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Logistic Kinetic Modeling and Interpretation of Mass Transfer in Supercritical CO_2 Extraction in Oregano, Chamomile and Moringa

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Abstract

The supercritical CO_2 extraction of essential oils from *Origanum vulgare* L., *Matricaria chamomilla* L., and *Moringa oleifera* Lam. was kinetically interpreted using a logistic mass transfer approach under different combinations of pressure and temperature. Extractions were performed in a fixed-bed SFE system operated for 210 min using high-purity CO_2 under pressures ranging from 100 to 500 bar and temperatures between 30 and 60 °C, depending on the vegetable matrix. The logistic model was parameterized through the total extractable mass (m_t), the characteristic time associated with the maximum extraction rate (t_m), and the kinetic slope parameter b. The highest extraction yields were obtained at 300 bar and 45 °C for oregano (2.807 g), 100 bar and 40 °C for chamomile (5.006 g), and 500 bar and 60 °C for moringa (5.433 g). Simultaneously, increasing pressure and temperature systematically reduced, decreasing from 16.737 to 8.75 min in oregano and from 15.01 to 9.73 min in moringa, indicating an intensification of convective-diffusional transport mechanisms. The model adequately reproduced the experimental extraction curves, particularly in Oregon, where SSD values remained below 0.03 under all evaluated conditions. Unlike highly parameterized phenomenological approaches, the proposed logistic formulation represented the extraction dynamics using kinetically interpretable parameters without requiring experimentally inaccessible internal coefficients. The results demonstrate that logistic modeling constitutes a mathematically simplified but kinetically robust alternative for the comparative analysis and preliminary optimization of supercritical extraction systems applied to aromatic and medicinal plant matrices.

Keywords: supercritical fluid extraction; logistic kinetic modeling; mass transfer kinetics; essential oils; convective-diffusional transport; aromatic and medicinal plants

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1. Introduction

The extraction of bioactive compounds from plant matrices using sustainable technologies is currently a major research area in food engineering, green chemistry, and the valorization of natural biomass (Kagueyam et al., 2025). In recent decades, scientific and industrial interest in essential oils and plant extracts has increased considerably due to the growing demand for natural compounds with functional, antioxidant, antimicrobial, and pharmacological properties applicable to food, cosmetics, nutraceuticals, and pharmaceuticals (Ivanova et al., 2025). This scenario has driven the development of extraction methods capable of maximizing yield while simultaneously preserving the chemical integrity of thermolabile and highly volatile compounds present in aromatic and medicinal species (Bolouri et al., 2022; Vianna et al., 2021). In this context, supercritical fluid extraction (SFE) has become established as one of the most relevant technologies in contemporary processes for

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the separation and purification of high-value-added natural compounds (Njewa et al., 2025; Travis et al., 2026; Vafaei et al., 2022).

Among the various solvents used in solid-state fermentation (SSF), supercritical carbon dioxide ($ScCO_2$) offers particularly favorable physicochemical and environmental advantages for the extraction of plant secondary metabolites (Pereira & Meireles, 2009). Its relatively low critical temperature (31.1 °C) and moderate critical pressure (7.38 MPa) allow operation under conditions compatible with the thermal stability of sensitive compounds, while simultaneously reducing the risk of oxidative degradation and chemical transformation (Ruiz et al., 2022). Furthermore, supercritical CO_2 possesses high diffusivity, low viscosity, and density that can be modulated by pressure and temperature-properties that facilitate solvent penetration into porous plant structures and improve mass transfer between the solid and fluid phases (Nozari & Kander, 2025). Unlike conventional techniques such as Soxhlet extraction, maceration, or hydrodistillation, $ScCO_2$ extraction significantly reduces the use of toxic organic solvents and yields extracts free of solvent residues, a characteristic especially relevant for food and pharmaceutical applications (Le, 2026). These advantages have favored the industrial expansion of SFE technologies in processes aimed at obtaining essential oils, oleoresins, phenolic compounds and lipophilic extracts from complex plant matrices (Fraguela-Meissimilly et al., 2023).

However, the extraction behavior in SFE systems depends on a complex interaction between thermodynamic phenomena, mass transfer mechanisms, and the structural characteristics of the plant matrix. Operating variables such as pressure and temperature simultaneously modify the solvent density, the solubility of the extractable compounds, the relative volatility of the metabolites, the fluid viscosity, and the molecular diffusivity within the solid matrix (Zhou et al., 2021). Increased pressure typically increases the density of supercritical CO_2 and, therefore, its solvent capacity for lipophilic and semi-volatile compounds, while temperature exerts dual and partially antagonistic effects on extraction, as it increases the vapor pressure of the compounds but can simultaneously decrease the density of the supercritical solvent (Cvitković et al., 2024). Consequently, small variations in operating conditions can generate highly differentiated kinetic responses among plant species with different chemical compositions and tissue architectures. In complex aromatic matrices, these differences are intensified due to the coexistence of terpenic, sesquiterpenic, phenolic compounds and lipid fractions with different thermodynamic affinities towards supercritical CO_2 (Masyita et al., 2022).

From an engineering perspective, understanding extraction kinetics is fundamental to the design, optimization, and scale-up of supercritical solvent extraction (SFE) processes. Extraction curves reflect the temporal evolution of mass transfer between the plant matrix and the supercritical solvent, simultaneously integrating external convective phenomena, intraparticle diffusional resistances, and mechanisms of progressive depletion of the accessible solute (Dimić et al., 2021). Generally, SFE processes exhibit an initial stage characterized by high extraction rates associated with the rapid removal of compounds present in surface or easily accessible regions, followed by an intermediate region where internal diffusional mechanisms predominate, and finally, an asymptotic stage of progressive depletion of the residual solute (Mohammed et al., 2021). Mathematical modeling of these curves allows for the quantification of kinetic parameters associated with the overall extraction rate, the comparison of operating conditions, and the establishment of predictive criteria for industrial applications.

Several mathematical models have been developed to describe supercritical extraction processes. Among the most widely used approaches are phenomenological models based on mass balances and concentration gradients, such as the broken and intact cell model. Cells (BIC), the Shrinking Core (SC) model, and hybrid mass transfer models have been used to describe these models (Aydi et al., 2020). Although these models have high descriptive capacity, they frequently require internal parameters that are difficult to determine experimentally, including effective diffusion coefficients, broken cell fractions, internal resistances, and specific thermodynamic properties of the plant matrix. As an alternative, logistic and (Yuan et al., 2026)semi-

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phenomenological models have gained increasing relevance due to their ability to adequately represent the temporal evolution of extraction using parameters with relatively straightforward physical interpretation and less mathematical complexity (Lorenzi et al., 2025). In plant systems rich in aromatic and lipophilic compounds, logistic functions have demonstrated adequate representation of the transition between the initial convective stage and the asymptotic region of progressive solute depletion (de Elguea-Culebras et al., 2022).

Among plant species of functional and pharmacological interest, *Origanum vulgare* L., *Matricaria chamomilla* L., and *Moringa oleifera* Lam. constitute particularly relevant matrices due to the presence of bioactive metabolites with high biological and industrial value. Oregano contains phenolic and terpenic compounds such as thymol and carvacrol, widely recognized for their antioxidant and antimicrobial properties (Chiș et al., 2023). Chamomile has a composition rich in α-bisabolol, bisabolol oxides, and chamazulene, compounds associated with anti-inflammatory, sedative, and healing activities (Srivastava et al., 2010). Moringa, for its part, has gained increasing importance due to its high concentration of flavonoids, phenolic compounds, and functional lipid fractions with antioxidant and nutraceutical potential (Gharsallah et al., 2023; Kou et al., 2018). Although individual studies on supercritical extraction exist in these species, comparative analyses of kinetic behavior under differentiated operating conditions remain limited, particularly in plant matrices cultivated in high-altitude Andean ecosystems, where climatic and edaphic factors can significantly modify the metabolic composition and extraction response of the plant system.

Despite the widespread use of phenomenological models in supercritical extraction, there remains a methodological need for simplified kinetic approaches that allow for the comparison of different plant matrices without requiring internal parameters that are difficult to determine experimentally, such as effective diffusion coefficients, broken cell fractions, or specific intraparticle resistances. This limitation is particularly relevant in exploratory and preliminary optimization studies, where data availability is often restricted to cumulative extraction curves.

In this context, the objective of this study was to kinetically interpret the supercritical CO_2 extraction of essential oils obtained from oregano leaves, chamomile flowers, and moringa leaves using a logistic mass transfer approach. Unlike more complex phenomenological approaches, the proposed model seeks to represent the temporal evolution of the extraction using parameters of direct physical interpretation, associated with the total extractable mass, the characteristic time of maximum extraction rate, and the kinetic slope of the process. The main contribution of thipreliminaryevaluating whether a parsimonious logistic formulation can comparatively describe plant matrices with different structural compositions and thermodynamic responses to supercritical CO_2, providing a useful tool for the preliminary analysis, kinetic comparison, and initial optimization of supercritical fluid extraction (SFE) processes in aromatic and medicinal species.

2. Materials and Methods

2.1. Plant Matter and Sample Pretreatment

Leaves of *Origanum vulgare* L. (oregano), flowers of *Matricaria chamomilla* L. (chamomile), and leaves of *Moringa oleifera* Lam. (moringa) were collected in Guaranda, Bolívar Province, Ecuador (1°35′ S, 78°59′ W; 2660 m a.s.l.). The collection area is characterized by a temperate subhumid climate, with an average annual temperature of 14–16 °C and marked diurnal variability, conditions that influence the synthesis and accumulation of secondary metabolites in plant tissues (Fabián Zambrano-Intriago et al., 2015; Morales et al., 2016).

The initial moisture content was determined using the standard gravimetric method AOAC 930.15 (1995), drying at 105 °C for 6 h until constant mass was reached. The values obtained were 80.0% for oregano, 77.2% for chamomile, and 54.8% for moringa (wet basis).

Drying was carried out using forced convection in an air-circulating oven at 40 °C for oregano and moringa leaves and at 35 °C for chamomile flowers. The different temperatures correspond to the distinct terpene composition of each matrix: chamomile flowers contain thermolabile sesquiterpene fractions, particularly α-bisabolol and chamazulene (boiling points = 178 °C and = 270 ° C, respectively), whose oxidative degradation accelerates above 40 °C (Kotnik et al., 2007). The drying process was continued until a final moisture content of 7–9% ± 1% (w/w) was reached, a range documented as optimal for maximizing the diffusivity of $ScCO_2$ in dehydrated plant matrices without compromising the integrity of the target compounds (Oliveira et al., 2011; Sharif et al., 2014).

Particle size reduction was performed using a cyclone mill (Retsch SM 100, Germany) operating under combined impact and shear forces, with a 1 mm mesh screen. Particle size is a determining factor in solid-fluid extraction kinetics: smaller particle diameters result in a higher surface area to volume ratio, which reduces the intraparticle diffusion length and decreases the internal resistance to solute mass transfer to the supercritical phase (Duba & Fiori, 2015; Mezzomo et al., 2009). Moisture content determinations were performed in triplicate for each species.

The ground material was stored in airtight low-density polyethylene containers at room temperature (25 ± 2 °C), protected from light radiation and separated by species, in order to minimize lipid oxidation, absorption of ambient moisture, and possible cross-contamination between matrices of different chemical composition.

2.2. Supercritical CO_2 Extraction System (SFE)

Supercritical fluid extraction, known by its acronym SFE (Supercritical Fluid Extraction), was carried out using carbon dioxide (CO_2) as a supercritical solvent in a Helix SFE laboratory system.

The extraction of compounds was carried out in a Helix SFE laboratory system, consisting of a high-pressure pumping module, a thermal control system, and a fixed-bed extraction cell. Carbon dioxide (CO_2) with a purity of 99.95% was used as the solvent. In each trial, 100 g of previously dried and ground plant material were loaded into the extraction cell. Before the start of the process, the system was stabilized to reach the operating pressure and temperature conditions established for each treatment, ensuring a steady-state regime prior to the dynamic stage.

CO_2 was supplied at a constant volumetric flow rate of 1 L/min, under continuous conditions. The extraction process was carried out in two stages: an initial static phase of 15 min, designed to promote solvent penetration into the solid matrix and the establishment of initial equilibrium, followed by a dynamic phase of 180 min in which solute mass transfer to the supercritical phase occurred. Operating conditions were defined according to the plant matrix. For oregano, pressures of 20 and 30 MPa were evaluated at temperatures of 35 and 45 °C; for chamomile, pressures of 10 and 20 MPa at temperatures of 30 and 40 °C; and for moringa, pressures of 40 and 50 MPa at temperatures of 50 and 60 °C. These combinations allowed for the exploration of the combined effect of solvent density and transport properties on extraction performance.

The resulting extract was collected in 50 mL vials and stored at 10 °C until analysis to prevent thermal or oxidative degradation of the extracted compounds. Each experimental condition was performed in duplicate, allowing for the evaluation of the reproducibility of the process under the established conditions.

2.3. Mathematical Modeling

Kinetic modeling of the supercritical fluid extraction (SFE) process was performed using experimental extraction curves obtained under constant temperature and pressure conditions. The cumulative mass of essential oil extracted was recorded over time throughout the extraction process. These experimental data were then used to fit a mathematical model based on coupled mass balances between the solid and fluid phases of the extraction bed (Machado et al., 2021; Pannusch et al., 2023).

The extraction system was represented as a one-dimensional cylindrical bed composed of solid plant particles axially permeated by supercritical carbon dioxide. The model considered two continuous phases: i) a solid phase corresponding to the plant matrix containing the extractable solute, and ii) a fluid phase consisting of the supercritical solvent and the dissolved compounds. The conceptual configuration of the system used for modeling is shown in Figure 1.

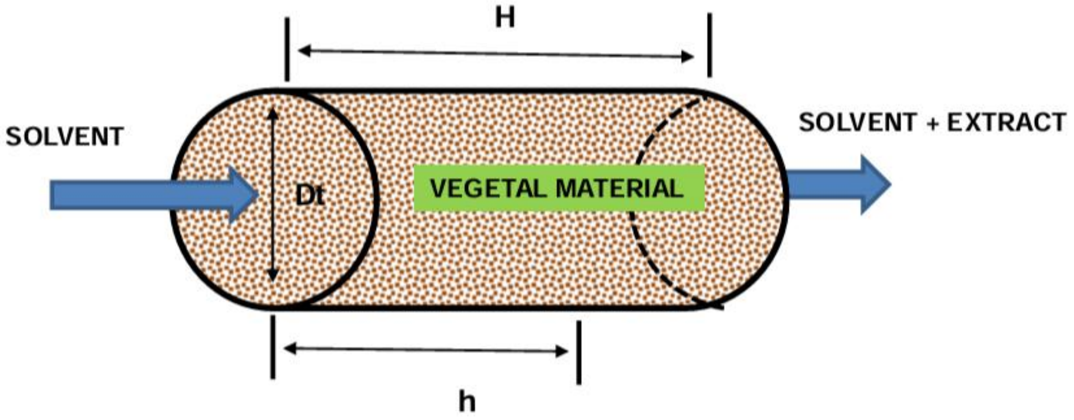

Figure 1. System for removing soluble compounds from the solid phase using supercritical solvent.

The system's behavior was described using partial differential equations derived from the mass balances for both phases. The mass balance for the fluid phase was expressed by equation 1, while the balance for the solid phase was represented by equation 2.

Mass balance in the fluid phase

$$\frac{\partial Y}{\partial t}+u\frac{\partial Y}{\partial h}=\frac{\partial}{\partial h}\left(D_{aY}\frac{\partial Y}{\partial h}\right)+\frac{J(X,Y)}{\varepsilon} \qquad (1)$$

Mass balance in the solid phase

$$\frac{\partial X}{\partial t}=\frac{\partial}{\partial h}\left(D_{aX}\frac{\partial X}{\partial h}\right)-\frac{J(X,Y)\,\rho}{(1-\varepsilon)\,\rho_s} \qquad (2)$$

where,

X and Y are the mass proportions of the solute (component to be extracted) in the solid and fluid phases, respectively; $u$is the pore velocity of the solvent; h is the axial coordinate in the extraction bed; $D_{aY}$is the axial dispersion coefficient; $D_{aX}$is the diffusion coefficient of the solid phase; $\rho_s$is the density of the solvent; ρ is the density of the solid; $\varepsilon$is the porosity of the bed; and J(X,Y) is the interfacial mass transfer flux.

As can be seen, equations (1) and (2) must consider all transport phenomena that can occur during the SFE process, namely, mass accumulation in the phases, mass variations due to convection and dispersion in the fluid phase, diffusion in the solid phase, and interfacial mass transfer. The model presented in this work does not consider accumulation or dispersion in the fluid phase, since these phenomena do not have a significant influence on the process compared to the effect of convection. Therefore, the mass balance equation for the fluid phase can be simplified, as Franca and Meireles did (De França & Meireles, 2000) (Equation 3).

$$\frac{\partial Y}{\partial h}=\frac{J(X,Y)}{\varepsilon} \qquad (3)$$

The boundary condition applied to the system corresponded to an initial concentration of zero solute at the inlet of the extraction bed:

$$Y(h=0,t)=0 \qquad (4)$$

The term interfacial mass transfer, represented as J(X, Y), can be interpreted in different ways. In this work, J(X, Y) was defined as a logistic function that depends on the extract composition throughout the process. To analyze the variation of this composition, essential oils from three plant materials were considered, and their compositions were measured as a function of time. The logistic equation, which is commonly used to model the growth of model populations, was chosen to describe the variation in the extract composition, resulting in Equation 5.

$$J(X,Y)=\frac{A\,b\,e^{\,b(t_m-t)}}{\left(1-e^{\,b(t_m-t)}\right)^2} \qquad (5)$$

As a result of integrating equation 3 and the boundary conditions defined in 4, the representative equation for the fraction of solute extracted in the fluid phase is given by equation 6.

$$Y(h = H, t) = \frac{H}{u\varepsilon} \cdot \frac{A\, b\, e^{\,b(t_m - t)}}{\left(1 - e^{\,b(t_m - t)}\right)^2} \qquad (6)$$

In equation 6, H is the total length of the extraction bed and A is a parameter of the logistic model. Finally, the equation for the total extraction curve was obtained by integrating equation 6 with respect to time using the initial condition given in equation 7.

$$m(h = H, t = 0) = 0 \qquad (7)$$

The result is as follows:

$$m(h = H, t) = \int_0^t Y\, Q_{CO_2}\, dt \qquad (8)$$

where QCO_2 represents the mass flow rate of the solvent within the extraction bed. For a particular plant species, the extraction curve can be represented by equation 9, which corresponds to the integration of equation 8.

$$m(h = H, t) = \frac{Q_{CO_2}\, H\, A}{u\varepsilon} \left[\frac{1}{1 + e^{\,b(t_m - t)}} - \frac{1}{1 + e^{\,b t_m}}\right] \qquad (9)$$

From the analysis of equation 9, it can be observed that as time approaches infinity, the mass of the extracted compound asymptotically approaches a fixed value. This value can be considered the total extractable mass of that compound under the given process conditions. Taking this into account and rearranging equation 9, a new equation for the extraction curve is obtained (Equation 10), given by:

$$m(h = H, t) = \frac{m_t}{e^{b t_m}} \left[\frac{1 + e^{b t_m}}{1 + e^{\,b(t_m - t)}} - 1\right] \qquad (10)$$

Reformulating the equation allowed the parameter to be replaced $A$by the total extractable mass of the extract (m_t, g), thus incorporating a parameter with direct physical meaning and experimentally determinable. Under this approach, the model was defined by the kinetic parameters b (min^{-1}) and t_m(min), associated with the extraction rate and the time at which the extraction rate reaches its maximum value, respectively.

The adjustment of kinetic parameters and the estimation of extraction curves were performed using nonlinear regression with the Microsoft Excel® Solver tool, applying the Generalized algorithm Reduced Gradient (GRG). The parametric estimation was carried out individually for each plant species evaluated, based on the experimental cumulative mass data obtained during the SFE process.

2.4. Construction of Extraction Kinetic Curves

Kinetic curves were constructed from the cumulative mass of extract obtained during the dynamic phase of supercritical CO_2 extraction. Under each experimental condition, the recovered extract was weighed gravimetrically and expressed as cumulative yield relative to 100 g of dried plant sample. Independent curves were generated for each species under the evaluated pressure and temperature combinations: oregano at 20 and 30 MPa with 35 and 45 °C; chamomile at 10 and 20 MPa with 30 and 40 °C; and moringa at 40 and 50 MPa with 50 and 60 °C. Each condition was tested in duplicate, and the resulting data were used to fit the logistic extraction model.

2.5. Parameter Estimation and Adjustment Criteria

The logistic model parameters were estimated using nonlinear regression in Microsoft Excel®, using the Solver tool and the Generalized algorithm Reduced Nonlinear gradient. The adjustment was performed independently for each plant species and operating condition. The objective function consisted of minimizing the sum of squared deviations between the experimental cumulative mass and the cumulative mass estimated by the model Equation 10).

$$SSD = \sum_{i=1}^{n} (m_{exp,i} - m_{mod,i})^2 \qquad (10)$$

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where $m_{exp,i}$ is the experimental cumulative mass at point i, $m_{mod,i}$ is the cumulative mass predicted by the model, and $n$corresponds to the number of kinetic observations available for each curve. The fitted parameters were m_t, t_m and b corresponding to the total extractable mass, the time associated with the maximum extraction rate, and the logistic slope kinetic parameter, respectively.

2.6. Reproducible Scope of the Modeling Procedure

The descriptive capacity of the logistic model was evaluated by comparing the experimental and predicted curves for each extraction condition. The quantitative fit criterion was the sum of squared deviations (SSD) between the experimental values and the values calculated by the model. The values obtained for each operating condition were reported along with the estimated kinetic parameters.

The graphical comparison between experimental and modeled data allowed us to evaluate the model's ability to represent the temporal evolution of the accumulated extract mass during the SFE process in the studied plant matrices.

3. Results and Discussion

3.1. Characterization of the Raw Material

The plant matrices evaluated showed differences in initial moisture content. Fresh oregano leaves registered the highest moisture content (80.0%), followed by chamomile flowers (77.2%), while moringa leaves presented the lowest initial value (54.8%). After convective drying, all samples reached final moisture contents between 7 and 9% (w/w).

The reduction in moisture was more pronounced in oregano and chamomile due to their higher initial water content. These differences reflect variations between leaf and flower matrices in water retention and in the physical structure of the plant tissue.

In supercritical CO_2 extraction systems, moisture content directly influences solvent diffusion and internal resistance to mass transfer within the solid matrix. Uwineza & Waśkiewicz (Uwineza & Waśkiewicz, 2020) and Bakhshabadi et al. (Bakhshabadi et al., 2025) noted that high water content can partially limit supercritical fluid penetration due to the occupation of the porous structure and modifications in solvent accessibility to lipophilic compounds. Similarly, Guo & Wu (Guo & Wu, 2025) reported that biomass preconditioning is a relevant factor in extraction kinetics due to its influence on diffusional phenomena and the effective solid-fluid contact surface area.

The moisture contents obtained in this study allowed extractions to be carried out under relatively homogeneous conditions between species, reducing the variability associated with the initial water content and favoring comparability in the kinetic modeling of the SFE process.

3.2. Kinetic Parameters of the Logistic Model

The kinetic parameters obtained by fitting the logistic model showed a consistent dependence on the operating pressure and temperature conditions in the three plant matrices evaluated. The results corresponding to the total extractable mass (m_t), the time associated with the maximum extraction rate (t_m), the slope kinetic parameter b, and the sum of squared deviations (SSD) are presented in Tables 1–3.

Table 1. Model parameters for 200 and 300 bars at 35 and 45 °C in the extraction of oregano oil.

Parameters	200 bar		300 bar	
	T = 35 °C	T = 45 °C	T = 35 °C	T = 45 °C
(m_t) (g)	1,787	1,881	2.371	2,807
(t_m) (min)	16,737	12,750	11.43	8.75
(b) (min^{-1})	0.019	0.023	0.010	0.013

SSD (squared deviation of error)	0.0019	0.029	0.016	0.015

Table 2. Model parameters for 100 and 200 bars at 30 and 40 °C in the extraction of chamomile.

Parameters	100 bar		200 bar	
	T = 30 °C	T = 40 °C	T = 30 °C	T = 40 °C
(m_t) (g)	3,896	5.006	4.103	4,801
(t_m) (min)	12,560	10.230	7.41	5,732
(b) (min^{-1})	0.027	0.017	0.018	0.050
SSD (squared deviation of error)	0.288	0.510	1.012	0.469

Table 3. Model parameters for 400 and 500 bars at 50 and 60 °C in the extraction of moringa oil.

Parameters	400 bar		500 bar	
	T = 50 °C	T = 60 °C	T = 50 °C	T = 60 °C
(m_t) (g)	3.207	3,972	4,859	5.433
(t_m) (min)	15.01	11.75	12.21	9.73
(b) (min^{-1})	0.025	0.027	0.037	0.027
SSD (squared deviation of error)	0.337	0.100	0.333	0.283

In oregano, the simultaneous increase in pressure and temperature produced a progressive increase in m_t, reaching a maximum value of 2.807 g at 300 bar and 45 °C. Concurrently, the parameter t_m decreased from 16.737 min to 8.75 min, indicating an acceleration of the overall extraction kinetics as the operational conditions intensified. This behavior is consistent with the influence of pressure on the density of supercritical CO_2 and, therefore, on its solvent capacity for lipophilic and semi-volatile compounds present in aromatic matrices (Vladić et al., 2021; Y. Yang & Hu, 2014). Simultaneously, the increase in temperature modifies the transport properties of the system, increasing molecular diffusivity and partially decreasing the internal solid-fluid mass transfer resistances (Yue et al., 2013). The systematic reduction of t_m observed in oregano suggests a progressive intensification of global mass transfer dynamics and an acceleration in the depletion of the readily accessible solute fraction as pressure and temperature increased. From a kinetic perspective, t_m can be interpreted as a temporal descriptor of the transition toward the region of maximum convective mass transfer, indirectly reflecting how rapidly the system reaches its highest instantaneous extraction efficiency under SFE conditions. (Bensebia et al., 2016).

This behavior is consistent with the progressive increase in supercritical CO_2 density as pressure and temperature increase within certain operating ranges. In SFE systems, higher solvent density generally increases solvation capacity and promotes the convective transfer of lipophilic compounds from the plant matrix to the fluid phase. Consequently, extraction tends to intensify kinetically during the initial stages of the process, simultaneously reducing the time required to reach the region of maximum mass transfer. This phenomenon has been extensively documented in supercritical extraction of essential oils and terpene compounds, where CO_2 density acts as one of the main determinants of the overall extraction capacity of the system (Guastaferro et al., 2026; Khaw et al., 2017).

In chamomile, the highest value of m_t was obtained at 100 bar and 40 °C, reaching 5.006 g, whereas the shortest characteristic time associated with the maximum extraction rate corresponded to 200 bar and 40 °C, with a t_m value of 5.732 min. Unlike the behavior observed in oregano and moringa, increasing pressure did not produce a proportional increase in the total extractable yield under all evaluated conditions. This behavior has been previously reported in plant matrices with complex terpene compositions, where the simultaneous effects of pressure and temperature can selectively modify the solubility of specific compounds and alter the balance between convective and

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diffusional transport mechanisms (Pourmortazavi & Hajimirsadeghi, 2007; Salgin, 2007; Topal et al., 2006). The greater thermal sensitivity observed in chamomile could be related to the thermodynamic nature of oxygenated and sesquiterpene compounds present in this species, whose extraction depends on both the solvent density and the relative volatility and solute-matrix interactions (Povh et al., 2001; Sliczniuk & Oinas, 2025). From a kinetic point of view, the decrease in (t_m) under higher operating conditions indicates an initial intensification of the extraction rate, although without an equivalent increase in (m_t), which shows a non-linear response of the system to pressure.

For moringa, the combined increase in pressure and temperature resulted in the highest overall extraction yield at 500 bar and 60 °C, reaching an m_t value of 5.433 g. Furthermore, the values of t_m progressively decreased as the operational conditions intensified, declining from 15.01 min to 9.73 min. This behavior suggests an acceleration of the overall extraction dynamics and a relative reduction in internal diffusional limitations under higher supercritical CO_2 densities. From a phenomenological perspective, the decrease in t_m indicates that the system reached the region of maximum convective mass transfer more rapidly, favoring a more intense extraction during the initial stages of the process. Similar behavior has been reported in supercritical extractions of *Moringa oleifera*, where elevated pressures significantly increase the solubility of lipid fractions and phenolic compounds in supercritical CO_2 as a consequence of enhanced solvent density and stronger solute-solvent interactions (Ngcobo et al., 2023; Rai et al., 2017; Zhao & Zhang, 2013, 2014). Additionally, the reduction of (t_m) under higher operating conditions coincides with observations made in phenomenological models of supercritical extraction, where the increase in pressure decreases the time required to reach the region of maximum mass transfer due to a higher rate of depletion of the accessible solute (Sovová, 1994, 2005).

The parameter b showed variations among species and operational conditions, reflecting differences in the kinetic slope of the fitted logistic curves. In general, higher b values were associated with faster transitions between the initial accelerated extraction stage and the asymptotic depletion region of the process. This behavior is consistent with previous reports on logistic and semi-phenomenological models applied to supercritical CO_2 extraction, in which the slope-related kinetic parameter indirectly reflects the relative intensity of convective and diffusional transport phenomena occurring during the extraction process (Bojanić et al., 2019; Pavlić et al., 2020; Zeković et al., 2017).

From a phenomenological perspective, the parameters and *b* can be interpreted as global kinetic descriptors of the interaction between the solvent capacity of supercritical CO_2 and the mass transfer resistances present in the system. While represents the total fraction potentially recoverable under specific operating conditions, it indirectly reflects the speed at which the system reaches the region of maximum convective transfer, constituting a temporal indicator of kinetic intensification. The parameter b, in turn, describes the transition between the initial stage dominated by accelerated extraction and the asymptotic region of progressive solute depletion. Under this interpretation, the logistic model not only acts as an empirical tool for mathematical fitting but also as a simplified approximation for describing the global evolution of convective-diffusional mechanisms in multicomponent SFE systems. Similar results have been previously discussed in semi-phenomenological models applied to supercritical extraction of aromatic and oilseed plant matrices (Dias et al., 2021; Huang, 2015; Suslova et al., 2023).

The relatively low SSD values obtained for the three species indicate good agreement between the experimental data and the curves predicted by the logistic model, particularly in oregano, where SSD values were below 0.03 under all evaluated conditions. Higher SSD values were observed in chamomile, especially at 200 bar and 30 °C (SSD = 1.012), which could reflect greater experimental variability or a more complex kinetic response of this plant matrix under certain operating conditions. However, overall, the results show that the logistic model was able to represent the temporal evolution of the cumulative mass extracted from the three species studied, adequately reproducing both the initial accelerated extraction stage and the experimentally observed asymptotic trend. This behavior is consistent with previous studies reporting the applicability of logistic and semi-

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phenomenological models to describe SFE processes in aromatic and medicinal plant matrices (Campos et al., 2005; R. Kant & Kumar, 2022; Paucarchuco-Soto et al., 2025).

3.3. Kinetic Behavior of the SFE Extraction Curves

The initial stage of the extraction curves was characterized by higher mass transfer rates, associated with the rapid removal of compounds located in surface regions and areas of low intraparticle diffusional resistance. As the process progressed, the slope gradually decreased due to the depletion of readily accessible solutes and the relative increase in internal diffusional limitations. This behavior is consistent with that reported by Sovová et al. (Sovová et al., 2016), Sovová (Sovová, 2012), and Oliveira et al. (Oliveira et al., 2011), who described SFE kinetics as evolving from an initial stage dominated by external convective mechanisms toward a regime partially controlled by intraparticle diffusion. Similarly, Sovová and Sovová (Sovová & Sovová, 2012) and Sovová (Sovová, 2022)noted that logistic curves adequately reproduce this kinetic transition in plant systems rich in volatile and lipophilic compounds.

The oregano growth curves, shown in Figure 2, demonstrated a highly sensitive kinetic response to the simultaneous increase in pressure and temperature. At 200 bar and 35 °C, the lowest initial slope and the lowest final cumulative yield were obtained, reaching approximately 1.8 g/100 g of sample at the end of the process, while the condition of 300 bar and 45 °C produced the curve with the steepest slope and highest cumulative yield, close to 2.5 g/100 g of sample. This behavior coincides with the values of (m_t) reported in Table 1, where the pressure increase from 200 to 300 bar raised the total extractable mass from 1.787 to 2.807 g, while the parameter (t_m) decreased from 16.737 to 8.75 min. The kinetic acceleration observed under higher operating conditions is consistent with the increased density of supercritical CO_2 and the simultaneous improvement of the system's transport properties, particularly molecular diffusivity and solid-fluid mass transfer (Lévai et al., 2017; Versteeg et al., 2024). Previous studies in species of the genus *Origanum* have reported similar trends, in which increased pressure favors the recovery of terpene compounds due to the increased solvent power of supercritical CO_2 (Gong et al., 2022; K. Kant et al., 2026).

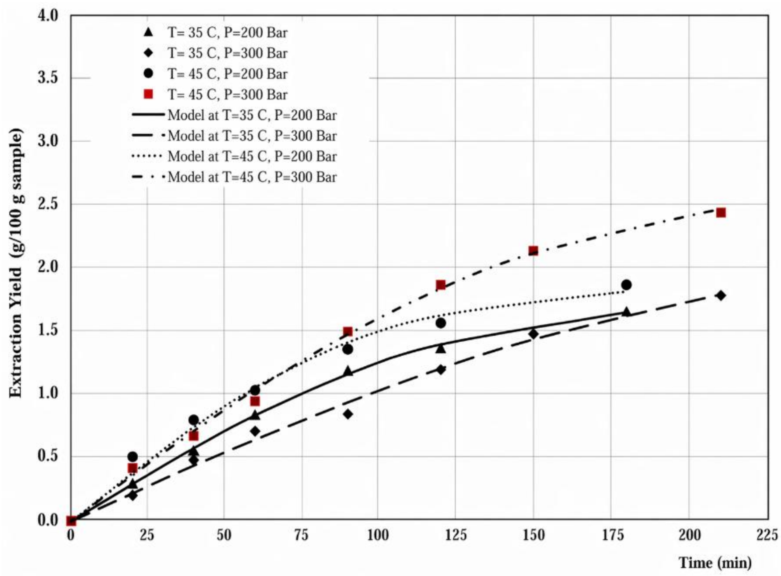

Figure 2. Experimental and logistic-modeled supercritical CO_2 extraction curves of oregano essential oil under different pressure and temperature conditions. Symbols represent experimental data, while continuous lines correspond to the fitted logistic kinetic model.

In Figure 3, corresponding to chamomile, the experimental and modeled curves exhibited a kinetic behavior different from that observed in oregano and moringa. Although the temperature increase from 30 to 40 °C produced a clear rise in cumulative yield under both evaluated pressures,

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the effect of increasing pressure on the overall extraction kinetics was neither proportional nor entirely linear. The condition of 100 bar and 40 °C generated the curve with the highest cumulative yield and one of the steepest initial slopes in the system, reaching approximately 5 g/100 g of sample toward the end of the process, consistent with the highest m_t value reported in Table 2 ($m_t = 5.006$ g).

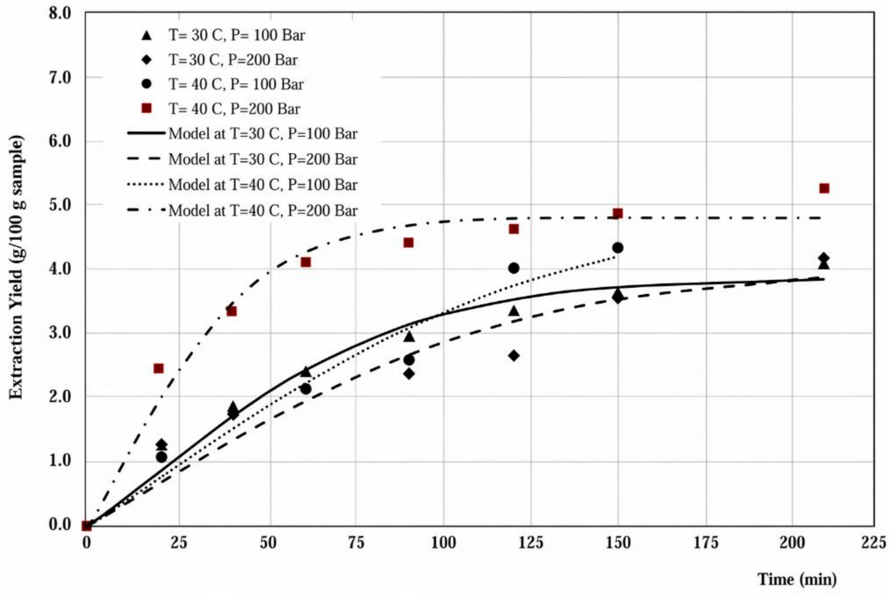

Figure 3. Experimental and logistic- modeled supercritical CO_2 extraction curves of chamomile essential oil under different pressure and temperature conditions. Symbols represent experimental extraction data, while continuous lines correspond to the fitted logistic kinetic model. The progressive asymptotic behavior of the curves reflects the gradual depletion of the readily accessible solute fraction during the extraction process.

Conversely, although the condition of 200 bar and 40 °C yielded the lowest t_m value (5.732 min), indicating a faster initial extraction rate, the total cumulative yield was slightly lower, reaching an m_t value of 4.801 g. This behavior suggests that an initial acceleration of mass transfer does not necessarily result in a proportional increase in the total extractable mass. From a phenomenological perspective, these results indicate that the increased pressure primarily enhanced the initial convective stage of the process, whereas the overall availability of extractable compounds remained conditioned by thermodynamic constraints and specific interactions between the supercritical solvent and the vegetal matrix.

From a thermodynamic perspective, this behavior could be associated with selective modifications in the relative solubility of oxygenated and sesquiterpene compounds present in chamomile as the density of supercritical CO_2 increases. In multicomponent systems, high pressure increases can preferentially favor the extraction of certain lipophilic fractions while simultaneously limiting the effective transfer of compounds with different relative volatility or solvent-matrix affinities (Díaz-Reinoso et al., 2006; Kaiser et al., 2004; Santivañez et al., 2026). Consequently, an initial acceleration of the convective stage does not necessarily imply a proportional increase in the total accumulated mass, particularly when the overall extraction depends on competing equilibria between internal diffusional mechanisms, metabolite volatility, and the solvent capacity of CO_2. This behavior suggests that the kinetic response of chamomile exhibited greater thermodynamic sensitivity to pressure-temperature interactions compared to oregano and moringa, likely due to the compositional complexity of its oxygenated terpene fractions.

The progressive separation between the curves obtained at 30 and 40 °C also indicates a high thermal sensitivity of the system. Several studies conducted on *Matricaria chamomilla* L. using supercritical extraction have reported that moderate temperature increases can simultaneously favor the vapor pressure of oxygenated compounds and molecular diffusivity, thus increasing mass

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transfer during the initial stage of the process (Jokić et al., 2012; Wenceslau et al., 2021). However, when the pressure increase excessively modifies the solvent density, selective changes in the relative solubility of certain terpene and sesquiterpene compounds can occur, altering the overall behavior of the extraction and the shape of the kinetic curves (Pourmortazavi et al., 2005, 2014).

The progressive deceleration observed in the final stages of the kinetic curves is consistent with the gradual depletion of the most accessible solute fraction within the plant matrix. During the initial phases of the SFE process, compounds located in surface or weakly retained regions are rapidly removed due to the predominance of external convective mechanisms. However, as extraction progresses, the availability of readily accessible compounds decreases, and mass transfer becomes increasingly conditioned by internal diffusional resistances and the migration of metabolites from less accessible regions of the plant structure. Consequently, the overall extraction rate tends to decrease progressively, generating the characteristic asymptotic region represented by the logistic model. This behavior has been extensively described in supercritical extraction of aromatic and oilseed plant matrices (Porter, 2007).

Additionally, Figure 3 showed greater experimental dispersion compared to Figures 2 and 4, particularly at 200 bar and 30 °C, the condition in which the highest SSD value (1.012) was recorded according to Table 2. This behavior suggests that the kinetic response of chamomile exhibited greater structural and compositional complexity under the evaluated operating conditions, possibly due to the coexistence of compounds with different volatilities, relative polarities, and thermodynamic affinities with supercritical CO_2.

The moringa curves presented in Figure 4 exhibited the most intense kinetic response among all evaluated matrices. Under the condition of 500 bar and 60 °C, both the steepest initial slope and the highest final cumulative yield were obtained, reaching approximately 5.5 g/100 g of sample at the end of the extraction process. In contrast, the condition of 400 bar and 50 °C produced the least steep curve and the lowest cumulative yield, close to 3.2 g/100 g of sample. These results are consistent with the parameters reported in Table 3, where the simultaneous increase in pressure and temperature increased the m_t value from 3.207 g to 5.433 g and reduced the t_m value from 15.01 min to 9.73 min. The observed behavior suggests a simultaneous intensification of the solvent capacity of supercritical CO_2 and of the convective and diffusional transport mechanisms responsible for mass transfer. Similar behavior has been reported in supercritical extractions of *Moringa oleifera* Lam., where elevated pressures significantly enhance the recovery of lipid fractions and phenolic compounds due to increased solvent density and stronger solute–solvent interactions (Iglesias Díaz et al., 2018; Marto De Souza et al., 2020). Likewise, Yang et al. (M. Yang et al., 2022) and Talavera et al. (Talavera et al., 2023) reported that the simultaneous increase in pressure and temperature particularly favors the extraction of less volatile compounds present in moringa leaves, which is consistent with the trend observed in the experimental curves of the present study.

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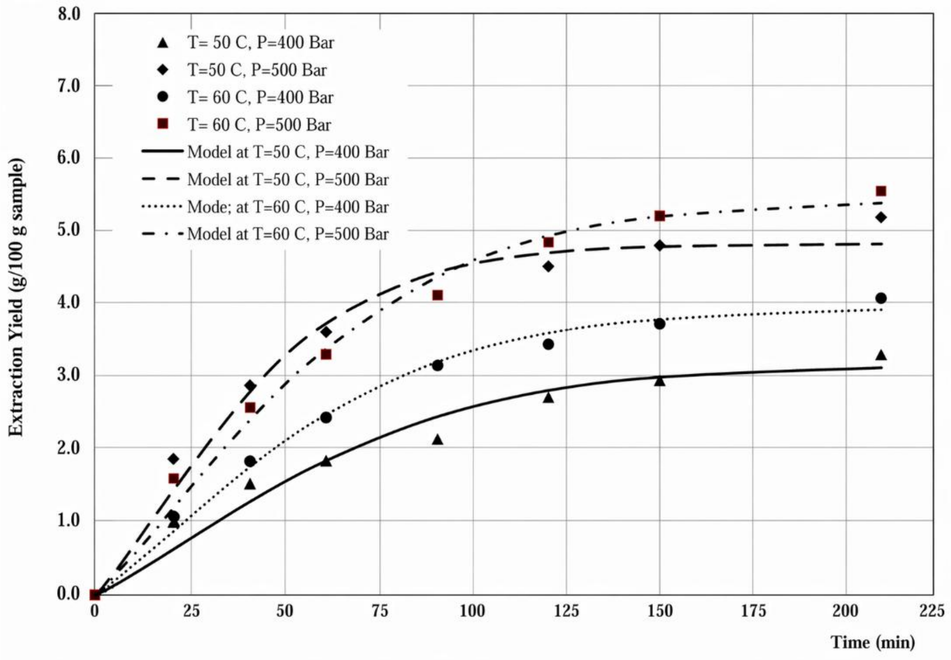

Figure 4. Variation of logistic kinetic parameters tm and b under different supercritical extraction conditions. Lower tm values indicate accelerated extraction dynamics associated with intensified global mass transfer conditions.

The comparison between the experimental and modeled curves presented in Figures 2–4 showed adequate agreement throughout most of the evaluated time interval, consistently reproducing both the initial accelerated extraction stage and the asymptotic region associated with progressive solute depletion. This correspondence is consistent with the relatively low SSD values reported in Tables 1–3, particularly for oregano, where SSD values remained below 0.03 under all evaluated operational conditions. Larger deviations were observed in chamomile, especially at 200 bar and 30 °C (SSD = 1.012), suggesting either a more complex kinetic response or greater experimental variability under that specific condition. Nevertheless, the overall results support the descriptive capacity of the logistic model to quantitatively represent the temporal evolution of supercritical fluid extraction in aromatic and medicinal plant matrices, consistent with previous studies conducted on similar supercritical systems (Jokic et al., 2010; Kruse et al., 2015).

3.4. Kinetic Implications of the Logistic Model in SFE Systems

The results obtained demonstrate that the logistic model consistently described the overall dynamics of supercritical CO_2 extraction in aromatic and medicinal plant matrices with contrasting physicochemical behaviors. Parameterization using (m_t), (t_m), and b allowed for the integration of the total extraction capacity, the characteristic process rate, and the transition between the initial convective stage and the diffusional region of progressive solute depletion into a single mathematical approach. From a phenomenological perspective, the systematic decrease in (t_m) under higher operating conditions indicated an intensification of mass transfer mechanisms and a relative reduction in intraparticle resistances, while the variations observed in b reflected structural and thermodynamic differences among the evaluated matrices. This behavior coincides with that previously described for SFE systems modeled using logistic and semi-phenomenological approaches, in which the temporal evolution of the extraction can be adequately represented by kinetic parameters with direct physical interpretation. (El Ahmadi et al., 2024; Martínez et al., 2003; Razgonova et al., 2025).

Unlike phenomenological models widely used in supercritical extraction, such as the Broken and Intact model Unlike biointensive cell fragmentation (BIC) or shrinking core approaches, the

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logistic formulation used in this study does not require the experimental estimation of effective diffusion coefficients, broken cell fractions, or internal parameters associated with specific intraparticle resistances. Although phenomenological models possess high mechanistic capacity, their application often depends on parameters that are difficult to determine experimentally and on more complex fitting procedures, particularly in heterogeneous and multicomponent plant matrices (Herzyk et al., 2024; Mouahid et al., 2024; Sovová, 2017). In this context, the good agreement observed between the experimental and modeled curves suggests that the logistic approach can parsimoniously represent the overall extraction dynamics, simultaneously preserving kinetic interpretability and mathematical simplicity. This characteristic is especially relevant in preliminary comparative studies and in the initial stages of optimization of single-particle extraction (SPE) processes applied to aromatic and medicinal matrices.

Unlike more structurally complex phenomenological models, such as BIC or Shrinking Core models, the logistic approach used in this study allowed for the adequate representation of experimental curves without requiring internal parameters that are difficult to determine experimentally, while simultaneously maintaining descriptive capacity in the face of variations in pressure, temperature, and the nature of the plant matrix. The good agreement observed between the experimental and modeled curves suggests that this approach is a useful tool for kinetic comparison between plant species and for the preliminary evaluation of operating conditions in SFE processes aimed at the valorization of bioactive compounds of natural origin. In this context, the proposed model represents a mathematically simplified, yet kinetically robust, approach to describing the supercritical extraction of essential oils in complex plant systems.

From a process engineering perspective, the reduction in parametric complexity achieved through the logistic approach can facilitate the preliminary analysis of operating conditions in SFE systems where the experimental availability of thermodynamic properties and transport coefficients is limited. The ability to comparatively represent plant matrices with different physicochemical behaviors using a reduced set of kinetic parameters is a potential advantage for exploratory studies, initial optimization stages, and comparative evaluation of aromatic and medicinal species. Although the model does not replace high-resolution mechanistic phenomenological approaches, the results obtained suggest that the logistic formulation can function as a parsimonious kinetic tool for describing global trends in supercritical extraction in multicomponent plant systems subjected to different pressure and temperature conditions.

Additionally, the logistic formulation presented a methodological advantage associated with the reduction of parametric complexity compared to traditional phenomenological models used in supercritical extraction. While high-resolution mechanistic approaches typically require multiple internal parameters dependent on thermodynamic properties and local mass transfer resistances, the proposed model adequately described the global evolution of the kinetic curves using a reduced set of easily interpretable parameters. From a computational and experimental perspective, this mathematical parsimony can favor the stability of the fit and simplify the comparative analysis between plant matrices subjected to different operating conditions, particularly in exploratory studies where the availability of detailed physicochemical parameters is limited.

Conclusions

The supercritical CO_2 extraction of essential oils from oregano, chamomile, and moringa showed differentiated kinetic responses under varying pressure and temperature conditions, confirming the strong dependence of SFE performance on the physicochemical characteristics of the vegetal matrix and the operational properties of the supercritical solvent. Increasing pressure and temperature intensified the global extraction kinetics, producing higher extractable masses and systematically reducing the characteristic time associated with the maximum extraction rate. The highest cumulative extraction yields were obtained at 300 bar and 45 °C for oregano, 100 bar and 40 °C for chamomile, and 500 bar and 60 °C for moringa, while the lowest values of were consistently associated with the most intensive operational conditions. Unlike oregano and moringa, chamomile exhibited a less

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proportional response to pressure increase, suggesting a more complex thermodynamic interaction between solvent density, terpene composition, and mass transfer mechanisms.

The logistic model adequately reproduced the temporal evolution of the extraction curves in the three evaluated species, capturing both the initial accelerated extraction stage and the asymptotic region associated with progressive solute depletion. The low SSD values obtained, particularly in oregano, confirmed the descriptive consistency of the proposed approach under different extraction conditions. From a phenomenological perspective, the parameters, and *b* provided kinetically interpretable descriptors associated with total extractable mass, characteristic extraction dynamics, and the convective-diffusional transition of the process. Although the proposed formulation does not replace high-resolution phenomenological models, the results demonstrate that the logistic approach constitutes a mathematically simplified and kinetically robust alternative for the comparative analysis and preliminary evaluation of supercritical extraction systems applied to aromatic and medicinal plant matrices.

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