxhlet. It gave a higher yield of extracted material, whose content of soluble hexane components (oil phase) was similar to that obtained with n-hexane. When ethanol was used as solvent, 70% less crystallizable waxes and at least 38% more tocopherols and phospholipids were extracted. In addition, ethanol showed great ability to extract sugar, mainly raffinose and sucrose, extracting over 75% of the initial sugar content.

Then, the kinetics of ethanolic extraction was studied at 50 and 60 °C in a batch reactor. At equilibrium conditions, it was observed that extraction could be limited by the solubility of the extractable material. Oil effective diffusivities were 9.94 10^{-10} at 50 °C and 3.11 10^{-9} m^2/s at 60 °C. From the point of view of the quality of the obtained products, this work demonstrated the feasibility of using ethanol as an alternative solvent to hexane in the oil extraction from sunflower collets.

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1. Introduction

The industrial oil extraction process has not changed much for the last few decades, although there have been some technical developments in optimization and better control. The conventional procedure for sunflower oil extraction involves seed preparation, mechanical extraction (in which a press cake or oilcake containing 16–24% of oil is obtained after continuous pressing), and a final stage which is the solvent extraction from ground oilcakes or expanded material, known as “collets” (porous cylinders obtained from pressed sunflower cakes by expanding). This last stage is commonly achieved by counter-current flow extraction using n-hexane as solvent (Li et al., 2014). The success of the industrial extraction process depends on how fast the compound to be extracted is dissolved, and on the balance achieved in the solvent phase. Solvent extraction is considered a mass transfer process between a solid phase (insoluble solid matrix), a liquid phase occluded inside the pores within the particle, and the miscella that moves through the spaces between the particles (Cacace and Mazza, 2003). Among the particles, the extracted material diffuses from the occluded liquid phase to the bulk liquid phase.

In the past, some alcohols were considered as possible solvents to extract oils from collets. But eventually, oil yields and some economic aspects favored the selection of hexane, an inflammable petroleum-derived solvent (Lusas et al., 1994). Nowadays it is known that this solvent can be emitted during extraction, being necessary its recovery because it has been identified as an air pollutant since it can react with other pollutants to form ozone and photochemical oxidants (Wan et al., 1995b; Hanmoungjai et al., 2000). Safety, environmental and health concerns have prompted increased interest in alternative solvents 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. In light of this new trend leading to 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).

Several studies have been carried out, both on laboratory and pilot scale, aimed to replace hexane with other hydrocarbons

Abbreviations: C_L, concentration in bulk phase (extracted material kg/miscella kg); C_s, concentration in solid-occluded miscella phase (extractable material kg/inert solid kg); d.b., dry basis; D_e, effective diffusivity (m^2/s); e.m, extracted material; R, collet average radium (m); K, equilibrium constant (C_s/C_L); M_t/M_{inf}, relation between mass extracted at time t and the one 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.

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(Conkerton et al., 1995; Wan et al., 1995a, 1995b) or alcohols (Abraham et al., 1988; Rittner, 1992; Hron et al., 1994; Sineiro et al., 1998) as solvents for oil extraction. Isopropanol and ethanol are the most promising solvents for the oil extraction from cottonseed (Abraham et al., 1988; Hron et al., 1994), sunflower seed (Sineiro et al., 1998) and soybean (Baker and Sullivan, 1983; Rittner, 1992). Ethanol is a worthy candidate to be studied as alternative solvent because it is cheap and it can be produced by fermentation from a large variety of biological materials using simple technology, and therefore labeled as "natural" or "biorenewable". In addition, although flammable, this alcohol is recognized as non-toxic and has less handling risks than hexane (Rittner, 1992). The use of ethanol as an extraction solvent also avoids eventual toxicity problems of meals for animal feedstuff (Ferreira-Dias et al., 2003), but it has been reported that the solubility of lipids in ethanol is drastically affected by the moisture content of the solvent and the extraction temperature (Rao and Arnold, 1956, 1957).

Due to the lower selectivity of ethanol towards triglycerides, during the extraction process other compounds such as phosphatides, polyphenols, pigments and soluble sugars are extracted jointly (Hron et al., 1982, 1994; Sineiro et al., 1996). After the ethanol extraction, and when the miscella cools down, it can be expected that part of the extracted material becomes insoluble (in ethanol) and separates as an emulsion. At about 38 °C, the gums obtained (mucilaginous material consisting of emulsified oil, phospholipids, pigments and sugars) lose some of their entrained miscella, agglomerate and sink to the bottom of the oil phase (Hron and Koltun, 1984). The aim of this work was to determine the performance of ethanol (extractive power, quantity and quality of extracted oil, and oil extraction kinetics) when used in the oil extraction from sunflower collets.

2. Materials and methods

2.1. Sample characterization

All experimental determinations were made with sunflower expanded material, known as "collets", which were kindly provided by a local factory. Collets were stored in polyethylene containers with screw caps in the dark at 4 °C until used in the extraction experiments. A sample of 20 collets was randomly selected to determine the average size of the collets. Collet dimensions, namely length (L) and radius (R), were measured using a gage with an accuracy of 0.01 mm. The initial moisture and oil content were determined according to IUPAC method 1.121 and 1.122 (IUPAC, 1992), respectively. The oil content of the solid was determined by an exhaustive extraction with analytical-reagent grade n-hexane (90%, bp 68–72 °C) in a Soxhlet apparatus. Similarly, the maximal ethanolic extraction yield was determined using analytical-reagent grade ethanol (95%, bp 78 °C). Solvents were removed from the miscellas firstly by rotary evaporation at 50 °C and low pressure, and then by nitrogen displacement until constant weights were reached.

The extracted material obtained using ethanol as solvent was fractionated in hexane-soluble material and other compounds (hexane-insoluble fraction) by phase separation with n-hexane. The hexane-soluble material constituted the lipid material that was used to study oil extraction kinetics.

2.2. Analyses of minor components

For the extracted material obtained using ethanol, contents of minor components (tocopherols, phospholipids, waxes and sugars) are expressed on a total extracted material basis and then referred to as moisture-free sunflower collets mass, in order to allow comparison with the results obtained using n-hexane as extraction solvent.

2.2.1. Tocopherol analysis

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) and a fluorescence detector (Waters 2475) with the excitation wavelength set at 290 nm and the emission wavelength set at 330 nm. The mobile phase used was n-hexane:isopropanol (99.5:0.5 v/v, HPLC solvent, J.T. Baker, Phillipsburg, USA) at a flow rate of 1.0 mL/min. Tocopherol content was determined by the external standard method. Areas were converted to concentrations using the standard curve of α-tocopherol (Sigma Chemical Co., 95%) in n-hexane in the relevant concentration range for the sample concentrations ($R^2 = 0.99$). Determinations were performed in triplicate.

2.2.2. Phospholipid analysis

Quantitative determination of phospholipids (PL) was carried out by enrichment using a diol solid-phase extraction cartridge (J.T. Backer Inc., Phillipsburg, NJ, USA) and subsequent analysis by HPLC-UV (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. Identification of PL was carried out by comparing the retention times with pure standards. The following PL reference standards with purities greater than 98% were supplied by Sigma Chemical Co. (St. Louis, MO, USA): L-α phosphatidylethanolamine (PE), L-α phosphatidylcholine (PC), L-α phosphatidylinositol (PI) and phosphatidic acid (PA). Calibration curves were obtained using standard solutions prepared by dissolving the standard PL in HPLC mobile phase at different concentrations. Determinations were performed in duplicate.

2.2.3. Wax determination

Wax composition was determined by separation on a silica gel chromatographic column and analysis by GLC (Carelli et al., 2012). Briefly, column chromatography was performed using a glass column (i.d. = 15 mm, length = 400 mm) with a double phase of silver nitrate-impregnated silica gel (3 g) placed at the bottom of the column and hydrated silica gel 2% (12 g) placed on top as a solid stationary phase. The waxes were eluted with n-hexane/ethyl ether (99:1 v/v) at a flow rate of 3 mL/min using Sudan I dye to control the end of the elution (Carelli et al., 2012). The eluted wax fraction was evaporated to dryness and diluted with n-heptane, and analyzed by capillary GLC with an on-column injection system. A Perkin Elmer AutoSystem XL gas chromatograph equipped with an FID detector, a temperature programmable on-column injector and a TotalCrom Workstation data processor version 6.3.1 (Perkin Elmer, MA, USA) was used. The capillary column was an HP-5 (5% diphenyl and 95% dimethyl-polysiloxane), fused-silica 15 m length × 0.32 mm i.d., 0.25 μm film thickness (Hewlett–Packard, Palo Alto, CA). C32 to C44 wax standards of 99% purity were obtained from Sigma Chemical Co. (St. Louis, MO, USA).The C32 standard was used as internal standard, and the purified sunflower wax recovered from a filter cake following the method proposed by Carelli et al. (2012) was used as standard for the identification of waxes with more than 44 carbon atoms. Waxes were categorized as follows: with less than 40 carbon atoms they were considered the oil soluble fraction, waxes with 40 and 42 carbon atoms were the partially soluble fraction, and waxes with more than 44 carbon atoms constituted the crystallized fraction. Determinations were performed in duplicate.

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2.2.4. Sugar content determination

Sugar content of the solid material was determined by an exhaustive extraction following AOAC method 925.05 (AOAC, 1990) with the modification proposed by Liu and Markakis (1987). Samples of approximately 4 g of sunflower collets were defatted by soaking the material in hexane for 20 min, and then subjected to extraction using 80 mL 80% ethanol in an 80 °C bath for 4 h with occasional shaking. The extract was cleaned by adding 2 mL of saturated lead acetate to precipitate proteins and then centrifuging down the impurities. The supernatant was diluted with distilled water and filtered. Enough anhydrous Na_2CO_3 was added to precipitate the lead. Finally the purified extract was diluted with distilled water to a final volume of 250 mL (extract). Four mL of the extract were lyophilized and then rehydrated with 4 mL of mobile phase, and then an aliquot was passed through a 0.45 μm MILLIPORE filter and injected into an HPLC system, following the method proposed by Martínez Ruiz (2005) with modifications. A Waters e2695 HPLC (Waters Associates, Milford, MA, USA) equipped with a Rezex ROA organic acid column (300 mm length, 7.8 mm i.d., Phenomenex, USA) and a refraction index detector (Waters 2414) was used. The mobile phase used was H_2SO_4 5 10^{-3} N at a flow rate of 0.3 mL/min, the column temperature was maintained at 20 °C, and the injection volume loop was 10 μL. The following reference sugars were supplied by Anedra (Argentina): glucose, fructose, arabinose, galactose, raffinose, rhamnose, sucrose, cellobiose, maltose, xylose, mannitol, starch, pectin and inulin. In order to obtain calibration curves, standard solutions were prepared by dissolving the reference sugars in HPLC mobile phase to different concentrations. The amount of sugar extracted using ethanol was determined by the difference between the sugar retained in the solid matrix after ethanol extraction and the initial sugar content. Determinations were performed in quadruplicate.

2.3. Equilibrium studies

The equilibrium studies were performed using a magnetically stirred batch system immersed in a temperature-controlled water bath. Samples of sunflower collets (approximately 10.0 ± 0.1 g) were subjected to ethanol extraction with different collet-to-solvent ratios: 1:4, 1:11 and 1:18 (g/mL). Solid and solvent were brought to extraction temperature (50 °C and 60 °C) separately before every experience. The miscella was withdrawn after 16 h (960 min), which was considered enough time to attain the equilibrium state. The amount of extracted material in the liquid phase was measured gravimetrically by solvent evaporation. The residual extractable material in the moisture-free sunflower collets was determined as the difference between the maximal extractable material determined by Soxhlet and the extracted material in the liquid phase. The partition coefficient was determined as the ratio of the concentration of the residual extractable material in the moisture-free sunflower collet to the concentration of the extracted material in the miscella. Extractions were replicated three times for each experimental condition. For the sake of comparison, equilibrium was also analyzed using n-hexane as extraction solvent.

2.4. Solvent extraction experiments

In order to determine the extraction kinetic parameters, experiments were performed in a similar way to Baümler et al. (2010), working at 50 and 60 °C, with extraction times from 0 to 960 min (considered as infinite time). The extraction mixture consisted of approximately 10.0 ± 0.1 g of sunflower collets and 180 mL of ethanol (95%, bp 78 °C), corresponding to a collet-to-solvent ratio of 1:18 (g/mL). The agitation rate was kept constant in all experiments, being sufficient to maintain a well-mixed fluid and the particles in suspension. At the end of contact time, the contents of the flasks were immediately filtered, and the miscella was concentrated using a rotary evaporator, not exceeding 50 °C. The remaining solvent traces were removed under a nitrogen stream to constant weight. All the extractions were carried out in triplicate.

The extracted material obtained using ethanol as solvent was fractionated as described in Section 2.1.

2.5. Mathematical modeling

2.5.1. Equilibrium

During solvent extraction, the concentration of the extracted material in the occluded phase was considered in equilibrium with the concentration of the extractable material in the moisture-free sunflower collet matrix, according to a ratio which was experimentally determined by the following expression:

$$C_s = K^* C_L \tag{1}$$

where C_s is the concentration of the extractable material in the solid phase at the radial position r = R, K is the equilibrium or partition constant, and C_L is the concentration of the extracted material in the occluded phase at the same radial position R, i.e. at the interface.

Thus, equilibrium is reached between the solution surrounding the particles (miscella) and the extractable material contained in the solid.

2.5.2. Oil extraction kinetics

Modeling of the oil extraction kinetics was made following the theory 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), who considered that the extraction process is accomplished through two main mechanisms: a washing process of the extractable material on the seed surface, and a diffusion process, which can take place in one or two phases, depending on the proportion of broken and intact cells that remain after pre-extraction treatments. The rate of dissolution of the extractable material into the solution was described by a modified model of Fick's Law of diffusion in non-stationary state for cylindrical particle geometry, suspended in a homogeneous medium with a constant concentration without volume restriction (Pérez et al., 2011):

$$\frac{M_t}{M_{inf}} = 1 - \sum_{n=1}^{\infty} A_n \, exp(-B_n \, t) \tag{2}$$

where M_t and M_{inf} represent the mass of oil that diffuses at time t and infinite, respectively, and A_n and B_n are the diffusion model-fitting parameters which depend on the particle geometry (Crank, 1975). For cylindrical particle geometry their expressions are:

$$A_n = \frac{4}{R^2 \lambda_n^2} \tag{3}$$

$$B_n = D_e \, \lambda_n^2 \tag{4}$$

where D_e is the effective diffusion coefficient (m^2/s), R is the average radium (m), and λ_n are roots of $J_0(R\lambda_n) = 0$, where J_0 is the Bessel function of the first kind of zero order.

For a sufficiently long time, Eq. (2) can be simplified to:

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$$\frac{M_t}{M_{inf}} = 1 - A\ exp(-B\ t) \quad (5)$$

where the exponential coefficient is given by $B = D_e\lambda_1^2$ and the pre-exponential coefficient by $A = \left(1 - \frac{M_0}{M_{inf}}\right) A_1\ exp(B\ t_0)$. Coefficient A is associated with the average value of the material extracted in the washing step (M_0, kg solute/kg dry defatted meal).

The mathematical model represented by Eq. (5) was applied to fit the experimental oil extraction data for sunflower collets at different temperatures using nonlinear regression (Systat Software, 2008).

2.6. 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 the means of pairs of treatments with a significance level $p \leq 0.05$. Physical and chemical properties of the raw material were expressed as the means of n determinations with 95% confidence intervals. The number of replicates (n) carried out in each case 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% (Fernández et al., 2012). The null hypothesis (H_0) and the alternative hypothesis (H_1) were proposed: 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, *common A model* when only B varies with temperature or solvent, and *common B model* when only A depends on temperature or solvent); 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) obtained by the following equations (Boché and Lavalle, 2004; Fernández et al., 2012):

$$F_o = \frac{\frac{\sum_{i=1}^{q}\left(x_i^{mod} - y_i\right)^2 - \sum_{i=1}^{q}\left(x_i^{diffAB} - y_i\right)^2}{(q-b)-(q-d)}}{\frac{\sum_{i=1}^{q}\left(x_i^{diffAB} - y_i\right)^2}{(q-d)}} \quad (6)$$

$$F_c = F[0.05, d-b, q-d] \quad (7)$$

where x_i^{mod} and x_i^{diffAB} are the simulated values of M_t/M_{inf} obtained with the model being compared (common A, common B or global model) and the different A and B model, respectively; y_i is the mean value of the three replicated measurements; q is the number of total measurements; b and d are the number of parameters to be estimated from the model being compared and the different A and B model, respectively. For the global model b = 2, for common A and common B models b = 3, and for the different A and B model four parameters must be estimated (d = 4).

3. Results and discussion

3.1. Characterization of the raw material

The raw material (sunflower collets) was characterized physically and chemically, giving the following mean values accompanied by the standard error: L = 49.17 ± 7.57 mm; R = 9.56 ± 0.34 mm; initial moisture content = 6.0 ± 0.6% d.b.; oil content = 22.8 ± 0.6% 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%), presenting in minor amounts 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%).

The extraction yield obtained by Soxhlet, and the chemical composition of the extracted material using ethanol and n-hexane are presented in Table 1. It can be observed that the yield of extracted material when the solvent used was ethanol is higher than that for n-hexane. The material extracted with ethanol had 69% of soluble hexane components or lipid fraction that represents 22.2 ± 0.5% d.b., this value being similar to that for the material extracted with hexane (22.8 ± 0.6% d.b.).

Some authors point out the lower selectivity of ethanol towards oil, with the consequent extraction of other compounds such as phosphatides, polyphenols, pigments and soluble sugars (Hron et al., 1982, 1994; Sineiro et al., 1996), which is in agreement with our results. On the other hand, it was found that ethanol has a similar capacity to extract lipid material to that of n-hexane. Therefore, due to the simultaneous extraction of other compounds, the results obtained in this work when ethanol was used as solvent are referred to as "extracted material" instead of "extracted oil".

In Table 1, contents of minor components (tocopherols, phospholipids, waxes and sugars) are expressed on a total extracted material basis for each solvent. From these results, the content of extractable minor components in the solid, or moisture-free sunflower collets, was estimated as kg of component per kg of moisture-free sunflower collets in order to demonstrate the differences in extractability. As it can be observed, tocopherols and phospholipids extracted using n-hexane and ethanol did not show significant differences; but when the results are expressed in g or mg of extracted compound per kg of moisture-free sunflower collets on d.b., the results show a greater extractability (over 38%) with ethanol. This result could be partially explained by the difference between solvent polarities (Li et al., 2014). Ethanol can extract more polar lipids, such as phospholipids, than n-hexane. Some authors reported the use of ethanol to fractionate phospholipids from a solid matrix (Montanari et al., 1999). Among the minor compounds in oilseeds, tocopherols are intrinsically bound to oil body structures (Fisk et al., 2006), they are amphipathic molecules, with the hydrophobic tail associating with membrane lipids and the polar head groups remaining on the membrane surface (Sattler et al., 2004). The higher tocopherol yield obtained could be the result of the breakdown of the collet structure caused by moisture contribution by the use of the ethanol azeotrope.

When waxes are considered, the material extracted using ethanol had a significantly lower content, being its composition different from that obtained with n-hexane as solvent (Table 1). Ethanol extracts 70% less crystallizable waxes than hexane, which would imply a less rigorous winterization or dewaxing stage in the refining process.

Sugars are not extracted with n-hexane, but they are with ethanol. This partially explains the higher yield obtained with the latter solvent. Sugar composition of the extracted materials is presented in Table 1. It is possible to observe that ethanol has a great ability to extract sugars, mainly raffinose and sucrose, extracting over 75% of the initial sugar content. Thus it could increase the nutritional value of the meal, because consumption of the indigestible sugars raffinose and stachyose is associated with flatulence and abdominal discomfort (Rackis, 1975).

3.2. Equilibrium constant

The equilibrium constant or partition constant, defined as the

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Table 1
Extraction yield and chemical composition of the material extracted by Soxhlet with ethanol and hexane from sunflower collets.

Analytical determination		Extraction solvent	
		Ethanol	Hexane
Yield of extracted material	(% d.b.)	32.2 ± 1.3[b]	22.8 ± 0.6[a]
	hexane-soluble material (%)	69.0 ± 1.3	100
Phospholipids	(g/kg e.m.)	2.90 ± 0.01[a]	2.52 ± 0.29[a]
	(g/kg of solid in d.b.*)	0.93 ± 0.32 10^{-2a}	0.58 ± 6.68 10^{-2b}
	PE (%)	9.1 ± 0.8[a]	13.3 ± 1.6[a]
	PA (%)	16.1 ± 0.8[b]	24.4 ± 2.2[a]
	PI (%)	35.5 ± 1.2[a]	30.6 ± 2.7[a]
	PC (%)	39.3 ± 1.1[b]	31.7 ± 2.1[a]
Tocopherols	(mg/kg e.m.)	499 ± 125[a]	512 ± 63[a]
	(mg/kg of solid in d.b.*)	160.76 ± 40.21[a]	116.95 ± 14.50[a]
	Alpha (%)	99.0 ± 0.1[a]	98.2 ± 0.7[a]
	Beta (%)	1.0 ± 0.2[a]	1.8 ± 0.9[a]
Waxes	(mg/kg e.m.)	329 ± 8[a]	670 ± 2[b]
	(mg/kg of solid in d.b.*)	105.78 ± 2.50[a]	152.93 ± 0.48[b]
	Oil soluble (%)	24.5 ± 0.1[b]	12.9 ± 0.04[a]
	Partially oil soluble (%)	34.2 ± 0.3[b]	19.3 ± 0.2[a]
	Crystallizable (%)	41.3 ± 0. 3[a]	67.8 ± 0.2[b]
Sugars	(g/kg e.m.)	105.66 ± 11.45	–
	(g/kg of solid in d.b.*)	34.02 ± 3.69	–
	Raffinose (%)	33.3 ± 2.6	–
	Sucrose (%)	59.7 ± 3.4	–
	Glucose (%)	2.1 ± 0.3	–
	Galactose (%)	1.5 ± 0.2	–
	Fructose (%)	2.1 ± 0.3	–
	Rhamnose (%)	1.3 ± 0.8	–

Data are mean values ± standard errors.
Values in the same row with the same letter are not significantly different ($p > 0.05$) by the LSD Fisher method.
d.b. = dry basis.
e.m. = extracted material.
*solid in d.b. means moisture-free sunflower collets.

ratio of the residual extractable material in the solid phase to the extracted material in the bulk miscella ($K = C_S/C_L$), varied according to the nature of the solvent, the collet-to-solvent ratio and temperature considered (Table 2). The statistical analysis was performed separately for each solvent due to their different selectivity. Interactions between temperature and the collet-to-solvent ratio were detected; for this reason, temperature was chosen as partition variable for the ANOVA (Table 2). The equilibrium constant is related to the level of difficulty to extract solutes from the solid matrix. When ethanol was used, the equilibrium constant was strongly influenced by temperature, decreasing with increasing temperature. Therefore, the extractability of the material increased with temperature. It was observed that the collet-to-solvent ratio was also important, the extractability being higher when the solvent proportion was increased.

In contrast, when the extraction solvent was n-hexane, the equilibrium constant values were lower, making clear the superior oil extraction capacity of this solvent. In this case, temperature did not affect this parameter.

The ratio of the concentration of extractable material between the solid phase and the drained miscella is shown in Fig. 1. For ethanol, the shape of the curve exhibits a linear region at lower concentrations and a moderately curved behavior at higher concentrations, similar to those reported by Abraham et al. (1988), who studied oil extraction from cotton seed using ethanol, and by Pérez et al. (2011), who analyzed oil extraction from different ground sunflower seeds using n-hexane as solvent at 50 °C. Experimental data were adjusted according to the following equation (Pérez et al., 2011):

Table 2
Equilibrium constant at 50 and 60 °C and different collet-to-solvent ratios. Comparison between ethanol and hexane as extraction solvents.

Collet-to-solvent ratios (g/mL)	$K_{ethanol}$	K_{hexane}
50 °C		
1:4	17.13 ± 0.22[c]	0.49 ± 0.01[b]
1:11	10.51 ± 0.56[b]	0.34 ± 0.04[a]
1:18	7.55 ± 0.84[a]	0.54 ± 0.03[b]
60 °C		
1:4	8.17 ± 0.86[b]	0.55 ± 0.02[b]
1:11	5.14 ± 0.46[a]	0.18 ± 0.01[a]
1:18	3.52 ± 0.40[a]	0.60 ± 0.09[b]

In the same column and for each temperature, values with the same letter are not significantly different ($p > 0.05$) by the LSD Fisher method.
K = ratio of the residual e. m. in the solid*phase to the e. m. in the bulk miscella.
e.m. = extracted material.
*solid means moisture-free sunflower collets.

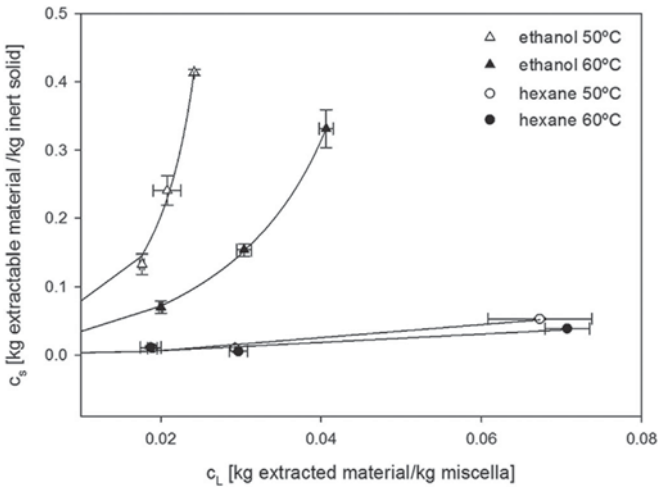

Fig. 1. Relationship between the extractable material occluded in the solid matrix and the extracted material in the miscella at equilibrium (bullets: experimental data; solid lines: fitting model).

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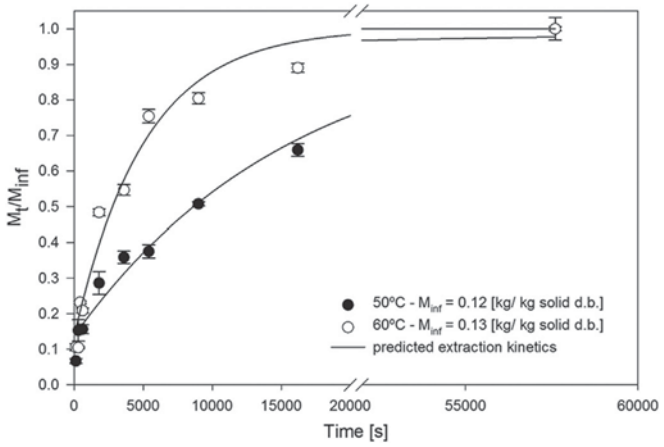

Fig. 2. Experimental (bullets) and predicted (lines) oil extraction kinetics at 50 °C and 60 °C using ethanol as solvent.

$$C_S = \frac{a\,C_L}{1 + b\,C_L} \tag{8}$$

where the constant a is the slope of the linear region, and the constant b represents the curvature that is significant at higher concentrations. Both constant values were obtained by nonlinear regression, giving $a = 3.43 \pm 0.43$ and $b = -33.16 \pm 1.19$ at 50 °C ($r^2 = 0.99$), and $a = 2.34 \pm 0.05$ and $b = -17.57 \pm 0.16$ at 60 °C ($r^2 = 0.99$). For n-hexane, the correlations were linear, $C_S = a\,C_L$, being $a = 0.70 \pm 0.09$ at 50 °C ($r^2 = 0.91$) and $a = 0.50 \pm 0.07$ at 60 °C ($r^2 = 0.89$). Patricelli et al. (1979) also obtained a linear relation in their study of sunflower oil distribution between the liquid and solid phase using crushed and laminated partially-decorticated sunflower seeds, hexane at 22 °C and low solid-to-solvent ratio. The differences in the fitting curve slopes are associated with the oil solubility in the solvent used, as well as the raw material used. On a molecular level, there is a driving force, or potential, that causes the oil to dissolve in the solvent. If the oil is only partially miscible in the solvent, as in the case of ethanol, then this force decreases as the concentration of oil in the solvent increases and goes to zero at the saturation concentration (Abraham et al., 1988). This could explain the curvature obtained when ethanol was used as extraction solvent.

3.3. Oil extraction kinetics using ethanol as solvent

As mentioned above in Material and Methods (Section 2.1), the material extracted with ethanol was fractionated using n-hexane. The material soluble in n-hexane was used to study the oil extraction kinetics. Because the oil is only partially miscible in ethanol, the driving force decreases as the concentration of oil in the solvent increases and goes to zero at the saturation concentration; therefore in the oil extraction experiences, a high collet-to-solvent ratio (1:18) was used to keep the driving force large.

Experimental and predicted oil extraction data of M_t/M_{inf} at different temperatures using ethanol as solvent are presented in Fig. 2. The extraction rate increased markedly with temperature; the change in yield can be attributed to the fact that a rise in temperature increases the solubility and diffusion of the oil while decreasing viscosity. Table 3 shows the obtained coefficients of the model used to represent oil extraction for all the studied cases: different A and B model, common A model, common B model and global model (as explained in Section 2.6). For the temperature analysis, the comparison of the model with different A and B coefficients with the common B and global models showed significant differences ($F_o > F_c$). On the other hand, the comparison of the model with different A and B coefficients with that using a common A coefficient did not present significant differences ($F_o < F_c$), indicating that only the B coefficient depends on temperature within the range studied. Thus, in order to represent the oil extraction kinetics using ethanol as solvent and to obtain the diffusion coefficients, the common A model was selected. D_e values determined by Eq. (4) were 9.94 10^{-10} at 50 °C and 3.11 10^{-9} m^2/s at 60 °C, values that were lower than those reported for n-hexane (1.68 10^{-8} at 50 °C, 2.25 10^{-8} m^2/s at 60 °C) (Baümler et al., 2010).

Experimental oil extraction results obtained using ethanol were also compared with reported data of sunflower collet oil extraction using n-hexane as solvent (Baümler et al., 2010). For the solvent analysis, the comparison of the different A and B model with the common A, common B and global models showed significant differences in all cases ($F_o > F_c$), indicating that both parameters A and B depend on the solvent used, as it can be easily deduced from the experimental data (Fig. 3) and the parameters of the kinetic model (Table 4). Comparing the experimental data, it is worth mentioning that at the equilibrium condition the oil yields obtained with hexane were 45% higher than those obtained when ethanol was used, thus extracting almost the total lipid content determined by exhaustive extraction (23.5 ± 0.4% d.b.) (Baümler et al., 2010). Moreover, the equilibrium ethanolic extraction improved by 10% when temperature was increased by 10 °C, whereas the hexane extraction did not change significantly.

4. Conclusions

This work demonstrated the feasibility of using ethanol as an alternative solvent to hexane in the oil extraction from sunflower collets. Oil extraction was described by modified nonlinear

Table 3
Coefficients obtained from the different models proposed for oil extraction yield using ethanol as solvent.

Fitting description	Coefficients	Temperature (°C)		F_o	F_c
		50	60		
Different A and B	A × 10^1	8.69 ± 0.19	8.88 ± 0.35	–	–
	B × 10^5	6.42 ± 0.59	20.81 ± 2.51		
	R^2	0.98	0.97		
Common A	A × 10^1	8.62	8.62	0.84	4.49
	B × 10^5	6.29 ± 0.47	19.66 ± 1.98		
	R^2	0.98	0.97		
Common B	A × 10^1	9.34 ± 0.40	7.90 ± 0.46	53.82	4.49
	B × 10^5	11.07	11.07		
	R^2	0.89	0.90		
Global (Common A and B)	A × 10^1	8.62 ± 0.42		37.48	3.63
	B × 10^5	11.07 ± 1.86			
	R^2	0.58			

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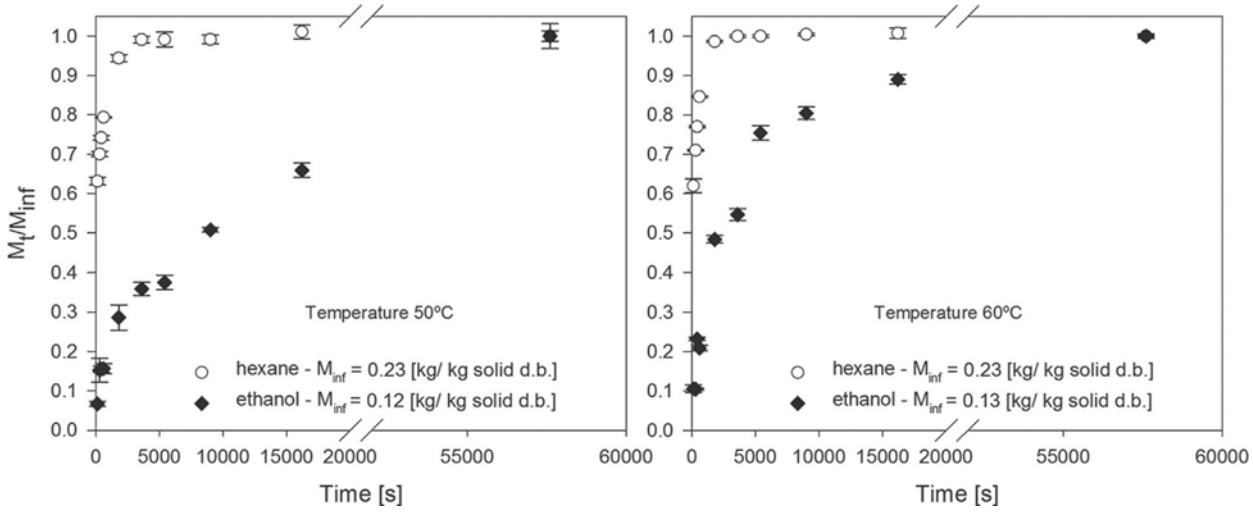

Fig. 3. Comparison between the oil extraction kinetics using ethanol as solvent and reported data of sunflower oil extraction using n-hexane (Baümler et al., 2010).

Table 4
Comparison of the coefficients obtained from the different models proposed for fitting the oil extraction yield data when ethanol and n-hexane were used as solvent. Results of the ESS.

Fitting description	Coefficients	Solvent		F_o	F_c
		Ethanol	n-hexane (Baümler et al., 2010)		
50 °C					
Different A and B	$A \times 10^1$	8.62	4.23 ± 0.08	–	–
	$B \times 10^5$	6.29 ± 0.47	116.00 ± 4.78		
	R^2	0.98	0.99		
Common A	$A \times 10^1$	5.73	5.73	526.6	4.49
	$B \times 10^5$	2.62 ± 2.05	199.70 ± 18.12		
	R^2	0.40	0.95		
Common B	$A \times 10^1$	9.29 ± 0.38	2.16 ± 0.43	174.90	4.49
	$B \times 10^5$	10.69	10.69		
	R^2	0.91	0.54		
Global (Common A and B)	$A \times 10^1$	5.73 ± 1.06		902.77	3.63
	$B \times 10^5$	10.69 ± 6.92			
	R^2	0.32			
60 °C					
Different A and B	$A \times 10^1$	8.62	4.80 ± 0.11	–	–
	$B \times 10^5$	19.66 ± 1.98	180.20 ± 7.46		
	R^2	0.97	0.99		
Common A	$A \times 10^1$	6.11	6.11	128.50	4.49
	$B \times 10^5$	10.66 ± 4.58	253.70 ± 16.38		
	R^2	0.74	0.97		
Common B	$A \times 10^1$	9.57 ± 0.46	2.65 ± 0.39	45.50	4.49
	$B \times 10^5$	32.26	32.26		
	R^2	0.93	0.74		
Global (Common A and B)	$A \times 10^1$	6.11 ± 1.07		250.70	3.63
	$B \times 10^5$	32.26 ± 16.91			
	R^2	0.49			

diffusion models derived from Fick's second law, which involved 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. Only parameter B depended on temperature, therefore the model selected was that which considered parameter B depending on temperature (common A model). The same analysis was performed to evaluate the solvent dependence of the parameters. As expected, results demonstrated that both parameters depended on the solvent used.

The extracted material obtained using ethanol consisted of two phases: a hexane-soluble fraction and a hexane-insoluble fraction that could be separated by simple fractionation using n-hexane. Both fractions consisted of partially degummed sunflower oil with a relatively low crystallizable wax content and a hexane-insoluble fraction composed of oil, phospholipids, pigments and sugars. This confers an interesting property to ethanol: that of providing partially degummed sunflower oil on the one hand, as well as a higher recovery of PL in the other phase (hexane-insoluble fraction). This hexane-insoluble fraction could be refined and used as sunflower lecithin. In addition, it was demonstrated that sugars are extracted when ethanol is used as solvent. Thus the sugar content in the residual solid material, especially the indigestible raffinose, was reduced and this increased its nutritional value.

It was observed that other compounds, different from

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triglycerides, were extracted when ethanol was used as solvent. Knowledge of 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 subsequent purification steps. This aspect will be further studied in future work.

Conflict of Interest statement

The authors have declared no conflict of interest

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