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Solid-liquid Extraction of Soluble Carbohydrates from Soybean Meal: an Experimental Study, Kinetics, and Modeling

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HIGHLIGHTS

- SPC is obtained by solid-liquid extraction process with hydroalcoholic solvent.
- Box-Behnken was applied to evaluate the effect of operational parameters.
- Soluble carbohydrate extraction from DSM is limited by intraparticle diffusion.
- Diffusion coefficient of stachyose, raffinose, sucrose, and glucose was estimated.

Abstract: Soybean Protein concentrate is a product from the soy processing industry with high value, but to obtain it is necessary to evaluate the favorable operational conditions to extract soluble carbohydrate from soybean meal with low loss of protein. The solid-liquid extraction of soluble carbohydrates compounds from soybean meal was evaluated in view to estimate the influence of the operational parameters and the kinetic of soluble carbohydrates extraction. The influence of temperature (45-65°C), mean diameter (0.6-1.4 mm), and mass/solvent ratio (5-15 mg/mL) was investigated by Box-Behnken 3^{3-1} central composite design. The soluble carbohydrate compounds over time were investigated using three mathematical models (equilibrium-dependent, Peleg, and intra-particle diffusion). The results at Box-Behnken indicated that higher temperatures and DSM to the solvent ratio resulted in increased extraction yield of the soluble carbohydrates, while the DSM particle size showed a minor influence. According to the kinetics data, the extraction process approached equilibrium after around 120-180 min. The conditions that maximized the extraction were 60°C and DSM to the solvent ratio of 10 mg/mL, resulting in the reduction of the total soluble total carbohydrate content in DSM of 29.5% to 15.1%, resulting in soy protein concentration in DSM of 65.8%, compatible with the standard protein content of SPC product. The intraparticle diffusion model was found to be the most suitable to describe the extraction process due to the best fit with the experimental data.

Keywords: Deffated soybean meal; batch process extraction; stachyose; raffinose; intraparticle diffusion.

INTRODUCTION

The Soybean [Glycine max (L.) Merrill] is one of the most cultivated grains in the world, being largely for the production of vegetable oil and protein. Currently, Brazil is the world's largest producer of soy, with the 2020/2021 harvest having an estimated production of 139,978 million tons [1-2]. About 78–80% of soybeans result in bran, 18–20% in oil, and the rest in the form of low-value, high-fiber feed. Soybean meal (SBM) is obtained from the partial removal of the oil contained in the soybean, which is carried out through direct solvent extraction [3].

SBM is the main source of protein used in the poultry and livestock industries worldwide. Of all SBM sold in the United States, over 50% is used in poultry diets and 26% is used in swine diets. The main reason for SBM's popularity is the quality and unique amino acid composition that complements many cereal grains [4]. Soy protein concentrate (SPC) is produced by extracting soluble carbohydrates from SBM using alcohol, acid, or hot water [5]. Soy protein concentrates (SPCs) contain a minimum of 65% protein (dry basis) and are mostly flours of which the water or alcohol soluble components, especially flatulence-promoting sugars and strong flavor compounds, are leached [6-7].

SPC is a product with greater added value, compared to soybean meal, as it has higher protein content and lower amounts of antinutritional factors (antigens, trypsin inhibitors, oligosaccharides, and phytic acid). This allows this product to be applied in feed for the fish diet, as well as in the feeding of piglets and calves in the weaning phase [8]. According to Deak and coauthors [7], SPC yields 75% of the defatted flake weight and can be processed by three basic procedures: extraction with 20 to 80% aqueous ethyl alcohol, acid leaching or denature the protein with moist heat and extract with water. As described in patent PI0704760-6 A2, it is preferable to use the hypro bran (48% of protein), from soybean waste after oil extraction, and a hydro-alcoholic solution (ethanol of 62% w/w). The amount of alcohol can vary from 3.0 to 6.0 liters per kg of bran [9].

The SPC yield and quality depend on the efficiency of the soluble carbohydrates extraction process from the soybean meal. The yield and quality of the SPC produced depend on the efficiency of the extraction process of soluble carbohydrates from soybean meal. Thus, the operational variables associated with the solid-liquid extraction process (soybean meal granulometry, extraction time, temperature, and the soybean meal mass to solvent volume ratio) must be carefully studied. To optimize this process, therefore, it is necessary to evaluate the appropriate process conditions by experimental design and the kinetic studies associated with their corresponding mathematical modeling, whether empirical or phenomenological [10].

Studies on the quantification and characterization of soybean meal carbohydrates are found in the literature [11-13], however, there are no related studies of solid-liquid extraction of the soluble carbohydrate from DSM with hydroalcoholic solvent, with a systematic evaluation of operating parameters, as well as their respective process modeling Thus, this study aimed to evaluate the influence of process variables (temperature, particle diameter and soybean meal to solvent ratio) and kinetics in the extraction of soluble carbohydrates from SMB soybean meal. Furthermore, different models were used to reproduce the kinetic data and evaluate the mass transfer mechanisms involved in the process.

MATERIAL AND METHODS

Materials

A defatted soybean meal (DSM) was obtained from IMCOPA (Araucária, PR, Brazil). Sugars standards (stachyose, raffinose, sucrose, and glucose) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethanol absolute was purchased from Neon (Suzano, SP, Brazil).

Extraction from defatted soybean meal

The extractions were conducted in batch mode operation. Solvent (ethanol/water at 62% of ethanol w/w) previously heated up to the temperature of extraction, was transferred for the glass flasks containing DSM sample. The mixture was immediately closed and placed in a thermal bath (glycerol) to start the extraction. A heating plate with magnetic stirring and a thermometer was used to keep and check the temperature during all times of extraction. After extraction, the DSM particles were immediately separated using filter paper and the liquid fractions were submitted to determinations of sugars and total soluble solids (total yield).

Our study evaluated different variables in the process of extracting sugars from DSM. Firstly, an experimental design Box-Behnken 3^{3-1} was made to evaluate the effect of the variables: temperature (45°C,

55°C, and 65°C), DSM to the solvent ratio (5.0 mg/mL, 10. mg/mL, and 15 mg/mL) and particle size of DSM (0.6 mm, 1.0 mm, and 1.4 mm). All assays were conducted for 20 minutes with ethanol solution (62% w/w). Second, the kinetics of the batch solid-liquid extraction was studied at different time intervals (5, 15, 30, 60, 120, 240 and 360 min) at different temperatures (45°C, 55°C, and 65°C), DSM to the solvent ratio of 10 mg/mL and particle size of 1.0 mm. The samples of solvent extract were filtered and stored in amber vials under refrigeration (4°C) until analysis.

Extraction from defatted soybean meal

The kinetics of soluble carbohydrate extraction of soybean meal was evaluated using three mathematical models. The equilibrium-dependent model, intra-particle diffusion model, and the Peleg model were applied to describe the kinetics curves obtained experimentally at 45°C, 55°C, and 65°C (particle size of DSM of 1.00 mm and DSM to the solvent ratio of 10 mg/mL).

Equilibrium-dependent model

This model is based on the solute mass transfer between the surface solid and liquid solvent. The driving force is the linear gradient between the solute concentration at the time and the equilibrium solute concentration, without any internal solid diffusion resistance [14].

$$\frac{dC}{dt} = k \cdot [C_\infty - C(t)] \quad (1)$$

Where C is the solute concentration in the liquid phase (mg L-1), k is the solute transport coefficient (min-1) and C_∞ is the solute concentration equilibrium (mg L-1), t is the processing time (min). Integrating the differential equation (1), with the boundary condition (t=0, C=0), the equilibrium-dependent model is obtained (Eq. 2).

$$C(t) = C_\infty \cdot [1 - e^{-k \cdot t}] \quad (2)$$

The Peleg model

The empirical Peleg model [15], adapted to solid-liquid extraction process modeling, as described by Eq. (3), where K_1 is the Peleg rate constant (min L mg^{-1}), K_2 is the Peleg capacity constant (L mg^{-1}). For solid-liquid extraction, Co is usually equal to zero.

$$C = Co + \frac{t}{K_1 + K_2 . t} \quad (3)$$

Intra-particle diffusion model

This model considers the solute mass transfer is limited by internal diffusion. The extraction of a solute from spherical particles with radius R, considering the solute diffusion constant ante the mass flux is described second Fick's law, as Eq. (4)

$$\frac{\partial X}{\partial t} = D_{EF} \cdot \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial X}{\partial r}\right)\right] \quad (4)$$

The analytical solution for Eq. (04), express in average carbohydrate concentration in the solid particle (X), is described by Eq. (4) [16]. The experimental values of the carbohydrates concentration in the solid particle were obtained by Eq. (5). Eq. (6) is the mass balance that correlates the amount of carbohydrate in DSM particle and carbohydrate concentration in the hydroalcoholic solvent phase.

$$(\mathrm{t}) = X_0 + (X_\infty - X_0) \cdot \left[1 - \frac{6}{\pi^2} \cdot \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot exp\left(-\frac{n^2 \cdot \pi^2 \cdot D_{EF}}{R^2} \cdot t\right)\right] \quad (5)$$

$$\mathrm{X(t)} = X_0 - \frac{V}{M} \cdot C(t) \quad (6)$$

Where X∞ is the solute concentration in the solid particle at equilibrium (mg g-1); X0 is the initial solute concentration in the solid particle (mg g-1), V is the total water extraction volume (L) and M is the DSM mass used in the batch extraction (g), DEF is the effective coefficient of diffusion for the solute inside the solid particle (mm^2 min-1)

DSM characterization and soluble carbohydrate quantification

The DSM samples were subjected to particle size analysis, following the official methodology established by MAPA [17]. The #7, #9, #12, #16, and #28 mesh sieves were used. The sieving was carried out in a vibrator device, turned on for a period of 10 minutes. The chemical composition of DSM was determined by analyzing the humidity, ash, total protein, and total fiber contents according to the protocols described in AOAC [18]. Lipid content was determined using the Bligh and Dyer method [19], and total carbohydrate content was obtained from the difference from 100 % of the sum of the remaining contents.

The total solid extraction content was determined by evaporation to constant mass at 373.15 K in a circulation oven (Nova Etica, model RV-10, Brazil). The most relevant soluble carbohydrates present in the DSM (stachyose, raffinose, sucrose, and glucose) were quantified for all extracts obtained from DSM [20]. Sugars determinations were performed using an ACQUITY UPLC H-Class System with refractive index detector (Waters, Miliford, MA, EUA) and a column Aminex Bio-Rad HPX-87H (300 x 7.8 mm, 9 μm). The injection volume was 10 μL, the mobile phase was water with 5 mmol/L of H_2SO_4 and the elution flow was 0.6 mL/min. The temperature column and detector were maintained at 50 °C. Sugars in the extracts were identified comparing their retention times to standard sugars. The quantification of individual sugars was by external calibration.

Statistical analysis

The regression coefficients for the linear and interaction terms were determined by multiple linear regressions and the Student t-test was used to verify their statistical significance. Analysis of variance (ANOVA) was applied to validate models. StatSoft STATISTICA software (version 10.0) was used for all of the calculations. The relative mean errors (RME) and coefficient of determination (R^2) were determined as the evaluation criteria for the kinetic models.

RESULTS

DSM characterization

The chemical composition of the fractioned DMS samples at different sieve sizes was showed in Table 1. The different particles sizes of DSM showed statistical differences for each assay evaluated, probably due to the heterogeneous morphology of the DSM sample retained from each sieve size. Although the analysis of variance and Tukey's test report statistical differences between each sieve size, the composition showed similar for all analysis and particle size: the humidity is almost 12.5%, the total amount of lipids, ash, and fiber content was lower than 13% of the DSM total chemical composition, and all particle size have soluble carbohydrate and protein compositions higher than 25.93% and 47.49%, respectively. Thus, all fractions of DSM can be suitable for the production of SPC.

Table 1. Proximate chemical composition of soybean meal fractions*.

Particle size (mm)	Fraction** (%)	Protein (%)	Humidity (%)	Total Fiber (%)	Ash (%)	Lipid (%)	Carbohydrate (%)
> 2.80	8.7	48.46 ± 0.14^{B}	12.05 ± 0.03^{C}	3.85 ± 0.13^{B}	6.35 ± 0.09^{B}	0.70 ± 0.03^{C}	28.59 ± 0.06^{B}
2.00	13.7	49.42 ± 0.12^{A}	12.39 ± 0.05^{A}	3.84 ± 0.04^{B}	6.29 ± 0.05^{B}	0.67 ± 0.02^{C}	27.39 ± 0.13^{D}
1.40	26.7	48.67 ± 0.11^{B}	12.39 ± 0.04^{A}	4.28 ± 0.12^{A}	6.16 ± 0.17^{B}	0.85 ± 0.01^{B}	27.65 ± 0.29^{CD}
1.00	20.5	47.49 ± 0.07^{C}	12.16 ± 0.07^{BC}	3.52 ± 0.12^{C}	6.23 ± 0.13^{B}	0.66 ± 0.05^{C}	29.94 ± 0.15^{A}
0.60	15.5	49.66 ± 0.08^{A}	12.46 ± 0.02^{A}	2.90 ± 0.08^{D}	6.23 ± 0.04^{B}	0.63 ± 0.03^{C}	28.11 ± 0.10^{C}
< 0.60	14.8	49.53 ± 0.08^{A}	12.19 ± 0.05^{B}	3.12 ± 0.11^{D}	7.99 ± 0.06^{A}	1.23 ± 0.01^{A}	25.93 ± 0.19^{E}

* Means with the same lower case letters in the same column represent no statistical differences according to Tukey's test ($p < 0.05$).
** Mass fraction of DSM retained in the mesh sieves of #7, #9, #12, #16, and #28, respectively.

Evaluate soluble carbohydrate solid-liquid extraction

The effect of some operational variables that could affect the total soluble carbohydrate extraction yield was initially studied by experimental design Box-Behnken 3^{3-1}, with the operational variables: temperature (45°C, 55°C, and 65°C), DSM to the solvent ratio (5.0 mg mL^{-1}, 10 mg mL^{-1}, and 15 mg mL^{-1}) and particle size of DSM (0.6 mm, 1.0 mm, and 1.4 mm). Table 2 reports the yield of total solid extract (TSE), stachyose,

raffinose, sucrose, and glucose. Total carbohydrate soluble was also reported in Table 2. According to the analysis of variance (ANOVA), the operational parameters have a significant influence on the total solid extract and soluble carbohydrate extraction at hydro alcoholic solvent (ethanol 62% w/w). Temperature and DSM to the solvent ratio showed the most relevant effects for the soluble carbohydrate extraction (Figure 1(a)), while the total solid extraction showed statistical of all operational parameters (Figure 1(b)).

Table 2. Total solid and soluble carbohydrate extract from solid-liquid extraction process of DSM*.

Treatments*	Total Solid extract (g/100g)	Stachyose (g/100g)	Raffinose (g/100g)	Sucrose (g/100g)	Glucose (g/100g)	Total soluble carbohydrates (g/100g)
45-0.6-10	14.94 ± 0.50^{B}	$2.19 \pm 0,02^{G}$	$0.77 \pm 0,03^{C}$	$5.27 \pm 0,07^{E}$	$0.53 \pm 0,03^{BC}$	8.76 ± 0.09^{E}
45-1.4-10	11.59 ± 0.32^{D}	1.68 ± 0.02^{I}	0.57 ± 0.03^{D}	3.86 ± 0.07^{G}	0.27 ± 0.03^{D}	6.37 ± 0.09^{H}
45-1.0-05	11.94 ± 0.09^{D}	1.73 ± 0.01^{I}	0.74 ± 0.02^{C}	4.38 ± 0.04^{F}	0.48 ± 0.01^{C}	7.32 ± 0.04^{G}
45-1.0-15	14.06 ± 0.42^{BC}	2.01 ± 0.03^{H}	0.56 ± 0.05^{D}	4.31 ± 0.11^{F}	0.30 ± 0.01^{D}	7.19 ± 0.12^{G}
55-0.6-05	15.90 ± 0.09^{B}	2.33 ± 0.01^{DE}	1.00 ± 0.02^{B}	5.87 ± 0.04^{D}	0.65 ± 0.02^{A}	9.85 ± 0.04^{D}
55-1.4-05	12.25 ± 0.62^{CD}	0.70 ± 0.01^{J}	0.21 ± 0.02^{E}	1.59 ± 0.04^{H}	0.12 ± 0.01^{E}	2.63 ± 0.04^{I}
55-0.6-15	19.91 ± 0.44^{A}	3.03 ± 0.03^{C}	0.98 ± 0.05^{B}	6.37 ± 0.11^{C}	0.55 ± 0.04^{BC}	10.93 ± 0.13^{C}
55-1.4-15	15.91 ± 0.71^{B}	2.25 ± 0.03^{FG}	0.60 ± 0.05^{D}	4.44 ± 0.11^{F}	0.31 ± 0.03^{D}	7.60 ± 0.13^{F}
65-0.6-10	20.98 ± 0.54^{A}	3.09 ± 0.02^{BC}	1.18 ± 0.03^{A}	6.23 ± 0.07^{C}	0.54 ± 0.03^{BC}	11.05 ± 0.09^{C}
65-1.4-10	19.34 ± 1.37^{A}	3.13 ± 0.02^{B}	1.20 ± 0.03^{A}	6.64 ± 0.07^{B}	0.66 ± 0.03^{A}	11.64 ± 0.09^{B}
65-1.0-05	15.89 ± 0.30^{B}	2.37 ± 0.01^{D}	1.00 ± 0.02^{B}	5.80 ± 0.04^{D}	0.59 ± 0.02^{AB}	9.75 ± 0.04^{D}
65-1.0-15	20.47 ± 0.96^{A}	3.59 ± 0.03^{A}	1.20 ± 0.05^{A}	7.00 ± 0.11^{A}	0.49 ± 0.02^{BC}	12.48 ± 0.12^{A}
55-1.0-10	15.79 ± 0.74^{B}	2.29 ± 0.02^{EF}	0.81 ± 0.03^{C}	5.24 ± 0.07^{E}	0.48 ± 0.03^{C}	8.82 ± 0.09^{E}

Means with the same lower case letters in the same column represent no statistical differences according to Tukey's test ($p < 0.05$).
* Experimental conditions: temperature (°C), DSM particle size (mm), DSM to the solvent ratio (mg/mL). Extraction time: 20 minutes.

As reported in Table 2, the soluble carbohydrate composition showed the sucrose as the major carbohydrate extracted during the hydroalcoholic extraction process of the soybean meal, equivalent to 60% of total soluble carbohydrates extracted, while the oligosaccharides stachyose and raffinose represents almost 35%, and glucose in the minor composition, about 5% of the total soluble carbohydrate estimated. The oligosaccharides observed is similar that reported by Oliveira and coauthors [21], who reported concentration of raffinose and stachyose ranging from 0.392 to 1.104 g/100g and 2.236 to 4.405 g/100g, respectively, in a study with 28 genotypes/cultivars registered in the EMBRAPA Soybean Gemplasm Bank.

The amount of soluble carbohydrate content observed in the total soluble extract varies between 47.8% and 61.9%, while the maximum amount of soybean protein content in the total soluble extract was 13.7%. To the SPC process is desirable to remove soluble carbohydrates with the lowest loss of soybean protein possible. Although the carbohydrates were more soluble in an aqueous solvent, the use of a hydroalcoholic solvent (with a partial composition of water) prevents the undesirable protein extraction with high soluble carbohydrate extraction that could be applied to concentrate the DSM (almost 48% w/w) to SPC (higher than 65% w/w) [9].

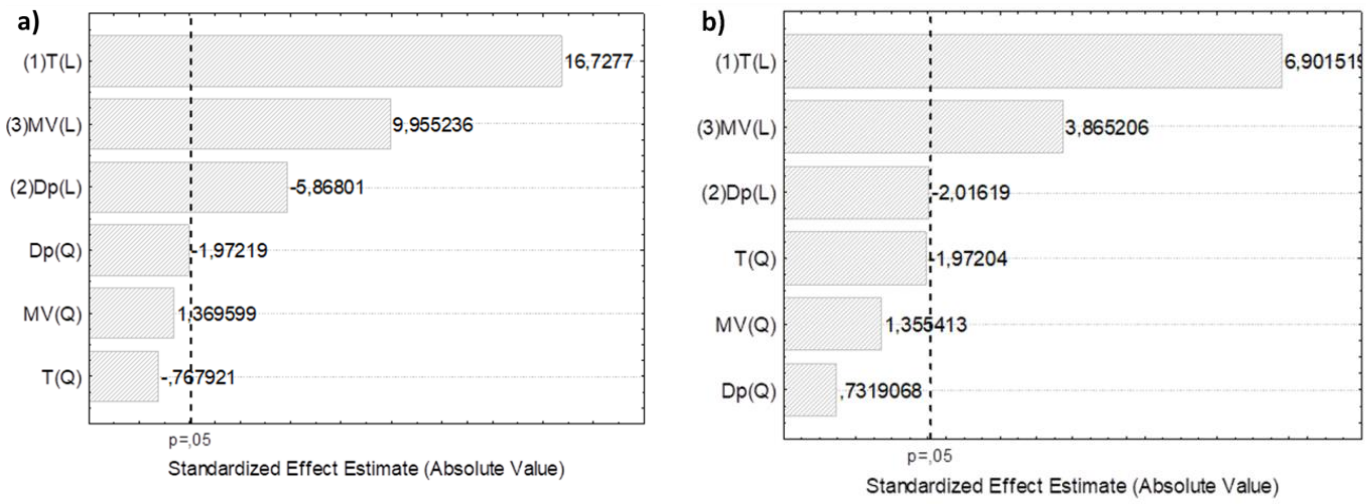

Figure 1. Pareto analysis of the variables on the total solid (a) and total soluble carbohydrate (b) extraction. T – temperature (°C), MV - DSM to the solvent ratio (mg/mL), Dp – DSM particle size, L – linear dependence, Q – Quadratic dependence.

Extraction kinetics of the soluble carbohydrate

The extraction kinetics curves (Figure 2) for the compounds obtained from DSM showed typical behavior, under all experimental conditions, similar as reported in studies of solid-liquid extraction of an interesting solute (phenolic, anthocianins, lipids) from leaves, grans and pulps [10, 12, 14, 22]. Initially, there was a fast extraction rate until 50 minutes of the batch extraction process, followed by a slow extraction stage with a decrease in the extraction rate over time. As reported in several studies of solid-liquid extraction in batch mode operation, the extraction process can thus be easily separated into two stages: a washing stage, step with the solute onto the surface are leached into the bulk liquid phase; and an intraparticle diffusion rate under the porous particles, where the solvent penetrates the solid and dissolves the solute, which diffuses to the surface. The porosity and tortuosity of the paths inside the solids offer resistance to diffusion, making the extraction rate lower than the first step [10, 22]. The soluble carbohydrate extraction approaches to equilibrium due by limiting the soluble carbohydrate saturation of the hydroalcoholic solvent, or even by depletion and difficulty in extracting the solute inside the DSM particle.

The batch process extraction with hydroalcoholic solution promotes the rich of soybean protein due to the extraction of soluble carbohydrates as shown in Figure 3. For extraction conducted at 65°C and DSM to the solvent ratio of 10 mg/mL, the total carbohydrate content reduces 29.5% to 15.1% while the protein concentration in DSM increase from 47.5% to 56.8% after 360 minutes. The amount of protein obtained after 360 minutes corresponding to 65.8 on a dry basis, which corresponding to the SPC concentration (over 65% on a dry basis) [23]. To obtain a higher protein concentration in the SPC or obtained at least 65% of protein (dry basis) in lower operational time than observed in our study, is necessary to increase the solvent temperature (until near the hydroalcoholic solvent boiling point) and increase the DSM to the solvent ratio above the 10 mg/mL evaluated in this study.

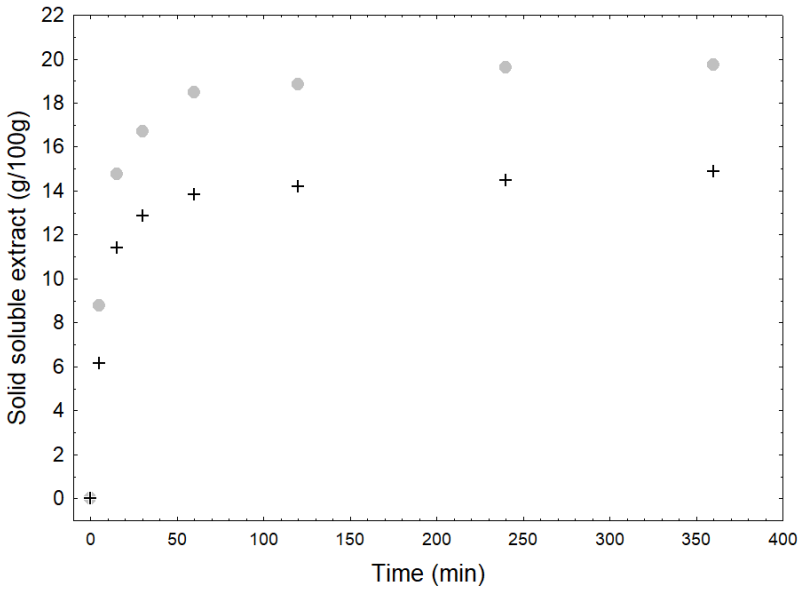

Figure 2. Solid-liquid extraction in batch mode operation: kinetics of total solid extract (●) and total soluble carbohydrate (**+**). Operational conditions: Temperature of 65°C, DSM to the solvent ratio of 10 mg/mL, DSM particle size of 1.0 mm.

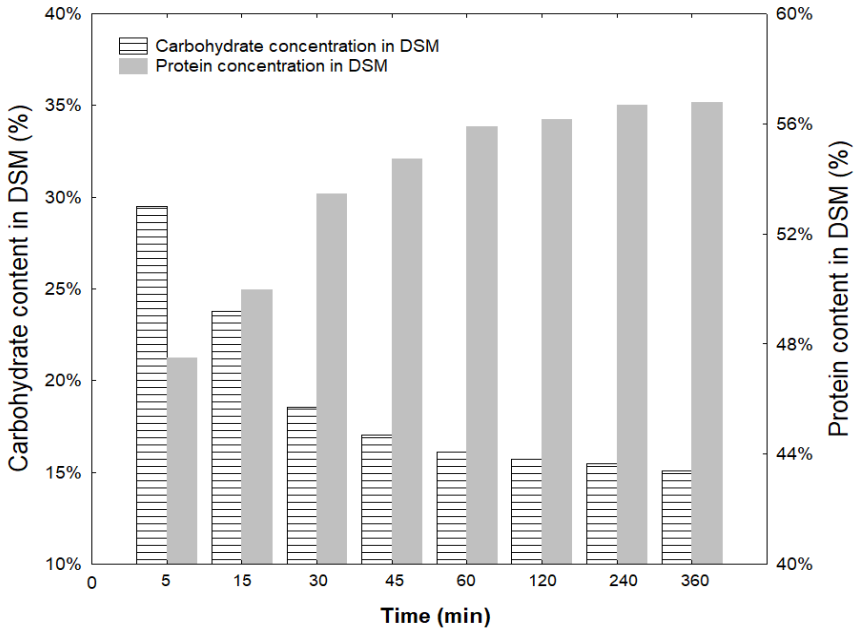

Figure 3. Solid-liquid extraction in batch mode operation: total soluble carbohydrate (▤) and soy protein (▬) content in DSM particle over the solid-liquid extraction in batch mode operation. Operational conditions: Temperature of 65°C, DSM to the solvent ratio of 10 mg/mL, DSM particle size of 1.0 mm.

The extraction kinetics curves for the soluble carbohydrate evaluated in this study (stachyose, raffinose, sucrose, and glucose) showed behavior similar at the total soluble carbohydrate (Figure 3) for the range of temperature evaluated. Initially, there was a fast increase in the soluble carbohydrate concentration in the hydroalcoholic phase, followed by a slow extraction stage with a decrease in the extraction rate over time (Figure 4a-d).

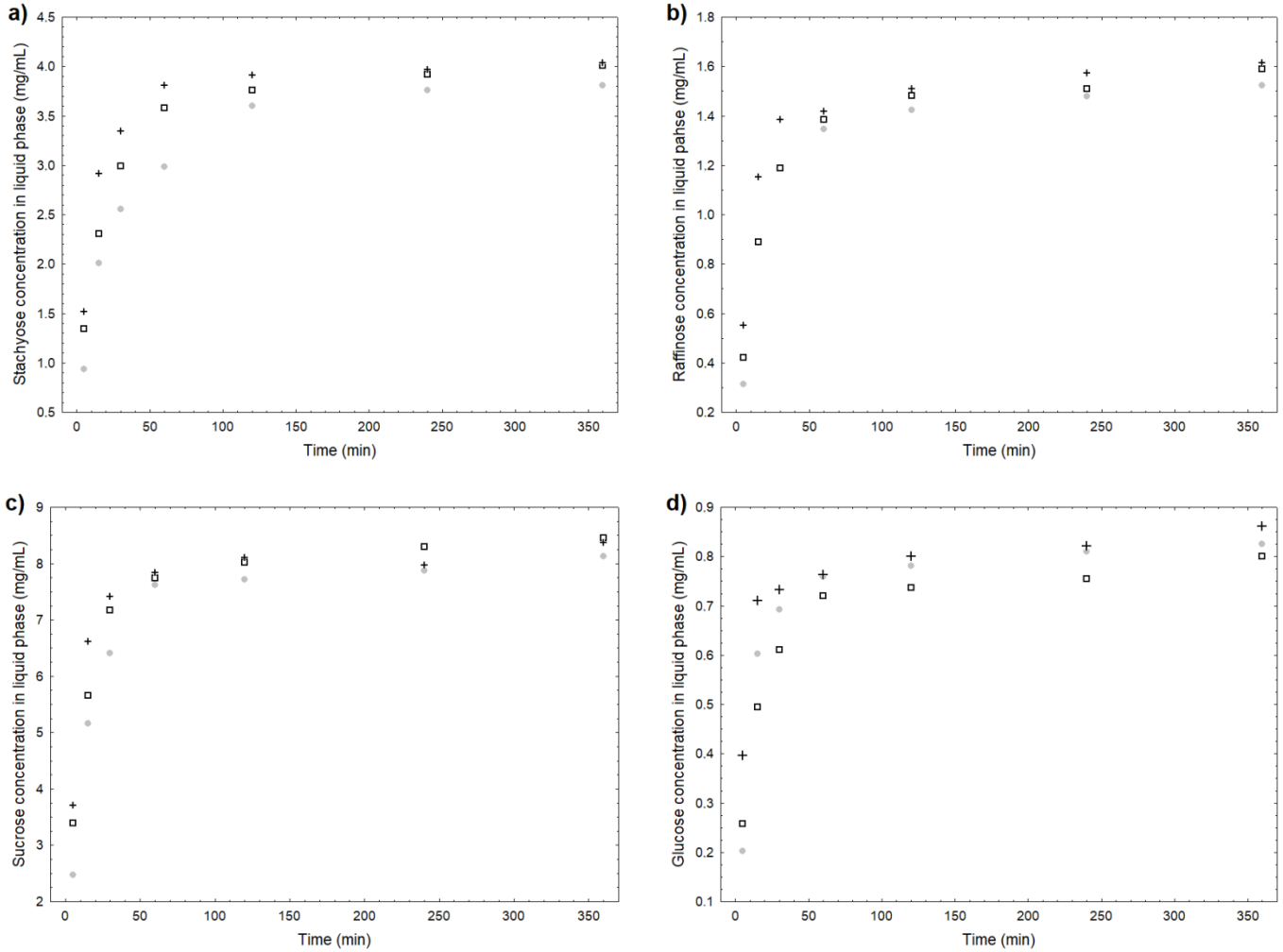

Figure 4. Hydroalcoholic kinetics for stachyose (a), raffinose (b), sucrose (c), and glucose (d).Operational condition: DSM to the solvent ratio of 10 mg/mL, DSM particle size of 1.0 mm, Temperature: 45°C (●), 55°C (□), and 65°C (+).

High temperatures increase the extraction rate of carbohydrates, probably due to the increases in their solubility in the solvent system and the increase of the carbohydrate diffusion in the solvent. Also, high temperatures promote the solvent viscosity decrease of the solvent, which is favorable for carbohydrate diffusion in the solvent inside of the DSM particle. Furthermore, most of the carbohydrate extraction occurs at the beginning of the process (washing stage), when 70-90 % of the total soluble carbohydrates removed during the all extraction process is obtained in the first 60 minutes, while at 120 minutes the amount of soluble carbohydrate extracted is statistically equal of 360 minutes ($p<0.05$), what suggest the extraction system tends to equilibrium, limited by carbohydrate solubility in the solvent system and the lower concentration gradient between DSM internal particle and liquid solvent carbohydrate concentration. In our study, the temperature of 65 °C reaches equilibrium condition more quickly than at lower temperatures, but a temperature of 45 °C is sufficient to deplete the soluble sugars present in the soybean meal until the solvent solubility.

Ekvall [24] evaluated the extraction of raffinose and stachyose from leguminous vine pea. The high amount of oligosaccharides and glucose was obtained with hydroalcoholic solvent (50% ethanol), after 60 minutes, with yield extraction of 28.4% and 16.3% of raffinose and stachyose, respectively, with a boiling point solvent extraction. The authors concluded that the extraction process time is the most relevant operational parameter to develop the leaching of oligosaccharides from vine pea.

Mathematical modeling of soluble carbohydrate extraction

Modeling the solid-liquid extraction process is a very important tool for the development of the solid-liquid extraction process, as the process optimization or design of the unit operations and equipment applied in the leaching process. Thus, the goal of empirical and phenomenological mathematical models is to provide an

output (yield of solid-liquid extraction or the soluble carbohydrate concentration) base on input data, such as temperature, DSM to the solvent ratio, DSM particle size, and operational time.

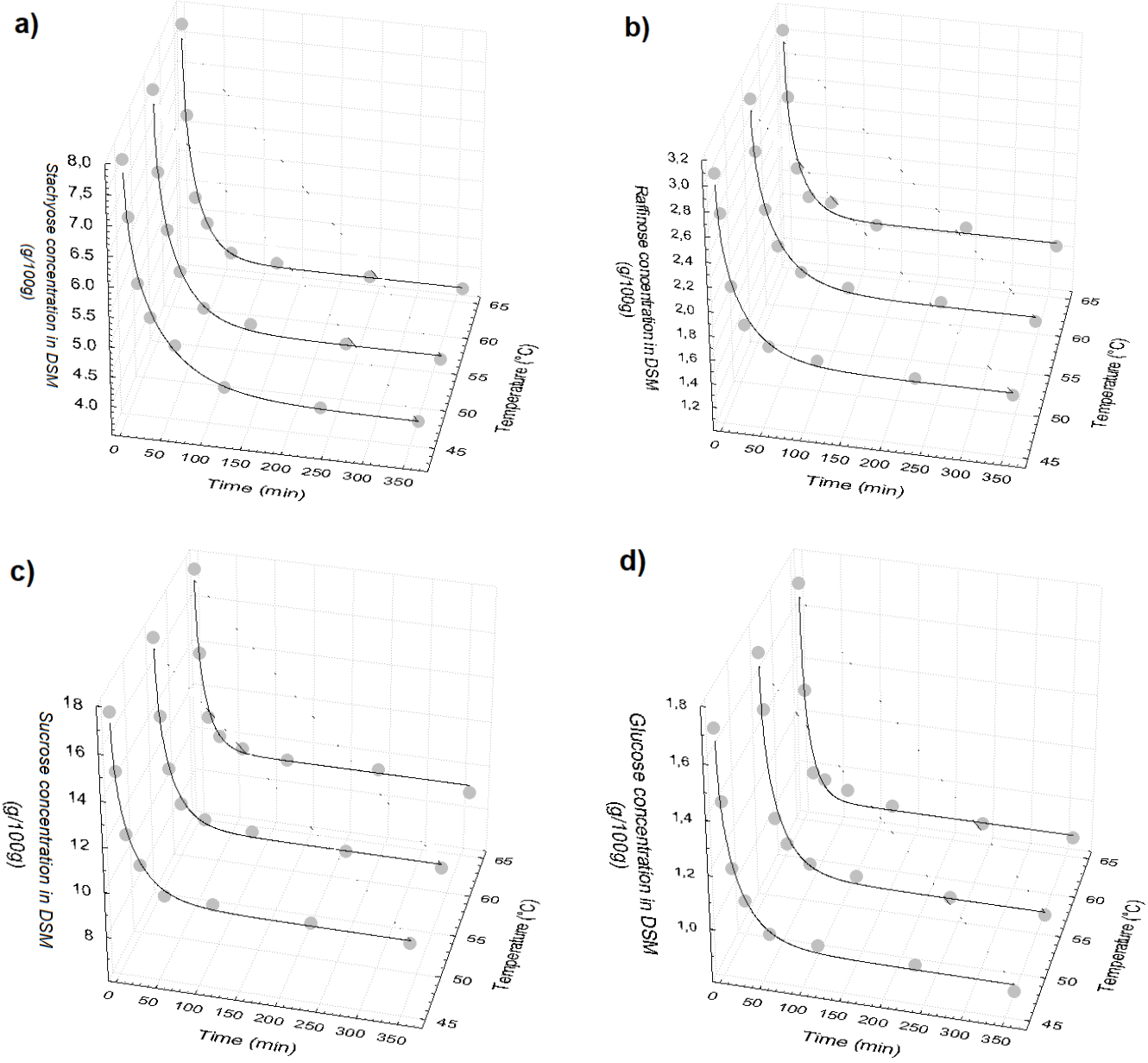

Figure 5. Comparison between the extraction kinetics results obtained experimentally and the intraparticle diffusion model for (a) stachyose, (b) raffinose, (c) sucrose, and (d). Symbols are experimental data and lines are model results: Operational condition: DSM to the solvent ratio of 10 mg/mL, DSM particle size of 1.0 mm.

Table 3. Modeling parameters of stachyose, raffinose, sucrose, and glucose extraction from DSM*.

Model	Parameter	45°C	55°C	65°C
Stachyose				
Equilibrium-dependent model	k x 10^2	4.82 ± 0.60	6.21 ± 0.69	9.12 ± 0.72
	Co	3.53 ± 0.12	3.81 ± 0.09	3.85 ± 0.07
	R^2	94.81	96.04	97.34
	RME (%)	8.86	6.41	3.70
Intraparticle diffusion	D_{EF} x 10^2 (mm^2/min)	1.95 ± 0.23	2.97 ± 0.20	4.50 ± 0.55
	Xoo (g/100g)	3.93 ± 0.09	3.79 ± 0.12	3.75 ± 0.08
	R^2	98.95	99.41	99.12
	RME	1.56	1.34	1.72

Cont. Table 3

Peleg	K_1	4.06 ± 0.27	2.67 ± 0.12	1.79 ± 0.15
	K_2	0.25 ± 0.01	0.24 ± 0.01	0.24 ± 0.01
	R^2	99.35	99.86	98.76
	RME	2.14	1.74	3.01
Raffinose				
Equilibrium-dependent model	k x 10^2	5.54 ± 0.36	5.81 ± 0.40	8.98 ± 0.73
	Co (g/L)	1.49 ± 0.03	1.49 ± 0.02	1.52 ± 0.03
	R^2	97.95	98.15	97.28
	RME	4.73	4.16	3.05
Intraparticle diffusion	D_{EF} x 10^2 (mm^2/min)	2.72 ± 0.66	2.74 ± 0.41	4.54 ± 0.89
	Xoo (g/100g)	1.54 ± 0.07	1.49 ± 0.45	1.48 ± 0.05
	R^2	97.15	98.76	97.93
	RME	3.17	2.55	3.04
Peleg	K_1	8.15 ± 1.08	7.65 ± 0.49	4.69 ± 0.60
	K_2	0.63 ± 0.02	0.61 ± 0.01	0.61 ± 0.02
	R^2	97.66	99.41	97.24
	RME	4.33	2.84	4.99
Sucrose				
Equilibrium-dependent model	k x 10^2	6.95 ± 0.42	8.57 ± 0.75	12.01 ± 0.76
	Co	7.76 ± 0.11	8.13 ± 0.15	7.96 ± 0.10
	R^2	98.41	96.21	97.83
	RME	3.33	5.24	2.34
Intraparticle diffusion	D_{EF} x 10^4 (mm^2/min)	3.44 ± 0.51	4.44 ± 0.39	6.34 ± 0.82
	Xoo (g/100g)	9.46 ± 0.21	9.20 ± 0.12	9.34 ± 0.16
	R^2	98.67	99.40	98.46
	RME	2.13	1.63	1.93
Peleg	K_1	1.19 ± 0.11	0.87 ± 0.06	0.63 ± 0.60
	K_2	0.12 ± 0.01	0.12 ± 0.01	0.61 ± 0.01
	R^2	98.65	99.48	97.23
	RME	3.78	1.53	3.40
Glucose				
Equilibrium-dependent model	k x 10^2	7.15 ± 0.74	7.02 ± 0.61	13.6 ± 1.48
	Co	0.82 ± 0.03	0.75 ± 0.02	0.80 ± 0.02
	R^2	93.34	96.98	96.89
	RME	9.73	8.46	3.46
Intraparticle diffusion	D_{EF} x 10^4 (mm^2/min)	3.41 ± 0.43	3.91 ± 1.14	7.29 ± 1.46
	Xoo (g/100g)	0.93 ± 0.18	0.89 ± 0.04	0.88 ± 0.24
	R^2	98.26	98.96	97.02
	RME	2.06	3.56	3.63
Peleg	K_1	10.78 ± 2.21	12.16 ± 0.83	5.62 ± 0.88
	K_2	1.16 ± 0.05	1.24 ± 0.02	1.78 ± 0.03
	R^2	94.06	92.23	94.98
	RME	8.45	12.42	6.10

* Experimental conditions: temperature (°C), DSM particle size of 1.0 mm, DSM to the solvent ratio of 10 mg/mL.

The different model parameters for the soluble carbohydrate compounds (stachyose, raffinose, sucrose, and glucose) are summarized in Table 3. All models showed R^2 values ranged from 0.94 to 0.99 for stachyose, from 0.97 to 0.99 for raffinose, from 0.96 to 0.99 for sucrose, and from 0.93 to 0.98 for glucose, indicating that the models used can describe the extraction process in batch mode operation, of these compounds. The equilibrium-dependent model showed the highest RME and lower R^2, in general, indicating the poorest fit. This could be because the model neglects the carbohydrates diffusion inside the DSM particle solid, which is the internal mass transfer phenomenon that can be relevant for the solid-liquid extraction processes, in most cases.

The Peleg model presented a good fit for the soluble carbohydrates extraction in batch mode operation with hydroalcoholic solvent, except for glucose. The inverse of the rate constant ($1/K_1$) relates to the extraction rate potential at the beginning of the extraction process, while the inverse of the Peleg capacity constant

($1/K_2$) suggests the maximum extraction yield. Based on these values, for each carbohydrate, it was verified that the extraction rate increases at the beginning of the process when the temperature increases, while the capacity to remove soluble carbohydrate is similar for each temperature, in the range evaluated.

The intraparticle diffusion model showed a good fit for experimental data obtained for the range of temperature evaluated in this study. The soluble carbohydrate experimental and model data were plotted under (Figure 5a-d). Some deviations, related by RME in Table 3, could be related to a possible change in the DSM heterogeneous structure. Therefore, the intra-particle diffusion model can be useful to predict the soluble carbohydrate extraction in a leaching process with hydroalcoholic solvent and their diffusion coefficients.

The diffusion coefficients obtained varied from $1.95x10^{-2}$ to $4.50x10^{-2}$ mm² min^{-1} for stachyose, from $2.72x10^{-2}$ to $4.54x10^{-2}$ mm² min^{-1} for raffinose, from $3.34x10^{-2}$ to $6.34x10^{-2}$ mm² min^{-1} for sucrose and from $3.41x10^{-2}$ to $7.31x10^{-2}$ mm² min^{-1} for glucose. As expected, the diffusivities of the simple saccharides (glucose and sucrose) are higher than the oligosaccharides (raffinose and stachyose), which correlated with the lower solubility of these oligosaccharides in this hydroalcoholic solvent. The diffusion coefficient of glucose and sucrose is higher than raffinose and stachyose in order of 76% at 45°C and 40% at 65°C, which suggests the mono and disaccharides are easier to extract than the oligosaccharides.

The temperature is an important role in the mass transfer diffusion, with higher diffusion coefficients being obtained at higher temperatures, what is observed in the kinetic extraction of stachyose (Figure 5a) and raffinose (Figure 5b): higher initial rate of the carbohydrate extraction (high rate of carbohydrate concentration decay in DSM grain) at 65 °C than 45 °C, that approaches the equilibrium faster, while the residual amount of carbohydrate inside the DSM particle lower than at 45°C.

Since there are no data reported in the literature about the diffusion coefficient of these carbohydrates in the extraction process of DSM, the values calculated were only compared with those reported by Baumler [25], who studied diffusion of sugars (raffinose and sucrose) during oil extraction from sunflower collets using ethanol as solvent. The average values for the total sugars diffusion coefficient in ethanol varied from $3.9x10^{-2}$ to $9.06x10^{-2}$ mm² min^{-1} within a temperature range of 50-60°C, indicating that the prediction model used in our study gives accurate and realistic results reported.

CONCLUSION

The data obtained in this study suggest the solid-liquid extraction of soluble carbohydrate from DSM using hydroalcoholic solvent (ethanol/water of 62% w/w) is viable to obtain SCP. Batch extraction process at 65°C and DSM to the solvent rate of 10 mg/mL, promotes leaching of soluble carbohydrates. Temperature and DSM to the solvent rate are operating parameters that influence the yield of the carbohydrate extraction process. The highest extraction yield for the soluble carbohydrate extracted from DSM particle was obtained at 65 °C and DSM to the solvent ratio of 10 mg/mL, with the total carbohydrate content reduces of 29.5% to 15.1% and soy protein concentration in DSM particle of 65.8% (dry basis), required to the standard protein concentration for SPC production. The kinetics study and the use of mathematical models suggest the internal mass transfer is the most relevant resistance mechanism to the extraction of soluble carbohydrates from DMS particles. Also, it was determinate the diffusion coefficient of each carbohydrate was evaluated and the sucrose and glucose showed a higher diffusion coefficient than the oligosaccharides, in order of 40% at 65°C.

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