Experimental data acquisition and mathematical model for soluble protein extraction from Argentinian extruded expeller soybean meal

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Abstract Extruded expeller soybean meal is a byproduct of the soybean oil extraction, which is frequently used in Argentina by animal feed millers. In this work, the soluble protein extraction stage is studied as the first step of a challenge project in order to obtain a soy protein product from this byproduct. Extruded expeller meals from 4 different Argentinian processing plants were used to obtain 41 experimental data sets, using 1 to 3 consecutive extraction cycles operating at temperatures from 55 to 65 °C. Firstly, 16 data sets were used to estimate the values of the distribution constant and the diffusivity of proteins within the particle, both as function of the extraction temperature. The remaining 25 data sets were used for validation purposes. Extraction yields were analyzed considering the impact of the operating conditions, while a good agreement between experimental and predicted extraction yields was achieved as the reported statistical parameters indicate.

Keywords Soybean · Extruded expeller meal · Soluble protein · Extraction

List of symbols

α Volume ratio (—)

ε Volume fraction (—)
 θ Time coordinate (s)
 Θ Total extraction time (s)
 μ Viscosity (kg/m s²)
 ρ Density (kg/m³)
 τ Fick's number (—)
 ϕ Dimensionless ratio (—)
 A Arrhenius constant (m²/s)
 c Extraction cycle (—)
 C Soluble protein concentration (mg/ml)
 $\bar{C}$ Average protein concentration (mg/ml)
 CT Total protein concentration (mg/ml)
 D Mass diffusivity (m²/s)
 E Activation energy (kJ/mol)
 G Gibb's free energy (kJ/mol)
 h Planck constant (kg m²/s)
 H Enthalpy (kJ/mol)
 k Global mass transfer coefficient (m/s)
 K Distribution constant (—)
 MW Molecular weight (kg/kmol)
 n Sample origin (—)
 N Avogadro constant (1/mol)
 r Spatial radial coordinate (m)
 R Radius (m)
 Re Reynolds's number (—)
 R_g Gas constant (kJ/mol K)
 S Entropy (kJ/mol K)
 Sc Schmidt's number (—)
 Sh Sherwood's number (—)
 T Temperature (°C or K)
 v Agitation velocity (m/s)
 V Volume (m³)
 W Mass (kg)
 Y Extraction yield (%)

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Subscripts and superscripts

- 0 Initial
- β At solid particle
- γ At solvent phase
- a Protein
- i At interphase
- # At activation state

Introduction

In the last decades, soybean and its derivatives have become one of the most important Argentinian export goods, as result of a combination between the possibility of territorial expansion of this crop, and the worldwide significance played by new agricultural technologies in developing countries (Reboratti 2010). In 2013, exports of soybean products (oil and meal) were in the order of 23 billion dollars, representing 26% of the Argentinian's total sales abroad, according to the business chamber that represents producers of grains and cereals, the Cámara de la Industria Aceitera-Centro de Exportadores de Cereales (Hilbert and Galligani 2015).

The main products obtained from soybean processing are meal and oil. Soybean meal is a high protein vegetable product that is used by animal feed millers and the soy protein industry. Two industrial methods are used to process soybeans into meal and oil: hexane (chemical) extraction or expeller-pressed (mechanical) extraction. Soy protein products, including soy protein concentrates (SPC) and soy protein isolates (SPI), have become increasingly used as ingredients because of their high nutritional quality and versatile functional properties (Wang et al. 2004). SPC is defined as an edible protein product with a protein content of at least 65% protein on a moisture free basis, whereas SPI is a product containing 90% or more protein on a moisture free basis (ANMAT 2018; FAO 2018).

Most large processing facilities use hexane extraction since it is more efficient. In Argentina, solvent extraction represents approximately 90% of the soybean oil industry (Hilbert and Galligani 2015). Expeller pressed extraction is used by smaller facilities serving mainly local markets. In this process, heat and high pressure are applied to the expeller in order to extract oil from the soybean. While less efficient than hexane extraction, this extraction method is typically implemented by small-scale farmers, and cooperatives and represents the remaining 10% of the national soybean oil production (Hilbert and Galligani 2015).

The protein in the soybean meals produced from the extruding-expelling (EE) processing is heat-denatured by extrusion. Using this method, EE meals with different oil contents and protein denaturation degrees are obtained because of the processing conditions and equipment

specifications. The main advantages of this method are that the extraction process does not require solvent, as well as a lower initial capital investment is necessary when compared with traditional methods (Wang et al. 2004).

Most likely, because of the lower installed small-scale capacity for the EE technology and the higher residual oil content and lower protein content compared to defatted soy flakes from the solvent extraction process, fewer research works (Heywood et al. 2002; Wang et al. 2004) have been published related to the production of SPC and SPI from EE meals.

On the other hand, many technological and academic advances have been made for the production of SPC and SPI from defatted soy flakes and flour (Sunley 1995; Liu 1997; Badui Dergal and Valdés Martínez 2006). The most wide spread technologies used at industrial scale are alcohol and acid leaching for SPC and isoelectric precipitation for SPI (Shanmugasundaram 2011). Meanwhile, some innovative solutions for the conventional method have been proposed in the technological and academic literature. In the case of SPC, (Konwinsky 1992) applies for a technological patent proposing a previous agglomeration stage of the flakes before the aqueous extraction in order to include fine particles that are disposed along the process. (Russin et al. 2007) studied the size particle effect on the extraction of soy protein. Another patent application presented by (Cho et al. 2006) adds an enzymatic hydrolysis after isoelectric precipitation in order to increase the acidity resistance. In the patent application presented by (Chajuss 2012), an extraction step with aqueous alcohol following the solvent extraction to remove roasting and desolventization was proposed.

Additionally, alternative methods for SPI production have been analyzed, including ultrafiltration, reverse osmosis and swollen gel (Johnson et al. 1989). The most widely spread out protein extraction methods that have been implemented at large scale are aqueous extraction, studying the effect of protein extraction in the presence of salts, especially calcium chloride (Maltais et al. 2006), as well as the application of ultrasound during this stage (Bishnu 2009).

In this context, it is concluded that most technological advancement has been directed up to this point towards obtaining SPC and SPI from defatted soy flour. On the other hand, due to the increased interest in the expansion of the Argentinian social economy, an optimal process for producing SPC and/or SPI products from EE meals represents an important challenge for promoting social and growth economies as well as an opportunity for adding value to this byproduct.

This paper presents the evaluation of the aqueous extraction stage of soluble soy protein from EE meals produced in Argentina, with the intent of its subsequent use

in future works as raw material to produce SPC or SPI. This stage is thoroughly studied in this work, as several experimental runs for 1 to 3 consecutive extraction cycles and extraction temperatures from 55 to 65 °C have been carried out for EE meals from different processing plants. Then, a mathematical model to describe the kinetics extraction of soluble proteins is presented and validated.

The proposed contribution describes the mechanism of the water solvent extraction of soluble soy protein in order to evaluate and compare mass transfer rates under different operating conditions. Differences for the mass transfer coefficients (including diffusivities, global mass transfer coefficients and distribution constants) are substantiated from a physical point of view. Therefore, a complete mathematical model to describe the mass transfer mechanism for aqueous extraction of soy protein is developed using first principles equations through DAEs and semi-empirical correlations, and validated by means of experimental runs.

Experimental data acquisition

The extruded expeller soybean samples used for the experimental runs were obtained by the expeller-pressed method from various processing plants ($n = n_1, n_2, n_3, n_4$) located in the Argentinian central region. Different samples were taken into account because of the variability in the EE meal composition as consequence of differences in the processing conditions and equipment implemented during the extruding-expelling process. For example, the adopted temperature and residence time in the extruder influence the remnant available soluble protein within the meal. As result of the aforementioned variations in the extruding-expelling process, both the total initial protein content of the EE meal as well as its percentage of solubilization are important parameters, which turns out to be the protein available for extraction using the methodology hereafter studied. In addition, the heat treatment is linked to the anti-nutritional factors reduction and the protein digestibility. For adequate functional properties of soybean, a solubility index above 90% is required (Caprita and Caprita 2010). Suitable protein solubility generally correlates with optimum gelation, emulsifying and foaming ability of the protein (Lakemond et al. 2000). Protein solubility values lower than 74% reflect that lysine is unavailability for human and animals (Parsons et al. 1991). The values of protein solubilization in KOH were determined according to the method of (Araba and Dale 1990).

EE meals were ground into flour using a Blade mill (Sojamet, Argentina). For sieving, a sieve shaker (Ro-Tap, US) and sieves (Macotest, Argentina) corresponding to the ASTM series No. 4, 8, 12, 25, 40, 50, 100 and blind were

used. The fraction of interest for the subsequent extraction was comprised by particle sizes between 25-mesh through and 100-mesh retained.

EE meal is composed of three primary ingredients: proteins (water soluble and non-soluble ones), insoluble carbohydrates and non-protein water-soluble materials. AOAC procedure was used to determine nitrogen content where initial total protein concentration in the EE sample was calculated as nitrogen $\times$ 6.25 (AOAC 2005).

The most commonly implemented prior art method for isolating vegetable protein from soybean meal involves a general step of protein solubilization by addition of an alkali during the extraction stage (Heywood et al. 2002). During the primary extraction procedures, the alkaline extraction was divided into 2–3 stages, $c = c_1, c_2, c_3$. The adopted operating conditions were: extraction velocity—140 rpm, extraction time—15 min, extraction pH—8.5, solid to liquid ratio—1:20; whereas these values are in agreement with those proposed by (Wang et al. 2004). The temperature for the alkaline extraction was set at 55, 60 or 65 °C. The extraction was performed in a batch extractor with continuous stirring at the specified temperature in a thermostatic bath.

At regular time intervals, a liquid sample was obtained from the batch extractor. Here, soluble protein content was determined by the Bradford technique (Bradford 1976), using Bradford reagent and measuring the absorbance at a wavelength of 595 nm in a spectrophotometer (UV-1800, Shimadzu, Japan).

At the end of each extraction cycle, the solid and liquid phases were separated, and the solid fraction was used as raw material for the subsequent extraction stage. The same operating parameters used at the first extraction stage were maintained throughout the process.

In order to determine the soluble proteins molecular weight in the washing solutions after each extraction cycle, protein patterns were analyzed by SDS–PAGE according to the method of (Laemmli 1970). Protein samples were solubilized in 0.125 M Tris–HCl buffer and dyed with Coomassie blue R-250. The homogenate was incubated at 90 °C for 5 min, followed by centrifugation at 8000 g for 5 min at room temperature. Then, 20 μ g samples were loaded into the polyacrylamide gel. The electrophoretic pattern of proteins was determined using polyacrylamide 12% gel slabs with a constant current of 20 mA per gel.

The experimental data related to the EE samples are reported in Table 1, as well as the operating parameters used during the extraction process.

Table 1 Input data

Item	Symbol	Units	Value		
			for $T = 55\text{ }^{\circ}\text{C}$	for $T = 60\text{ }^{\circ}\text{C}$	for $T = 65\text{ }^{\circ}\text{C}$
Particle radius	R_{β}	m		2.150×10^{-4}	
Particle density	ρ_{β}	kg/m ³		1.134×10^3	
Average soluble protein molecular weight	MW_a	kg/kmol		3.300×10^4	
Initial total protein concentration	$CT_{a,0}$	%wb		for $n = n1$: 4.046×10^1 for $n = n2$: 4.159×10^1 for $n = n3$: 4.015×10^1 for $n = n4$: 4.398×10^1	
Protein solubility	$S_{a,0}$	%		for $n = n1$: 8.780×10^1 for $n = n2$: 8.790×10^1 for $n = n3$: 8.931×10^1 for $n = n4$: 8.846×10^1	
Agitation velocity	v	m/s		7.300×10^{-1}	
Extraction time	Θ	s		1.800×10^3	
Expeller weight	W_{β}	kg		1.500×10^{-1}	
Solvent volume	V_{γ}	m ³		3.000×10^{-3}	
Solvent density	$\rho_{\gamma}(T)$	kg/m ³	9.857×10^2	9.832×10^2	9.806×10^2
Solvent viscosity	$\mu_{\gamma}(T)$	Pa s	5.036×10^{-4}	4.660×10^{-4}	4.329×10^{-4}
Diffusivity of proteins within the solvent—Eq. (9)	$D_{a,\gamma}(T)$	m ² /s	1.910×10^{-10}	2.095×10^{-10}	2.289×10^{-10}
Reynolds number—Eq. (10)	$Re(T)$	–	6.144×10^2	6.623×10^2	7.110×10^2
Schmidt number—Eq. (11)	$Sc(T)$	–	2.675×10^3	2.226×10^3	1.928×10^3
Sherwood number—Eq. (12)	$Sh(T)$	–	3.289×10^2	3.229×10^2	3.173×10^2
Global mass transfer coefficient in the solvent phase—Eq. (13)	$k_{a,\gamma}(T)$	m/s	1.460×10^{-4}	1.573×10^{-4}	1.689×10^{-4}

Extraction mathematical model

Several authors (Garcia-Perez et al. 2010; Bäumler et al. 2011; Cissé et al. 2012) have proposed different possible mass transfer mechanisms to model the extraction process of a soluble solute from a solid matrix. For the extraction of proteins (soluble compound) from soy expeller (solid matrix) using water (solvent), the following phenomenological steps are considered:

- Solvent entry, penetration and diffusion inside the solid matrix. The solid particles are spherical and their radius is set to the mean experimental value. Size, shape and density of the particles do not change during the extraction process.
- Solubilization of the soluble compounds in alkaline media. The protein concentration is initially uniform within the solid particles.
- Solute transport to the surface of the solid matrix by diffusion according to the 1-D radial Fick's second law. The diffusion coefficient is independent of time.
- Convective migration of the extracted solute from the external surface into the bulk solution. The protein

concentration at the solid interface is at equilibrium with the one at the bulk solvent, where the protein concentration is homogeneous (perfect mixing) and only function of time. The volume of the solvent phase is kept constant.

Mass transfer

The internal mass transfer is described by Fick's second law in 1-D spherical coordinates according to Eq. (1), where $C_{a,\beta}$ is the protein concentration inside the particle, and $D_{a,\beta}$ is the diffusivity coefficient of proteins within the particle.

$$\frac{1}{D_{a,\beta}(T)} \frac{\partial C_{a,\beta}(n, c, T, r, \theta)}{\partial \theta} = \frac{\partial^2 C_{a,\beta}(n, c, T, r, \theta)}{\partial r^2} + \frac{2}{r} \frac{\partial C_{a,\beta}(n, c, T, r, \theta)}{\partial r}, \quad (1)$$

$$0 < r < R_{\beta}, \quad 0 \leq \theta \leq \Theta$$

The boundary conditions are introduced by Eqs. (2–3); the former corresponds to no mass transfer at the center of the sphere; and the latter represents the interfacial solute flux, where $k_{a,\gamma}$ is the global mass transfer coefficient in the

solvent phase, $C_{a,\gamma}$ is the concentration in the bulk solvent and $C_{a,i}$ is the concentration at the solid-solvent interphase.

$$\frac{\partial C_{a,\beta}(n, c, T, 0, \theta)}{\partial r} = 0, \quad 0 < \theta \leq \Theta \quad (2)$$

$$\begin{aligned} -D_{a,\beta}(T) \frac{\partial C_{a,\beta}(n, c, T, R_\beta, \theta)}{\partial r} \\ = k_{a,\gamma}(T) (C_{a,i}(n, c, T, \theta) - C_{a,\gamma}(n, c, T, \Theta)), \quad 0 < \theta \leq \Theta \end{aligned} \quad (3)$$

The initial condition, as introduced by Eq. (4), sets a homogeneous soluble protein concentration within the particles, computed considering the initial total protein concentration $CT_{a,0}$ and the initial protein solubility $S_{a,0}$. For the first cycle ($c = c1$), the initial protein concentration was determined as explained in “[Experimental data acquisition](#)” section for each EE sample; while for the subsequent cycles ($c = c2$ or $c = c3$), the initial concentration corresponds to the remnant one from the previous cycle.

$$C_{a,\beta}(n, c, T, r, 0) = CT_{a,0}(n, c)S_{a,0}(n, c), \quad 0 \leq r \leq R_\beta \quad (4)$$

According to (Bonfigli et al. 2017), the macroscopic mass transfer in both phases, in addition to the non-accumulation condition in the interface, can be reduced to Eq. (5), thus obtaining a system which is consistent with respect to the mass balances.

$$(1 - \varepsilon_\gamma) \frac{\partial \langle C_{a,\beta}(n, c, T, \theta) \rangle}{\partial \theta} = -\varepsilon_\gamma \frac{\partial C_{a,\gamma}(n, c, T, \theta)}{\partial \theta}, \quad 0 \leq r \leq R_\beta, \quad 0 < \theta \leq \Theta \quad (5)$$

The average protein concentration within the solid particles $C_{a,\beta}$ is determined by integrating radial concentrations over volume, as stated in Eq. (6).

$$\langle C_{a,\beta}(n, c, T, \theta) \rangle = \frac{\int_0^{V_\beta} C_{a,\beta}(n, c, T, r, \theta) dV}{\int_0^{V_\beta} dV}, \quad 0 \leq r \leq R_\beta, \quad 0 \leq \theta \leq \Theta \quad (6)$$

The interfacial equilibrium of the protein concentration $C_{a,i}$ is considered under the assumption of diluted solution, as expressed by Eq. (7), where $K(T)$ is the distribution constant.

$$C_{a,i}(n, c, T, \theta) = K(T)C_{a,\beta}(n, c, T, R_\beta, \theta), \quad 0 < \theta \leq \Theta \quad (7)$$

The protein mass balance at the equilibrium is given by Eq. (8).

$$\langle C_{a,\beta}(n, c, T, 0) \rangle V_\beta = \langle C_{a,\beta}(n, c, T, \Theta) \rangle V_\beta + C_{a,\gamma}(n, c, T, \Theta) V_\gamma \quad (8)$$

Input data

Table 1 lists the main model input data related to experimental parameters and physicochemical properties, obtained by means of analytical determination or from the literature.

The Polson correlation (Polson 1950) estimates the proteins diffusivity coefficient at the solvent phase $D_{a,\gamma}$, as given by Eq. (9).

$$D_{a,\gamma}(T) = 9.4010^{-15} \frac{T}{\mu_\gamma(T)(MW_a)^{1/3}} \quad (9)$$

The global mass transfer coefficient $k_{a,\gamma}$ is calculated using the correlation proposed by (Geankoplis 1993), according to Eqs. (10–13).

$$Re(T) = \frac{2R_\beta \rho_\gamma(T)v}{\mu_\gamma(T)} \quad (10)$$

$$Sc(T) = \frac{\mu_\gamma(T)}{D_{a,\gamma}(T)\rho_\gamma(T)} \quad (11)$$

$$Sh(T) = 2 + 0.95(Re(T))^{0.5}(Sc(T))^{1/3} \quad (12)$$

$$k_{a,\gamma}(T) = \frac{Sh(T)D_{a,\gamma}(T)}{2R_\beta} \quad (13)$$

Resolution strategy

The proposed mathematical model for extraction of soluble proteins from EE meals comprises Eqs. (1–8). Partial differential equations were discretized using the central finite difference method (CFDM) and the implicit method, which have first-order accuracy in time and second-order accuracy in space, and are unconditionally stable and convergent. This model was implemented in GAMS (General Algebraic Modeling System) and solved using CONOPT, an algorithm based on the reduced gradient method, as it involves around 3000 variables and non-linear constraints.

Results and discussion

Estimation of model parameters

In order to complete the proposed mathematical model for the EE meals soluble protein extraction, it becomes necessary to accurately estimate the distribution constant $K(T)$ and the diffusivity of proteins within the particle $D_{a,\beta}(T)$, since no suitable correlations have been found in the literature. For this purpose, and following the experimental procedure described in “[Experimental data acquisition](#)” section of this work, 16 data sets were acquired when

recovering soluble proteins from EE samples from four different processing plants using 2 to 3 consecutive extraction batch cycles operating at temperatures from 55 to 65 °C. This implies that 64 data points were taken, i.e., 4 for each data set, considering that the elevated cost of the analytical determinations constitute a bottleneck for data acquisition.

Following the procedure proposed by (Castillo-Santos et al. 2017), the distribution constant $K(T)$ is estimated as the slope of the protein equilibrium concentration between the solid and liquid phases, as presented in Fig. 1. By means of analysis of variance and Tukey pairwise comparisons, influence of the extraction operating temperature on the distribution constant is found to have statistical significance ($p < 0.05$). Values of $K(T)$ for each extraction temperature are listed in Table 2, being the coefficient of correlation (R^2) 78.7% and the adjusted coefficient of correlation (R^2_{adj}) 75.1%.

Afterwards, the diffusivity of proteins within the particle $D_{a,\beta}(T)$ can be estimated by computing the Fick's number that satisfies the Eqs. (14–15) presented by (Cacace and Mazza 2003), as plotted in Fig. 2. These equations provide an accurate estimation of the diffusivity when the Fick's number and the volume ratio are small, the dimensionless extract concentration is large, and the extraction time is short.

$$\frac{C_{a,\gamma}(n, c, T, \theta)}{C_{a,\gamma}(n, c, T, \Theta)} = (1 + \alpha(T)) \times \left(\frac{6}{\sqrt{\pi}} \phi(T) - 3(3 + \alpha(T))\phi(T)^2 + \frac{12(3 + \alpha(T))}{\sqrt{\pi}} \phi(T)^3 \right) \quad (14)$$

$$\alpha(T) = \frac{V_\gamma K(T)}{V_\beta}, \tau(T) = \frac{D_{a,\beta}(T)\theta}{(2R_\beta)^2}, \phi(T) = \frac{\sqrt{\tau(T)}}{\alpha(T)} \quad (15)$$

In addition, Arrhenius functionality is used to assess the impact of the extraction temperature in the process kinetics, according to Eq. (16), as a function of the pre-exponential constant A_a and the activation energy E_a .

$$D_{a,\beta}(T) = A_a \exp\left(-\frac{E_a}{RgT}\right) \quad (16)$$

Then, the obtained values of A_a , E_a and $D_{a,\beta}(T)$ for each extraction temperature are listed in Table 2, being the coefficient of correlation (R^2) 77.0% and the adjusted coefficient of correlation (R^2_{adj}) 73.2%.

It is also observed that the obtained values for the activation energy E_a , the diffusivity of proteins within the particle $D_{a,\beta}(T)$, as well as the distribution constant $K(T)$, are in the same order of magnitude than ones previously reported in the literature for soluble compounds extraction

from a vegetal matrix (Cacace and Mazza 2003; Castillo-Santos et al. 2017).

In addition, Eqs. (17–19) state the dependence of the parameters on the Arrhenius functionality with the activation entropy $\Delta S^\#$, activation enthalpy $\Delta H^\#$, and activation Gibbs's free energy $\Delta G^\#$ (Paunović et al. 2014; Jurinjak Tušek et al. 2016).

$$A_a = \frac{RgT}{Nh} \exp\left(-\frac{\Delta S^\#(T)}{Rg}\right) \quad (17)$$

$$\Delta H^\#(T) = E_a - RgT \quad (18)$$

$$\Delta G^\#(T) = \Delta H^\#(T) - T\Delta S^\#(T) \quad (19)$$

For example, the calculated parameters at an extraction temperature of 60 °C are: $\Delta S^\# = -4.918 \times 10^{-2}$ kJ/mol K, $\Delta H^\# = 1.120 \times 10^2$ kJ/mol, and $\Delta G^\# = 1.283 \times 10^2$ kJ/mol. These values are in the same order of magnitude than ones previously reported in the literature for the extraction of soluble compounds from a vegetal matrix (Paunović et al. 2014; Jurinjak Tušek et al. 2016).

Model validation

In order to validate the proposed model for the recovery of soluble protein from EE meals when using the previously obtained values for the mass transfer parameters, and following the experimental procedure described in “[Experimental data acquisition](#)” section of this work, 25 data sets were independently acquired when recovering soluble proteins from EE samples from 4 different processing plants using 2 to 3 consecutive extraction batch cycles operating at temperatures from 55 to 65 °C. This implies that 100 data points were taken, i.e., 4 for each data set, considering that the elevated cost of the analytical determinations constitute a bottleneck for data acquisition.

Then, the experimental protein concentration values are compared with the ones predicted by the model, while the root-mean-square error (*RMSE*) and correlation coefficient (R^2) are computed to provide a measure of the predictive capabilities of the model.

Figure 3 presents the confidence intervals for the experimental data, as it is the region where 95% of the regression lines are expected to be, and contain more than 50% of the experimental values for all the experiences here reported. Additionally, the recovered soluble protein content predicted by the model is also plotted, where the average root mean square error (*RMSE*) value is 0.191 and the average correlation coefficient (R^2) is 0.945, thus indicating a good agreement between the experimental and predicted values.

Fig. 1 Estimation of the distribution constant

Table 2 Estimated values of mass transfer coefficients

Item	Symbol	Units	Value		
			for $T = 55\text{ }^{\circ}\text{C}$	for $T = 60\text{ }^{\circ}\text{C}$	for $T = 65\text{ }^{\circ}\text{C}$
Distribution constant	$K(T)$	–	$3.941 \times 10^{-2} \pm 2.54 \times 10^{-3}$	$6.991 \times 10^{-2} \pm 2.00 \times 10^{-2}$	$1.232 \times 10^{-1} \pm 2.14 \times 10^{-2}$
Diffusivity of proteins within the particle	$D_{a,\beta}(T)$	m^2/s	$1.022 \times 10^{-11} \pm 1.26 \times 10^{-12}$	$1.921 \times 10^{-11} \pm 5.70 \times 10^{-12}$	$3.544 \times 10^{-11} \pm 5.47 \times 10^{-12}$
Arrhenius constant	A_a	m^2/s	$1.790 \times 10^7 \pm 3.131 \times 10^3$		
Activation energy	E_a	kJ/mol	$1.147 \times 10^2 \pm 1.97 \times 10^{-1}$		

Prediction of the extraction yield

Extraction yield ($Y(n, c, T)$) is a measure of the soluble protein recovery efficiency from the expeller, as defined by Eq. (20).

$$Y(n, c, T) = \frac{C_{a,\gamma}(n, c, T, \theta) V_{\gamma}}{C_{a,\beta}(n, c, T, R_{\beta}, 0) V_{\beta}} 100 \quad (20)$$

The expected extraction yield is presented in Fig. 4, for different number of processing cycles $c = c_1, c_2, c_3$ when the operating temperatures are set at 55, 60 or 65 °C. Here, it is observed that each subsequent cycle recovers increasingly less soluble protein than the previous ones, where a larger difference is found between the first and

second ones than between the second and third ones because of the decrease on the mass transfer driving force, being this difference more noticeable at higher extraction temperatures where the diffusivity is larger. Meanwhile, it is also noted that the largest increment in the extraction yield with respect to the operating temperature occurs in the first cycle.

Figure 4 also introduces the cumulative extraction yield which is attained when using successive extraction cycles. It is observed that increasing the operating temperature from 55 to 60 °C implies an average 16.9% increment in the extraction yield, while it averages an extra 13.7% when the temperature is further increased to 65 °C.

Fig. 2 Estimation of the diffusivity of proteins within the particle

Fig. 3 Confidence bands and predicted values for the soluble protein concentration

For a given operating temperature, an average 53% of the total recovered proteins are extracted in the first cycle, with average efficiencies of 30% and 17% in the second

and third ones, respectively. Moreover, a better performance for the whole extraction process is obtained when the operating temperature increases, as a consequence of

Fig. 4 Extraction yield for different number of cycles and operating temperatures

larger values for the mass transfer and kinetic coefficients (as previously shown in Tables 1, 2). Nevertheless, the processing temperature cannot be increased indefinitely, because bioactive compounds (like proteins) are relatively thermo-labile, being susceptible to degradation at temperatures higher than around 70 °C (Pingret et al. 2013).

Conclusion

A mathematical model to study soluble protein extraction from Argentinian expeller meals was developed as part of a challenge project that has the objective of producing soybean protein concentrate using the expeller byproduct. Experimental data using 1 to 3 extraction cycles and operating temperatures from 55 to 65 °C was acquired using expeller from 4 processing plants. Then, 16 data sets were used to estimate the distribution constants and the diffusivities within the solid particles. Semi-empirical correlations as well as experimental data (like the average molecular weights of the extracted proteins and the initial solubility of the proteins) were implemented in the model in order to adequately describe the mass transfer mechanisms. Then, 25 independent experimental data sets were used for validation purposes. The influence of the number of extraction cycles and operating temperature on the extraction yield was also analyzed, where it was found that

the larger cumulative extraction yield is achieved for the higher operating temperature (allowed by the degradation goal) and the maximum number of extraction cycles.

According to this, the model here developed will be expanded to optimize the design of the entire production process from a cost-effective point of view.

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