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Brunner Modeling for oil Extracts Obtained by Supercritical Technology from Fenugreek (*Trigonella foenum-graecum F.*) seeds and germinated seeds

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Abstract

Fenugreek seeds (Trigonella foenum-graecum) are well-known for their high content of bioactive compounds, which are responsible for their antidiabetic, hypolipidemic, anti-obesity, and anticancer properties. However, these compounds can also have antinutritional effects. Germination offers a viable method to enhance the nutritional value, bioactivity, and sensory properties of fenugreek seeds while reducing antinutritional factors. This process leads to an increase in antioxidant activity, total phenolic content, and polyphenol levels, improving the digestibility of proteins and starch, and boosting essential nutrients like vitamins and amino acids. This study investigates the extraction of bioactive compounds from germinated and non-germinated fenugreek seeds using pressurized propane. The mathematical modeling of the desorption phase with supercritical fluids (SCFs) revealed that convection dominates the extraction process's initial 30 minutes, leading to rapid extract acquisition. For prolonged extraction, diffusion becomes the key mechanism, requiring a detailed understanding of plant matrix properties for optimization. Despite the model's general effectiveness, observed discrepancies suggest that differences in the seeds' phenomenological states might affect the outcomes, indicating the need for parameter adjustments. This research underscores the potential of fenugreek seeds as a source of bioactive compounds and highlights the importance of refining extraction and modeling methods to enhance extract quality. These insights pave the way for industrial and pharmaceutical applications, aligning with the demand for sustainable natural products.

Keywords: fenugreek; germination; super-critical technology;

1. Introduction

Fenugreek seeds (Trigonella foenum-graecum) are widely recognized for their richness in bioactive compounds, including phenols, flavonoids, alkaloids, and saponins[1], [2]. Pharmacological and clinical studies have demonstrated the medicinal applications of these seeds, highlighting their antidiabetic[3], hypolipidemic[4], anti-obesity[5], and anticancer activities[6]. However, it is important to note that the saponins and alkaloids present in fenugreek seeds are also considered antinutritional factors.

Therefore, germination or sprouting, a process that transforms the dry, dormant seed into a living, growing organism[7], emerges as a simple and economically viable approach to enhance the nutritional value, bioactivity, and sensory profiles of food products while attenuating antinutritional factors[8]. Edible sprouts exhibit high bioactivity, notably their antioxidant capacity and a significant increase in the total amount of phenols and polyphenols[9], which occurs due to the intensification of the plant's secondary mechanisms activated during germination. Research indicates that sprouts also improve the digestibility of proteins and starch present in the seed, in addition to increasing the nutritional value of essential nutrients such as vitamins and amino acids[10].

The extraction of bioactive compounds from sprouts and seeds using pressurized propane in its pure form results in an extract with high concentrations of secondary metabolites, such as β-carotene, polyphenols, and vitamins, while being free of organic solvent residues[11], [12], [13].

The objective of this study is to model the desorption step of fenugreek seeds using the process proposed by Marques (1997)[14]. The finite volume method was employed to solve the system of equations describing the process. Global extraction curve data available in the literature (Marques, 1997) were used to obtain the necessary information for solving the balance equations.

2. Methodology

Seed Treatment

Fenugreek seeds were purchased from a local store and underwent aseptic treatment using a 1% sodium hypochlorite solution to eliminate microorganisms, especially those that could hinder the germination process. Subsequently, the seeds were soaked in distilled water for 24 hours to break dormancy and initiate the germination process. After the soaking step, the seeds were washed with deionized water.

Controlled Environment Germination

The treated seeds were placed in trays lined with paper towels moistened with deionized water, covered with aluminum foil, and kept in a dark environment for 96 hours at 25 °C.

Drying

After the germination period, the sprouted seeds were washed again with distilled water. Subsequently, both sprouted and unsprouted seeds were dried in an oven with air recirculation at 45ºC for 8 hours until they reached a moisture content of 9%-12% (w/w).

Pressurized Fluid Extraction (PFE)

The equipment used for extraction consisted of a syringe pump (Thar Technologies), a stainless steel extractor with a capacity of 100 grams, and micrometric valves for depressurization. The extraction temperature was maintained at 60 °C using a thermostatic bath, while the pressure was set to 40 bar. The extraction flow rate was controlled by a flow regulator valve fixed at 3 mL/min. Experimental extractions were conducted at the State University of Maringá, following methods described in previous studies by our research group. The extractions were performed using fenugreek seeds (FS) and germinated fenugreek seeds (GFS) in different proportions. Table 1 presents the experimental design used in this study.

Tabel 1. Experimental disgn extraction.

samples	ratio	(Bar/ºC)	corridas
GFS (FG1)	1:1	40/60	2
GFS/FS (FG2)	1:2	40/60	2
GFS/FS (FG3)	2:1	40/60	2

Mathematical Modeling

The mathematical formulation of desorption using supercritical fluid (SCF) follows the same approach as any desorption problem. To study the deterpenation of the oleaginous phase mixture of fenugreek using SCF desorption, the diffusion model in homogeneous solids applied to fixed bed extractors was chosen. In this context, it is essential to determine the mass transfer and dispersion coefficients for the fluid phase, the effective diffusion coefficient for the solid phase, and the adsorption isotherm. The modeling was conducted using the Brunner model, with a Nelder-Mead subroutine employed to minimize the error function.

The mass balance equations for the fluid phase for the bed element indicated in is:

$$\frac{\partial Y}{\partial t} = \frac{1}{Pe_b}\frac{\partial^2 Y}{\partial z^2} - \frac{\partial Y}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon}\frac{3L}{R_p}\frac{Bi}{Pe_p}\left(Y - X\big|_{\rho=1}\right) \quad (1)$$

$$in\ z = 0 \quad (2)$$

The Langmuir isotherm will be used to describe local equilibrium between fluid and solid phases as follows:

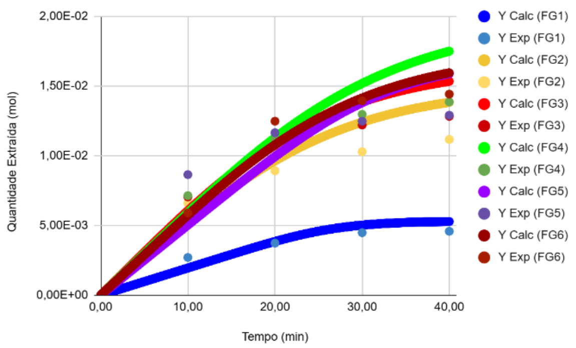
$$q = \frac{q_{max} bX}{1 + bX} \quad (3)$$

3. Results and Discussion

Based on the kinetic curves obtained from the modeled data and parameters related to the desorption of fenugreek seeds (FS) and germinated seeds (GFS) during the extraction with pressurized propane, it was observed that in all samples, as illustrated in Figure 1, the extraction process during the first 30 minutes is dominated by convection. This results in a steep curve slope and a higher amount of extract obtained. After this initial period, the desorption of oil in GFS and FS is determined by the diffusion phenomenon, where the solvent needs to penetrate deeper into the seed matrices to facilitate desorption.

However, it was noted that the model exhibited inadequate fitting for some experimental data, evidenced by significant discrepancies between runs under similar conditions, as observed in FG5 and FG6. The discrepancies in the quality of simulation may stem from the fact that the extractions are conducted from the same plant matrices but in different phenomenological states. This impacts not only the kinetic modeling but also the desorption phenomenon of the plant matrix under study.

Figure 1. kinetic curves of Brunner's model for the plant matrix in different proportions and phenomenological states



4. Conclusion

Seed germination proved to be a promising strategy for enhancing nutritional value and bioactivity while mitigating antinutritional factors such as saponins and alkaloids present in fenugreek seeds.

The mathematical modeling revealed that during the first 30 minutes of the extraction process, convection is the predominant mechanism, leading to rapid extract acquisition. However, for longer extractions, the diffusive phenomenon becomes the determining factor, necessitating a deeper understanding of the physical and chemical properties of plant matrices to optimize process efficiency. These findings indicate the need for model parameter adjustments to accommodate variations in the characteristics of germinated and non-germinated seeds.

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