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

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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

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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