

A MASS TRANSFER MODEL APPLIED TO THE SUPERCRITICAL EXTRACTION WITH CO₂ OF CURCUMINS FROM TURMERIC RHIZOMES (*Curcuma longa* L)

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Abstract - Increasing restrictions on the use of artificial pigments in the food industry, imposed by the international market, have increased the importance of raw materials containing natural pigments. Of those natural substances with potential applications turmeric rhizomes (*Curcuma longa* L), are one of the most important natural sources of yellow coloring. Three different pigments (curcumin, desmetoxycurcumin, and bis-desmetoxycurcumin) constitute the curcuminoids. These pigments are largely used in the food industry as substitutes for synthetic dyes like tartrazin. Extraction of curcuminoids from turmeric rhizomes with supercritical CO₂ can be applied as an alternative method to obtain curcuminoids, as natural pigments are in general unstable, and hence degrade when submitted to extraction with organic solvents at high temperatures. Extraction experiments were carried out in a supercritical extraction pilot plant at pressures between 25 and 30 MPa and a temperature of 318 K. The influence of drying pretreatment on extraction yield was evaluated by analyzing the mass transfer kinetics and the content of curcuminoids in the extracts during the course of extraction. The chemical identification of curcuminoids in both the extract and the residual solid was performed by spectrophotometry. Mass transfer within the solid matrix was described by a linear first-order desorption model, while that in the gas phase was described by a convective mass transfer model. Experimental results showed that the concentration profile for curcuminoids during the supercritical extraction process was higher when the turmeric rhizomes were submitted to a drying pretreatment at 343 K.

Keywords: extraction, drying, kinetic, supercritical CO₂, natural products, curcuminoids.

INTRODUCTION

The turmeric rhizome (*Curcuma longa*, L.) is one of the most important natural sources of yellow coloring. The pigments responsible for the yellow color characteristic of the oleoresin in turmeric are curcumin and two curcuminoids, desmethoxy-curcumin and bis-desmethoxy-curcumin (Govindarajan, 1980). These pigments are largely used in the food industry as substitutes for synthetic dyes like tartrazin. Curcumin is a yellow-orange crystalline powder, insoluble in water and ether but soluble in low-chain alcohols such as ethanol and methanol, acetone, acetic acid and dichloromethane. The extraction yield of oleoresin from turmeric rhizomes, using organic solvents such as ethanol, acetone and dichloromethane, lies between 5 and 13 [wt.%]. In general, the extraction of oleoresin from turmeric rhizomes is performed using ethanol as solvent (Krishnamurthy et al., 1975). In spite of the relatively high extraction yield obtained using acetone and ethanol, in the future the solvent extraction may be avoided as the standard procedure to obtain the curcuminoids since these pigments are unstable, and hence degrade when submitted to extraction with organic solvents at an elevated temperature. The residual solvent present in the extracts is another drawback of solvent extraction.

The supercritical separation technology using carbon dioxide as solvent makes possible not only the design of environment-friendly processes, but also the processing of biological materials (carbon dioxide has a relatively low critical temperature) and the possibility of obtaining products free of solvent residuals.

Since the development of processes for removing caffeine from coffee (Zosel, 1974) and extracting the essence of hops (Laws et al., 1980), the extraction of natural products with carbon dioxide in the near or supercritical state has received much attention.

In the last few years numerous applications of supercritical CO₂ for extraction of oily substances from different raw materials such as canola seeds (Lee et al., 1986), tucumã seed (França et al., 1991; Araújo, 1997), passion fruit (Corrêa et al., 1994), Turkish lavender flowers (Adasoglu et al., 1994), fungal material (Cygnarowicz-Provost et al., 1995), bacuri shell (Monteiro et al., 1999), and herbaceous and spice material (Ferreira et al., 1997; Reverchon, 1997), have been reported in the literature. Recently, there have been great interest in supercritical fluid extraction of pigments, including the carotenes from different raw materials, such as alfalfa (Favati et al., 1988), sweet potatoes (Spanos et al., 1993), microalgae (Mendes, 1995), buriti (França et al., 1999), and even the residue of the mechanical processing of palm oil (Birtigh et al., 1995; França et al., 1997).

In this work, turmeric rhizomes (*Curcuma longa*, L.) were submitted to extraction with supercritical CO₂ in a fixed bed to extract the oleoresin containing the curcuminoids. The turmeric rhizomes had previously been dried at 343 K. The extraction experiments were carried out in a supercritical extraction pilot plant at pressures between a 25 and 30 MPa and temperature of 318 K. A mass transfer model based on a linear first-order desorption for the solid phase and a convective one for the gaseous phase was applied to describe the kinetics of the extraction process.

MATERIALS AND METHODS

Materials

Tumeric rhizomes (*Curcuma longa* L) *in natura* were obtained from an experimental plantation administered by INCRA (Altamira-Pará-Brazil). Carbon dioxide, 99.99 [wt.%] pure, was provided by White Martins S/A.

Prior Treatment

The turmeric rhizomes were cleaned to remove the remaining sand, cut into small pieces (0.6 – 0.9 cm) and dried in an oven with air circulation (Fabbe, Model 179) at 343 and 378 K for 24 hours. Afterwards, they were ground with a comminuting mill (Framo-Gerätetechnik, Model A70). The dried solid material was sifted in a sieve shaker (Bertel, Model N800) fitted with sieves of different sizes (Tyler: 48, 65, 80, 100, 150 mesh). The dried material was packed in plastic bags and kept in a freezer at 268 K.

Experimental Setup

A schematic diagram of the extraction unit used in this work is shown in [Figure 1](#). It basically consists of an extractor (Metalwerksatt, TUHH) with 1000 cm³, a diaphragm-type compressor (Andreas Hofer, Mülheim, Germany, Model MKZ 120-50), a separator (Mechanical Workshop, UFPa) with 50 cm³, a thermostatic bath (Haake Mess-Technik GmbH, Karlsruhe, Germany, Model N3), a carbon dioxide reservoir, a gas flow meter (MF), and a control unit that displays the temperature and pressure inside the extractor. The detailed description of the extraction unit can be found in Chassagnez-Méndez (1998) and França et al. (1999).

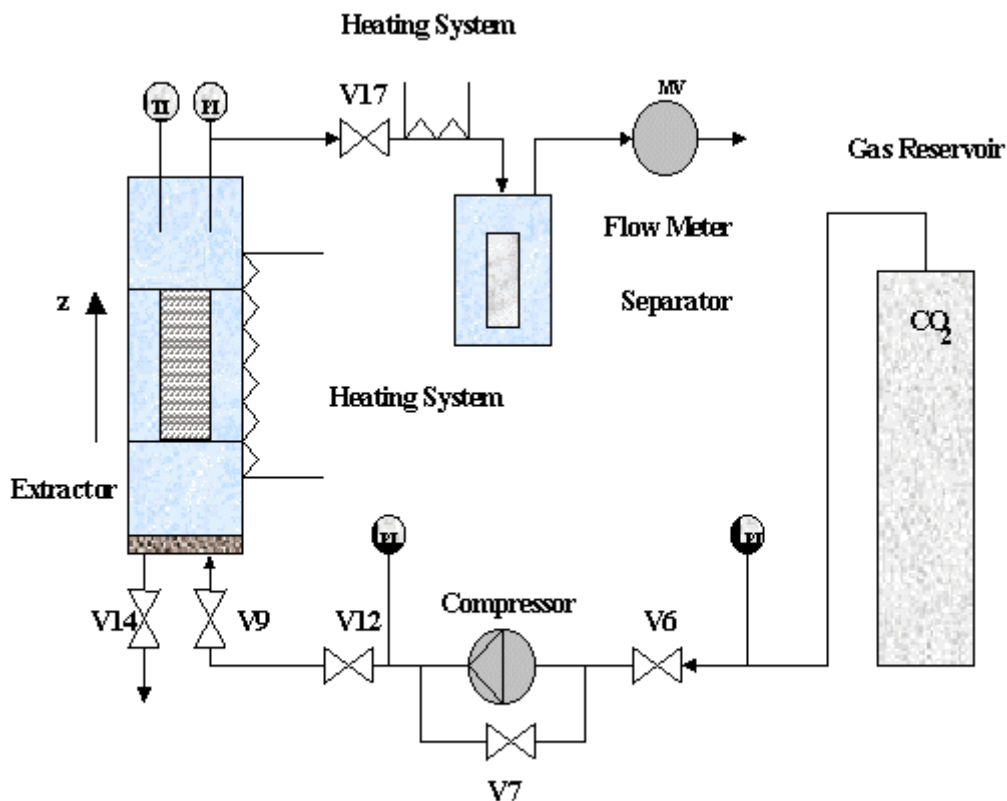


Figure 1: - Experimental setup.

Carbon dioxide was delivered at the required pressure by the membrane compressor and passed through a porous plate in order to assure a homogeneous flow of carbon dioxide along the fixed bed of 19.80 cm height and 1.76 cm internal diameter, placed inside the extractor. The supercritical carbon dioxide/oil resin was expanded in the separator. The expanded carbon dioxide passed through a gas flow meter and was released to the atmosphere. The pressure inside the extractor was measured by a Bourdon-type gauge (0-400 bar, ± 5 bar; Model DIN.S, Wika, Germany) and the temperature was monitored by a thermocouple (NiCr/Ni).

Curcuminoids (computed in terms of curcumin) present in both the oleoresin obtained in the extracts and the residual solid material were chemically analyzed by spectrophotometry.

In order to quantify the curcuminoids in the extracts, the oleoresin was diluted in ethanol (pa, Nuclear) and the samples were analyzed in a spectrophotometer (GBC, Model UV/VVIS 916) at 425 nm. The values obtained for the absorbance (A) were compared with a calibrated curve constructed using standard solutions of curcuminoids (pa., Merck, Darmstadt) diluted in ethanol (pa. Nuclear), and the concentration (C) was computed using the following equation:

$$A = 0.00434 + 0.1805 \cdot C \quad (1)$$

RESULTS AND DISCUSSIONS

The operating conditions and process parameters of the supercritical CO₂ extraction of oleoresin from tumeric rhizomes (*Curcuma Longa L*) are shown in [Table 1](#).

Table 1: Process parameters and operating conditions for the extraction of oleoresin from turmeric rhizomes (*Curcuma longa L*) with supercritical CO₂ at 318 K.

P [MPa]	Time [min]	T _{heating} [K]	m _{CO2} [kg/min]	Yield* [wt.%]
25	107	343	14.65	5.95
30	85	343	11.21	6.51
25	85	378	11.33	4.50
30	105	378	13.27	5.28

*mass of extracted oleoresin/mass of dried solid matrix.

The fixed bed characteristics of the dried rhizomes at 343 K were a density of 0.728 ± 0.026 g/m³, measured by the sand picnometry technique (Buczek and Geldart, 1986); a porosity of 0.442 ± 0.02 ; a mean particle diameter (\bar{D}_{SAUTER}) of 207 μ m, calculated as suggested by Massarani (1997); and a volume of 27.37 cm³.

The fixed bed characteristics of the dried rhizomes at 378 K were a density of 0.751 ± 0.048 g/m³, measured by the sand picnometry technique (Buczek and Geldart, 1986); a porosity of 0.428 ± 0.03 ; a mean particle diameter (\bar{D}_{SAUTER}) of $214 \mu\text{m}$, calculated as suggested by Massarani (1997); and a volume of 26.51 cm^3 .

[Table 1](#) shows that the maximum yield and the minimum solvent consumption was achieved at 30 MPa after a drying pretreatment of the tumeric rhizomes at 343 K. In supercritical extraction processes, the mechanical energy needed for the recompression of carbon dioxide and the extraction time play important roles in the economics of the process, and hence, the extraction of the oleoresin from the rhizomes of turmeric (*Curcuma longa* L) should be carried out at 30 MPa.

The mathematical model applied to describe the extraction kinetics states that mass transfer in the gaseous phase is described by a convective model without the dispersion term, considering the extraction rate to be proportional to the oleoresin concentration in the solid phase (linear first-order desorption). This phenomenon in the solid phase can be interpreted as a transport process with instantaneous equilibrium, based on the variations in solute concentration in the plant material and a small mass transfer resistance. This model was presented first by Tan and Liou (1988).

Mass Balance in the Fluid Phase

$$\frac{\partial C_f}{\partial t} + U \frac{\partial C_f}{\partial z} = - \frac{(1 - \varepsilon) \rho_s}{\varepsilon \rho_f} \frac{\partial C_s}{\partial t} \quad (2)$$

where C is the oleoresin concentration, ρ is the density, ε is the porosity of the bed, U is the superficial velocity of the solvent and z and t are the axial and temporal variable, respectively. The subscript f and s represent fluid and solid phase respectively.

Boundary Conditions

$$C_f = 0, t = 0 \quad (3)$$

$$C_f = 0, z = 0 \quad (4)$$

Mass Balance in the Solid Phase

$$(1 - \varepsilon) \rho_s \frac{\partial C_s}{\partial t} = -KC_s \quad (5)$$

Boundary Conditions

$$C_s = C_{0,t=0} \quad (6)$$

The solute concentration in the fluid phase is given by the following equation:

$$C_f(z = L; t) = \frac{(1 - \varepsilon) \rho_s}{\varepsilon \rho_f} C_o \left\{ \exp \left[-K \left(t - \frac{zL}{U} \right) \right] - \exp(-Kt) \right\} \quad (7)$$

The extracted oleoresin (m_{ext}) is given by the equation as follows

$$m_{\text{ext}} = \int_0^t m_{\text{CO}_2} C_f(z = L, t) dt \quad (8)$$

Since the physical characteristics of the fixed bed were determined experimentally and the operating conditions are known, including the solvent flux rate, m_{CO_2} , the linear first-order desorption constant (K) given by equation (5) is the only remaining adjustable parameter. [Table 2](#) shows the linear first-order constant and the equilibrium solubility for all the experiments.

Table 2: Linear first-order constant and the equilibrium solubility for all the experiments.

	T	Y	K
P [MPa]	[K]	[g _{oil} /Kg _{CO2}]	[1/min]
25	343	2.80	0.04006
30	343	3.78	0.07344
25	378	2.30	0.02084
30	378	2.94	0.02552

[Figure 2](#) illustrates the yield of the supercritical CO₂ extraction of oleoresin from the tumeric rhizomes submitted to a drying pretreatment, at pressures between 25 and 30 MPa and a temperature of 318 K. The results show that the drying pretreatment has a great influence on extraction yield. The tumeric rhizomes submitted to a drying pretreatment at 343 K showed higher yields in extraction experiments carried out maintaining the system pressure constant. This may be due to the fact that a drying pretreatment of the tumeric rhizomes at 378 K for 24 hours causes a higher volatilization of the oleoresin, hence affecting the extraction yield. It could also be observed that supercritical CO₂ extraction of the oleoresin from the tumeric rhizomes submitted to a drying pretreatment at pressures of 25 and 30 MPa, led to similar extraction yields. This physical observation emphasizes the fact that volatilization of the oleoresin takes place during the drying pretreatment at 378 K.

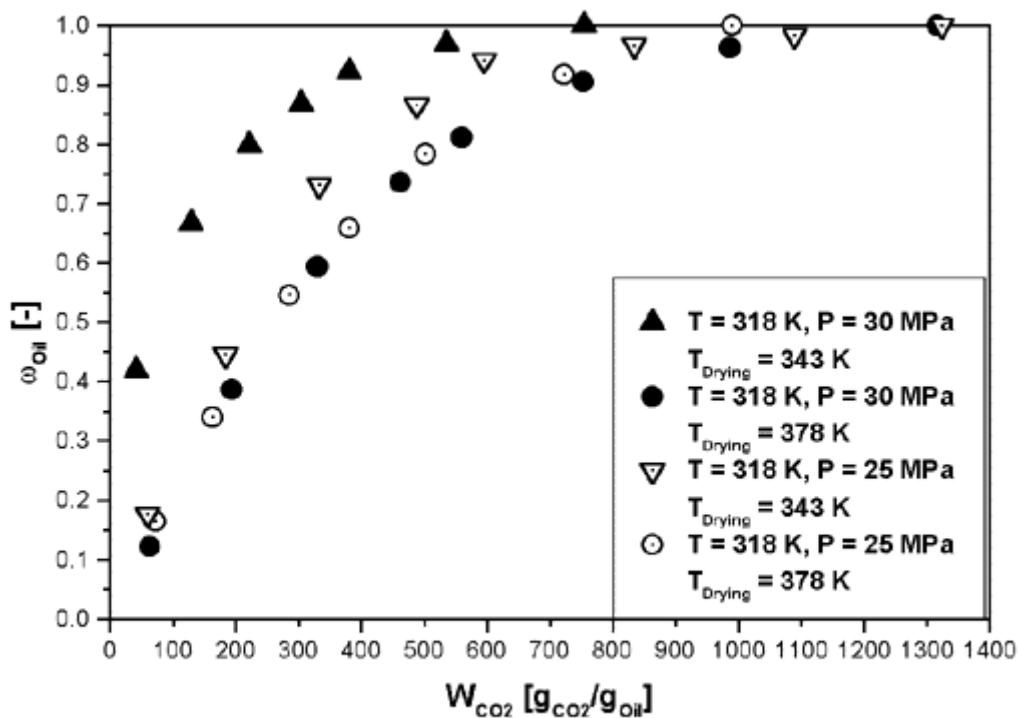


Figure 2: Yield of the supercritical CO₂ extraction of oleoresin from tumeric rhizomes

The weight fraction of curcuminoids (expressed in terms of curcumin) in the oleoresin obtained by supercritical CO₂ for all the extraction experiments is shown in [Figure 3](#). In all the experiments, the concentration of curcuminoids increases during the course of extraction. It is observed that the effect of both pressure and drying pretreatment on concentration becomes significant as the extraction time increases. A higher concentration of carotenoids in the oleoresin was achieved at 30 MPa when the rhizomes were submitted to a drying pretreatment at 343 K. It can also be observed that the drying pretreatment at 378 K causes a decrease in the curcuminoids content in the oleoresin.

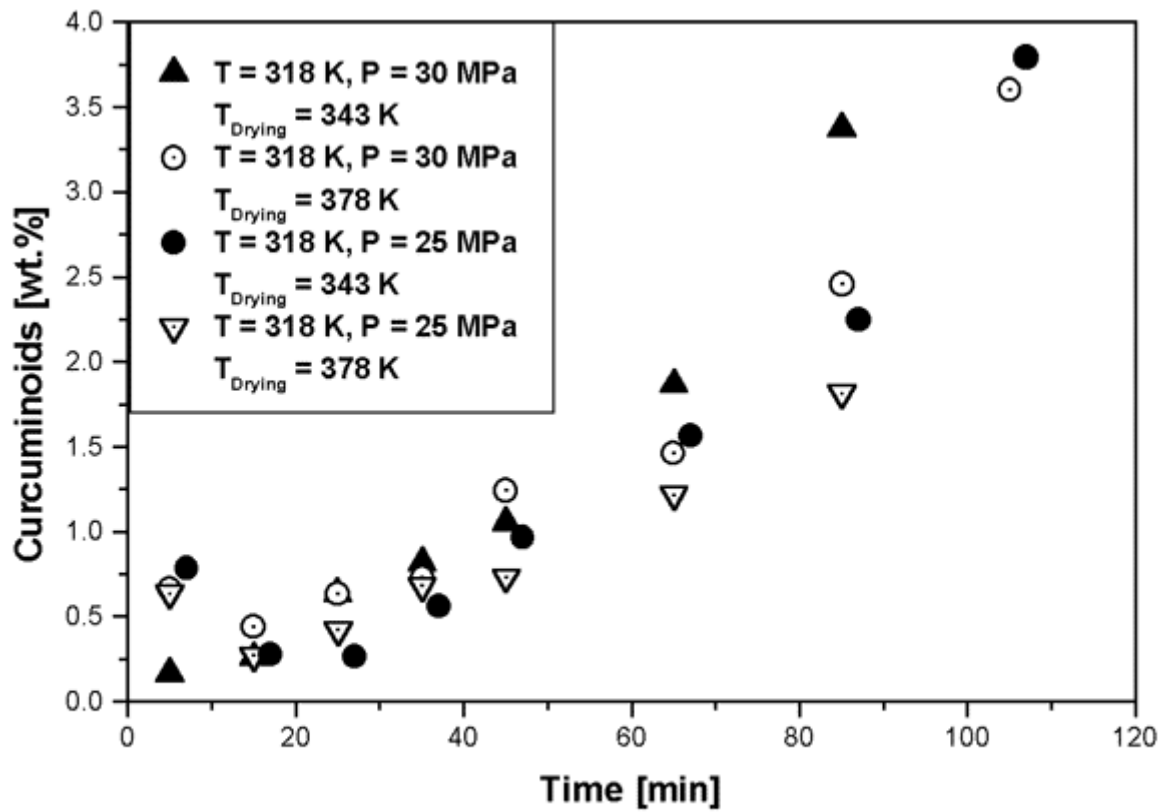


Figure 3: Concentration of curcuminoids in the oleoresin during the course of extraction.

The mathematical model regression applied to the extraction of oleoresin from tumeric rhizomes with supercritical CO₂ is depicted in [Figure 4](#). It could be observed that the proposed mass transfer model showed good agreement with the experimental data.

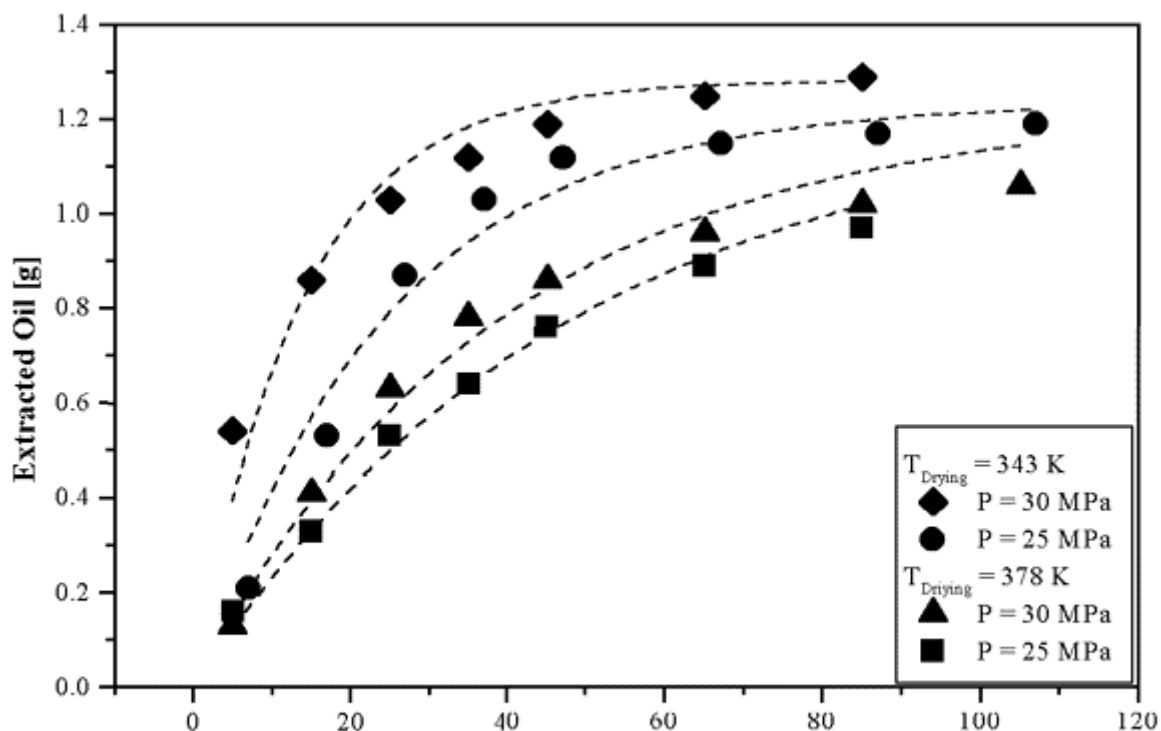


Figure 4: Model regression applied to the extraction of oleoresin from tumeric rhizomes with CO₂.

A comparison between the oleoresin extraction yields from the tumeric rhizomes, obtained by conventional solvent extraction (Krishnamurthy et al., 1976; George et al., 1981) and supercritical CO₂ extraction, shows that conventional solvent extraction obtains higher yields.

CONCLUSIONS

Based on evaluation and analysis of experimental extraction data, the following conclusions can be stated. For economic reasons, the extraction of oleoresin from turmeric rhizomes (*Curcuma longa*, L.) should be carried out at 30 MPa. The drying pretreatment of tumeric rhizomes at 378 K led to a decrease in both the extraction yield and the concentration of curcuminoids in the oleoresin. The extraction of oleoresin from tumeric rhizomes using organic solvents produces higher yields, as compared to supercritical CO₂ extraction. The proposed mass transfer model showed good agreement with the experimental data.

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