

Modeling of supercritical extraction of mannitol from plane tree leaf

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Abstract

The objective of this study was to investigate the theoretical feasibility of using supercritical fluid extraction of Mannitol from plane tree leaf as an alternative technology in the pharmaceutical industry. Simulation of an extraction column using dense liquid and supercritical carbon dioxide was modeled involving partial differential equations, using orthogonal collocation on finite elements. The important solvent extraction parameters such as the partition coefficient, mass transfer coefficient, dispersion coefficient, molecular diffusion and extraction efficiency (the amount of Mannitol extracted versus the amount of solvent used) were investigated as a function of the dimensionless Reynold's and Peclet numbers in order to optimize the extraction column geometry and the carbon dioxide operating conditions. The results of this study demonstrated that supercritical extraction is a viable technique for Mannitol production and that the process conditions for a large commercial extraction system do not require a high temperature in order to obtain a high extraction efficiency. However, at low pressures, the solubility of Mannitol in carbon dioxide would limit the success of the extraction process and at very high pressures the extraction technique may not be economically feasible. To investigate the authenticity of the mathematical model, the experimental data for the desorption of hexachlorobenzene from soil was compared with the theoretical results of this research. The model is able to predict the experimental data quite well without any adjustable parameters. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mannitol; Supercritical extraction; Plane tree leaf

1. Introduction

At present, Mannitol is produced by either hydrogenation or reduction chemical reaction of Mannose [1] and the extraction of Manna with liquid solvents. Both approaches have some disad-

vantages. In the chemical reaction procedure, Sorbitol is produced as a by-product which cannot be removed by simple distillation. Furthermore, the need for expensive metallic catalyst or a reducing agent such as sodium borohydride and also high temperature and pressure operating conditions make this method economically unfavorable. In the extraction process using normal hexane as the solvent, there are important economic, environ-

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mental and safety problems. Vacuum distillation is needed to purify the Mannitol but complete separation is still not possible. Since the Mannitol is used in the pharmaceutical industry, incomplete purification of Mannitol is unacceptable. The toxic and flammability properties of hexane are major disincentives to its use. Thus research in developing a safer and more effective method for Mannitol production is needed.

The main objective of this article is of the theoretical feasibility of the supercritical fluid extraction of Mannitol from natural resources. It has been found that Mannitol is contained naturally in the agricultural sources such as plane tree leaves, olive, seaweed, parsley, mushrooms, onions, strawberries, watermelons and grasses [2]. Since it has been experimentally shown that plane tree leaf contains as much as 80–90% Mannitol, this material was chosen as the object of this study.

Supercritical fluids have proved to be effective solvents for applications in chemical, petrochemical, pharmaceutical and environmental processes. They have liquid-like densities, gas-like viscosities and diffusivities at least an order of magnitude higher than that of normal liquid, which may result in superior mass transfer characteristics. Further, the solvent density, and hence the solvent effectiveness, can be controlled by small changes in temperature and pressure. Carbon dioxide is usually preferred as a supercritical fluid, because it is non-toxic and non-flammable, has a low critical temperature of 304.4 K and a moderate critical pressure of 72.8 bar [3–6].

In order to establish supercritical extraction as an alternative technology in the pharmaceutical industry for Mannitol production, simulation of an extraction column was carried out to determine the optimum range of operating conditions and the geometric configuration of the packed bed to be used.

2. Model description

The fixed bed consists of the shredded plane tree leaf containing Mannitol as the stationary phase with the flowing supercritical carbon diox-

ide as the mobile phase. The mathematical formulation of supercritical extraction systems is similar to the formulation of adsorbers, and some literature is available on adsorption processes [7,8]. Various models have been proposed to explain the effects of operating conditions and design variables on the device performance of pressure-swing adsorption [9–11], but relatively little information is available in the literature on the modeling of supercritical extraction.

Mathematically, the overall adsorption/desorption of the Mannitol from the solid matrix (plane leaf) can be described by a set of partial differential equations (PDEs). The complexity of the mathematical model depends on the simplifying assumptions considered. The following criteria are assumed in this study: (1) Axial dispersion is significant; (2) Radial dispersion is neglected because of the packed bed geometry (small column diameter); since the spreading of the concentration front in a chromatographic system is due entirely to the axial dispersion and bulk flow effects, the radial dispersion is thus insignificant and can be omitted; (3) Axial concentration gradients are important; (4) Radial concentration gradients are neglected; (5) The system is isothermal; (6) The packed column is isobaric; (7) There is local equilibrium in the pores of the shredded plane leaf; (8) The physical properties of the supercritical fluid are constant.

Since the Mannitol is transported through the column by both axial dispersion and bulk flow, the differential mobile phase mass balance is:

$$\frac{\partial C}{\partial \tau} - \frac{1}{\text{Pe}_b} \frac{\partial^2 C}{\partial z^2} + \frac{\partial C}{\partial z} + \frac{1 - \varepsilon}{\varepsilon} \frac{3L}{R_p} \frac{\text{Bi}}{\text{Pe}_p} (C - c_s) = 0 \quad (1)$$

The boundary conditions for this equation are:

$$\text{at } z = 0: \frac{\partial C}{\partial z} = \text{Pe}_b (C - C_0) \quad (1a)$$

$$\text{at } z = 1: \frac{\partial C}{\partial z} = 0 \quad (1b)$$

For desorption, the initial condition is given by:

$$C = C_0 \text{ when } \tau = 0 \text{ for all } z \quad (1c)$$

Assuming local equilibrium in the pores of the solid particles, the differential stationary phase mass balance is:

$$\left[\varepsilon_p + (1 - \varepsilon_p) \frac{\partial q}{\partial c} \right] \frac{\partial c}{\partial \tau} = \frac{1}{\text{Pe}_p} \frac{L}{R_p} \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left[\rho^2 \frac{\partial c}{\partial \rho} \right] \quad (2)$$

The relevant boundary conditions are:

$$\text{at } \rho = 1: \text{Bi}(C - c_s) = \frac{\partial c}{\partial \rho} \quad (2a)$$

$$\text{at } \rho = 0: \frac{\partial c}{\partial \rho} = 0, \quad \frac{\partial q}{\partial \rho} = 0 \quad (2b)$$

$$c = C_0, \quad q = q_0 \text{ when } \tau = 0 \text{ for all } \rho \quad (2c)$$

where q and c are related by the adsorption isotherm, $q = f(c)$. Using the Freundlich isotherm:

$$q = K \left(\frac{c}{C_{\text{sat}}} \right)^n \quad (3)$$

we have

$$\frac{dq}{dc} = \frac{Kn}{C_{\text{sat}}} \left(\frac{c}{C_{\text{sat}}} \right)^{n-1} = \frac{nq}{c} \quad (4)$$

3. The numerical solution technique

Several methods are available to solve the system of Eqs. (1)–(4). The most commonly used technique is the finite-difference method [12], which requires strict conditions for stability. For the case of a linear isotherm, the system can be solved analytically by the Fast Fourier Transform [13]; this method cannot be applied to non-linear isotherms, however Raghavan and Ruthven [14] used the orthogonal collocation method to solve this system of partial differential equations (PDE). However, as the profile along the bed becomes sharper, this method fails because of numerical oscillations. One way to overcome this difficulty is to apply orthogonal collocation on finite elements (OCFE). The OCFE technique combines the classical procedure of orthogonal collocation with the high accuracy of the finite element method.

4. Orthogonal collocation on finite elements

In Eqs. (1) and (2), the variables z and ρ take values in the interval $[0, 1]$. In the z direction, the interval is divided into N_{el} equally-spaced finite elements by fixing $(N_{\text{el}} - 1)$ interval node points, Z_k for $k = 1, \dots, N_{\text{el}} - 1$, with $Z_0 = 0$ and $Z_{N_{\text{el}}} = 1$. The length of each finite element is then:

$$L_{\text{el}} = \frac{1}{N_{\text{el}}} \quad (5)$$

Orthogonal collocation is applied inside each finite element, a process which requires the normalization of the variable in each element, given by:

$$s_k = \frac{z - Z_{k-1}}{L_{\text{el}}} \quad (6)$$

Only one element is considered in the radial direction for each particle, since a relatively simple profile is expected in the particle. In each element, orthogonal collocation points are calculated as roots of given polynomials and at each collocation point, the first derivative and the Laplacian of the unknown function (Mannitol concentration) are discretized using discretization matrices A and B which can be calculated from the collocation points [15]. In the axial direction, NP interior collocation points are considered and Legendre polynomials are used. In the radial direction (inside the shredded plane tree leaf particles), NR interior collocation points are considered and Jacobi polynomials in ρ^2 are used to take advantage of the problem symmetry [15]. This ensures that the condition at the center of the particle is automatically satisfied.

The orthogonal collocation on finite-elements method transforms the system of PDEs (Eqs. (1) and (2)) into a system of algebraic differential equations (ADEs) where the unknowns are the Mannitol concentrations at each node point. The mobile phase Mannitol concentration corresponding to the i th point in the k th finite element is denoted by C_i^k , and the plane tree leaf pore phase concentration corresponding to the j th point is denoted by $C_j^{i,k}$, where i and k have the same meaning as before.

At each interior collocation point (z or ρ direction), the corresponding differential equation (Eqs. (1) and (2)) is supposed to be satisfied. At each z -direction interior collocation point, Eq. (1) is transformed as follows:

$$\begin{aligned} \frac{dC_i^k}{d\tau} - \frac{1}{Pe_b} \frac{1}{L_{el}^2} \left[\sum_{l=1}^{l=NP+2} BZ_{i,l} C_l^k \right] \\ + \frac{1}{L_{el}} \left[\sum_{l=1}^{l=NP+2} AZ_{i,l} C_l^k \right] \\ + \frac{1-\varepsilon}{\varepsilon} \frac{3L}{R_p} \frac{Bi}{Pe_p} (C_i^k - c_{NR+1}^{i,k}) = 0 \end{aligned} \quad (7)$$

for all $i = 2, 3, \dots, NP + 1$ and for all $k = 1, 2, \dots, N_{el}$. Also at each ρ -direction interior collocation point, Eq. (2) is transformed as follows:

$$\begin{aligned} [\varepsilon_p + (1 - \varepsilon_p) f'(c_j^{i,k})] \frac{dc_j^{i,k}}{d\tau} \\ - \frac{1}{Pe_p} \frac{L}{R_p} \left[\sum_{l=1}^{l=NR+1} BR_{j,l} c_l^{i,k} \right] = 0 \end{aligned} \quad (8)$$

for all $i = 1, 2, \dots, NP + 2$ for all $k = 1, 2, \dots, N_{el}$, and for all $j = 1, 2, \dots, NR$, where $f'(c)$ is defined by Eq. (4).

The associated boundary conditions are:

Bed inlet: $z = Z_0 = 0$

$$\frac{1}{L_{el}^2} \left[\sum_{l=1}^{l=NP+2} AZ_{1,l} C_l^1 \right] - Pe_b (C_1^1 - C_0) = 0 \quad (8a)$$

Bed exit: $z = Z_{N_{el}} = 1$

$$\frac{1}{L_{el}} \left[\sum_{l=1}^{l=NP+2} AZ_{NP+2,l} C_l^{N_{el}} \right] = 0 \quad (8b)$$

An additional boundary condition at the surface of the plane tree leaf particle ($\rho = 1$) is given by:

$$\left[\sum_{l=1}^{l=NR+1} AR_{NR+1,l} c_l^{i,k} \right] - Bi (C_i^k - c_{NR+1}^{i,k}) = 0 \quad (8c)$$

for all $i = 1, 2, \dots, NP + 2$ and for all $k = 1, 2, \dots, N_{el}$.

Between each finite element ($z = Z_k, k = 1, 2, \dots, N_{el} - 1$), continuity of the flux is imposed:

$$\left[\sum_{l=1}^{l=NP+2} AZ_{NP+2,l} C_l^k \right] - \left[\sum_{l=1}^{l=NP+2} AZ_{1,l} C_L^{k+1} \right] = 0 \quad (9)$$

It has to be noted that:

$$C_{NP+2}^k = C_1^{k+1} \text{ for all } k = 1, 2, \dots, N_{el} \quad (9a)$$

The initial condition is:

$$\text{at } \tau = 0, C_i^k = c_j^{i,k} = C_0 \text{ for all } i, j, k \quad (9b)$$

Eqs. (7)–(9) form a system of $[N_{el}(NP + 1) + 1](NR + 2)$ ADEs with $[N_{el}(NP + 1) + 1](NR + 2)$ unknowns which can be written in the form:

$$\alpha \frac{du}{d\tau} + \beta u = 0 \quad (10)$$

with the initial condition:

$$\text{at } \tau = 0, u = u_0 \quad (10a)$$

where u is the vector containing the values of the Mannitol concentration at each grid point. Following Yu and Wang [16], the grid points were numbered in a way to reduce the bandwidth of the matrix β and decrease the computational time. This system with a 28×28 matrix was solved using a Gauss–Jordan algorithm computer program. In the aforementioned matrix, seven variables are related to the concentration of Mannitol in the mobile phase and the remaining 21 variables to the concentration of Mannitol in the stationary phase.

5. Parameter correlations

The parameters involved in the model are the mass transfer coefficient to the bulk phase, the axial dispersion coefficient in the fluid phase, the effective pore diffusivity in the particle and the Freundlich adsorption equilibrium parameters, K and n . These were evaluated using existing correlations and available data.

The mass transfer coefficient was estimated using the empirical correlation reported by Wakao [17]:

$$Sh = 2 + 1.1 Sc^{1/3} Re^{0.6} \quad (11)$$

Although this correlation was developed for convective processes, it has been used successfully for supercritical extraction [6].

The axial dispersion coefficients (D_l) for supercritical carbon dioxide in packed beds have been measured by Ghoreishi and Akgerman [18], and also Tan and Liou [19]. Using the method of propagation of errors, Ghoreishi and Akgerman [18] reported their experimental data with an accuracy of $\pm 8.6\%$ S.D. Tan and Liou [19] proposed an empirical correlation involving dimensionless groups, which generated their data with an average deviation of 8.5% as follows:

$$Pe_{pd} = 0.187Re^{0.265}Sc^{-0.919} \quad (12)$$

Since correlations based on dimensionless groups are useful for the scale-up of many processes, the correlation (Eq. (12)) was used in this research to evaluate the axial dispersion in supercritical carbon dioxide. The densities of supercritical carbon dioxide were evaluated from IUPAC data [20], and the viscosities were interpolated from the data of Tan and Liou [21]. The bed porosity of the packed column was assumed to be 0.5.

The effective pore diffusivity in the particle is given by:

$$D_p = \frac{\epsilon_p}{\tau_p} D_m \quad (13)$$

where D_m is the diffusion coefficient of the organic in the supercritical fluid, and τ_p is the tortuosity factor [22]. The tortuosity factor of solids is usually in the range of 2–8 and was held constant at a value of four using Mannitol in this study. The diffusion coefficient of Mannitol in supercritical carbon dioxide was calculated by the Taylor dispersion technique [23]. The particle porosity of shredded plane tree leaf evaluated, using the nitrogen desorption technique, was 0.12. Thus, the effective pore diffusivity was evaluated from Eq. (13) using the values of molecular diffusivity, particle porosity, and tortuosity.

At equilibrium, the distribution of Mannitol between the solid phase and the supercritical phase is determined by the adsorption isotherm. The adsorption isotherm of Mannitol on plane tree leaf in dense liquid and supercritical carbon dioxide was modeled using the Freundlich isotherm, as given by Eq. (3). The Freundlich constant, n , was assumed to be 1.0, so that a linear isotherm was used in this study. The Fre-

undlich constant, K , a distribution coefficient is defined as follows:

$$K = \frac{\text{Mass of Mannitol in the supercritical phase}}{\text{Volume of supercritical phase}} = \frac{\text{Mass of Mannitol in the plane tree leaf}}{\text{Mass of the plane leaf}} \quad (14)$$

This is analogous to the following equation:

$$K = \frac{\text{Mass of the plane tree leaf}}{\text{Volume of supercritical phase}} \quad (15)$$

In the modeling of the supercritical fluid extraction, two mobile and stationary phases are considered; considering the fact that the solute in the solid matrix (Mannitol in plane tree leaf) is extracted by the solvent, therefore it can be assumed that the mass of Mannitol in the mobile phase (supercritical fluid) would finally be the same as the mass of Mannitol in the stationary phase (plane leaf). Dividing the partition coefficient (Eq. (15)) by the density of the supercritical fluid at the system operating condition results in units of (g plane leaf)/(g supercritical fluid). Thus, the distribution coefficient determines the amount of the plane tree leaf which can be extracted using 1 g of supercritical fluid. It is imperative to realize that the K value defined in this study is not the thermodynamic distribution coefficient. The thermodynamic distribution coefficient is based on the ratio of mole fraction of Mannitol between two phases, namely, the mobile phase (supercritical fluid) and the stationary phase (plane leaf). Without a definitive molecular weight for plane leaf, the thermodynamic partition coefficient for the supercritical extraction of Mannitol will remain undefined. Since the saturation concentration (solubility) of Mannitol in the supercritical carbon dioxide has not been measured experimentally, the solubility of a similar compound, glucose, was assumed.

6. Optimization of extraction column geometry

In order to select the best dimensions (length, H , and diameter, D) for the cylindrical pressure

vessel used for the packed bed with the known volume, V , a suitable objective function which minimizes the capital cost was formulated using the following assumptions: (1) The ends of the vessel are 2:1 ellipsoidal heads; (2) The cost of fabrication for the ends is higher than for the sides; (3) The wall thickness (t') is a function of the vessel diameter, allowable steel stress, pressure rating of the vessel and the corrosion allowance; (4) There is no wasted material during fabrication. The objective function obtained is:

$$of = St' \rho' [2A + A'] \quad (16)$$

Using the numerical procedure developed by Happel and Jordan [24], the optimum $(H/D)_{opt}$ for different operating pressures was determined.

7. Results and discussion

The effects of the operating temperature and pressure of supercritical carbon dioxide on the desorption profile of Mannitol from the shredded plane leaf are shown in Figs. 1 and 2. In Fig. 1, the operating pressure of 1.5 kpsi was held constant while the operating temperature was changed from 290 to 330 K. The volumetric flow rate of carbon dioxide is held constant at $5.55e^{-8}$ m³/s and the configuration of the packed bed is

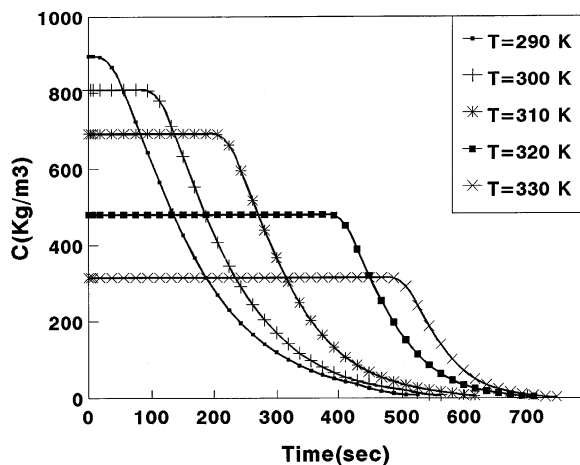


Fig. 1. Desorption profile of mannitol from plane leaf at different temperatures.

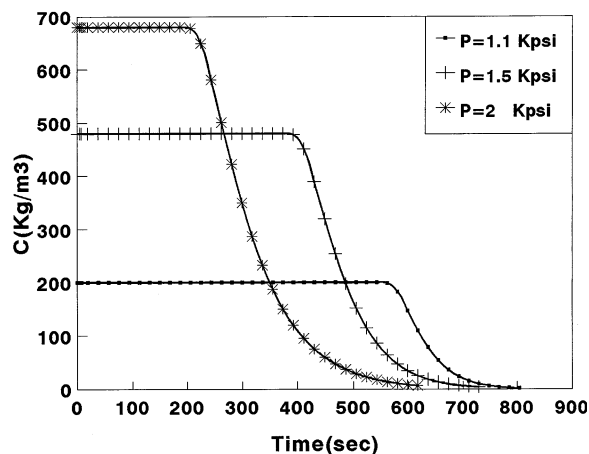


Fig. 2. Desorption profile of mannitol from plane leaf at different pressures.

considered to be 0.25 m length and 0.0046 m diameter. As shown in Fig. 1, the effect of temperature on the density of carbon dioxide can be realized by considering the shape and tail of the desorption profiles. At lower temperatures the saturation concentration or in other words, the solubility of Mannitol in carbon dioxide is higher than that of higher temperatures. Therefore, the shape of the desorption profile at lower temperatures such as 290 K is sharper than that at 330 K and consequently this results in a shorter residence time in the column.

Fig. 2 shows the effect of different operating pressures of extracting fluid on the desorption profile. For this figure, the temperature is held at 320 K and the same extraction column geometry was used. The same effect of density of carbon dioxide is realized on the behavior of desorption profile. As the pressure of flowing fluid inside the bed is increased, the solubility of Mannitol in carbon dioxide increases and a sharper profile is obtained. Theoretically, the long tail observed in the desorption profiles can be attributed to axial dispersion, mass transfer resistance. Thus, operating at higher pressures decreases the residence time required for complete recovery of solute (Mannitol) from the solid matrix (shredded plane leaf).

In Fig. 3, the effects of different pressures and Reynold's numbers at a constant temperature of

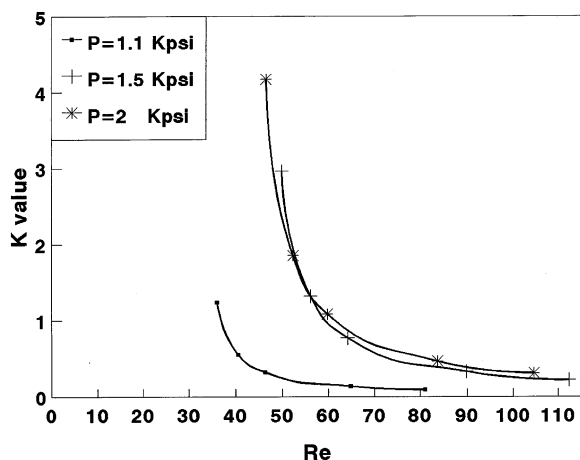


Fig. 3. Distribution coefficient at different pressures and Reynold's numbers.

320 K are shown on the partition coefficient. A residence time of 598 s is considered for this system. An increase in the operating pressure of carbon dioxide from 1.1 to 2 kpsi indicates that the distribution coefficient increases. The effect of varying temperature at constant pressure of 1.5 kpsi on the distribution coefficient is shown in Fig. 4. It is clear that a higher temperature decreases the partition coefficient.

The most likely explanation of the behavior of the partition coefficient relies on the density of carbon dioxide as the extracting supercritical

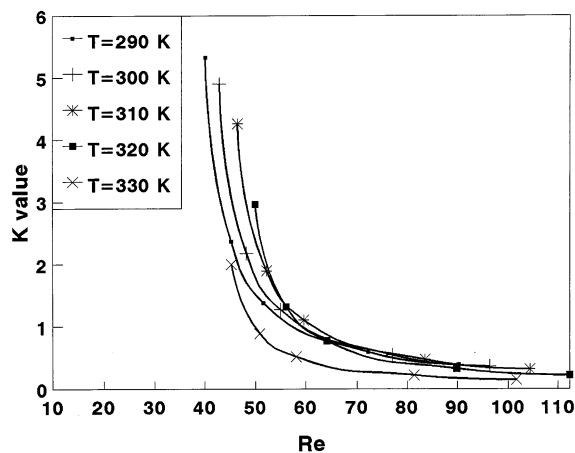


Fig. 4. Distribution coefficient at different temperatures and Reynold's numbers.

fluid. At temperatures and pressures above the critical point, carbon dioxide has densities that are higher than those of gases but similar to liquids. The liquid-like behavior of carbon dioxide results in greatly enhanced solubilizing capability. For instance, the increase in the K value at higher pressures (at 320 K) is due to changes in the ratio of the masses of the supercritical phase (mobile phase) to solid phase (stationary phase) which is a direct result of the density of carbon dioxide increasing from 0.25 to 0.72 g/cm³. The increase in partition coefficient indicates that 1 g of carbon dioxide is capable of extracting more Mannitol from plane tree leaf at 2 kpsi than at 1.1 kpsi.

By contrast, decreasing K value indicates that the amount of carbon dioxide needed to recover the Mannitol is more at 330 than 290 K. This can be attributed to a decrease in the density of carbon dioxide from 0.88 to 0.30 g/cm³. It is also important to realize that in the range above the critical point, retrograde behavior is observed. In the particular range of chosen operating conditions for the solvent, an enhanced retrograde solubility prevailed in such a manner that increasing temperature is more effective in decreasing solvent density (carbon dioxide) than increasing the solute (Mannitol) vapor pressure. At a Reynold's number of 50, temperature of 320 K and pressure of 2 kpsi, the partition coefficient in Fig. 3 predicts that 1 g of carbon dioxide is able to extract 4.25 g of shredded plane leaf.

The effects of different temperatures, pressures and Reynold's numbers of the packed column on the extraction efficiency are shown in Figs. 5 and 6. Fig. 5 clearly indicates that lower temperature results in a higher percentage extraction. Also, as shown in Fig. 6, higher extraction efficiency is obtained at higher pressures. These results are attributed to the solubility power of carbon dioxide at higher pressures and lower temperatures. The results presented in Figs. 5 and 6 are in agreement with those presented in Figs. 3 and 4.

As far as the dimensionless Reynold's number is concerned, it can be concluded that a moderate increase in Reynold's number up to 70 results in higher efficiency; subsequent increases do not significantly affect the extraction rate. A low Reynold's number results in a lower rate of dis-

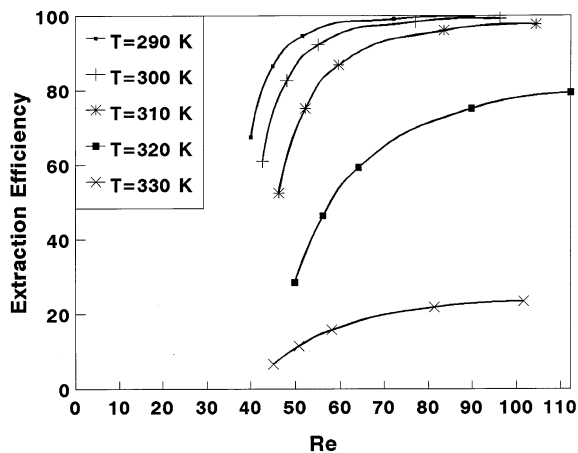


Fig. 5. Extraction of mannitol at different temperatures and Reynold's numbers.

person and mass transfer and a high Reynold's number increases the dispersion and mass transfer rate. Since a high rate of dispersion hinders the extraction rate and efficiency, the choice of a moderate Reynold's number seems to be the most suitable. Moreover, the results indicate that the process conditions do not require a high temperature in order to obtain an acceptable extraction rate. Very high pressure may make the process economically unfeasible.

In Figs. 7 and 8, the effect of different shredded plane leaf Peclet numbers (Pe_p) on the distribution

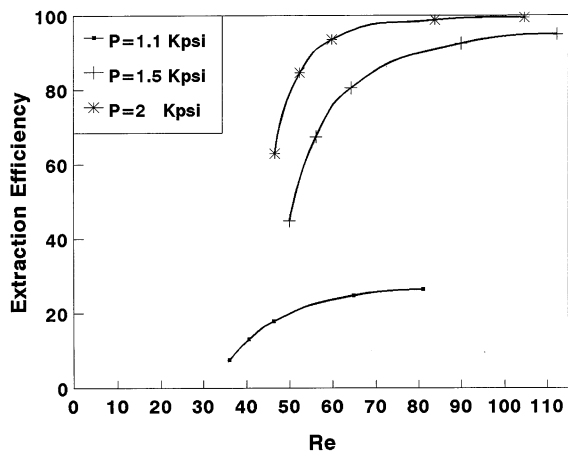


Fig. 6. Extraction of mannitol at different pressures and Reynold's numbers.

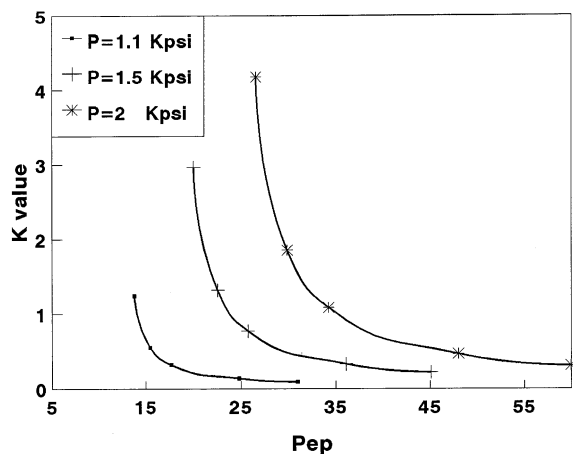


Fig. 7. The effect of particle Peclet number on the distribution coefficient at different pressures.

coefficient at different pressures and constant temperature has been investigated. Fig. 7 shows that increasing Peclet number reduces the K value, a phenomenon which can be explained as follows. The dimensionless Peclet number was changed by increasing the size of the shredded material which increases the axial dispersion coefficient [19]. Consequently, a higher rate of dispersion hinders the extraction process, so that a lower distribution coefficient is to be expected. The same effect has been studied at different operating temperatures and a constant pressure of 1.5 kpsi in Fig. 8. The

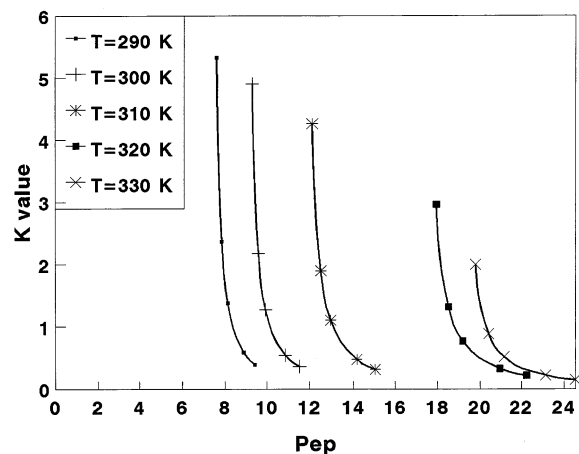


Fig. 8. The effect of particle Peclet number on the distribution coefficient at different temperatures.

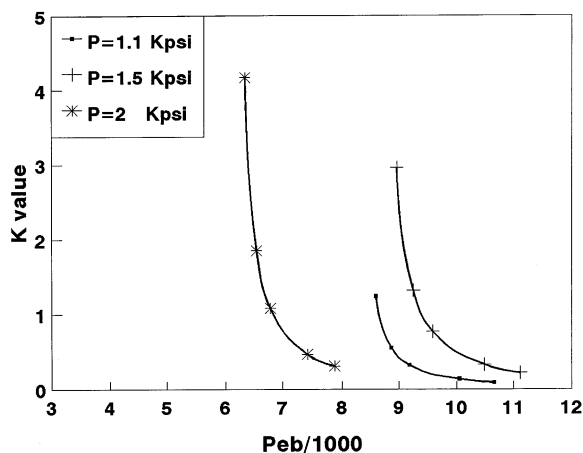


Fig. 9. The effect of bed Peclet number on the distribution coefficient at different pressures.

particle diameter of the shredded plane leaf was varied from 0.05 to 0.2 cm.

The effect of different Peclet numbers (Pe_b) for the packed bed on the partition coefficient has been studied at different pressures and temperatures and is shown in Figs. 9 and 10, respectively. For those figures, the bed Peclet number was changed by increasing the bed length and the interstitial velocity, both of which cause more dispersion, leading to the decrease in K value shown in both figures. The bed Peclet number was chosen as the independent variable (x -axis) be-

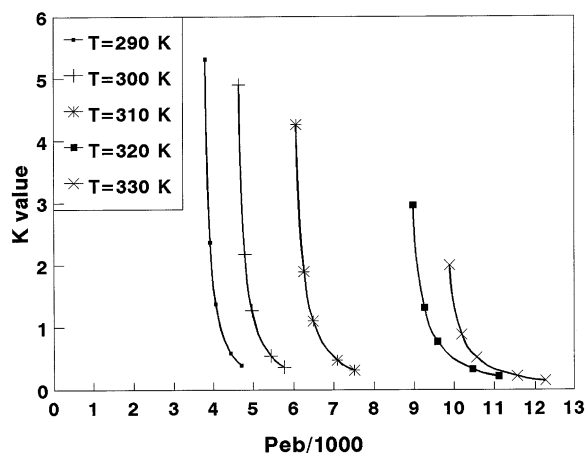


Fig. 10. The effect of bed Peclet number on the distribution coefficient at different temperatures.

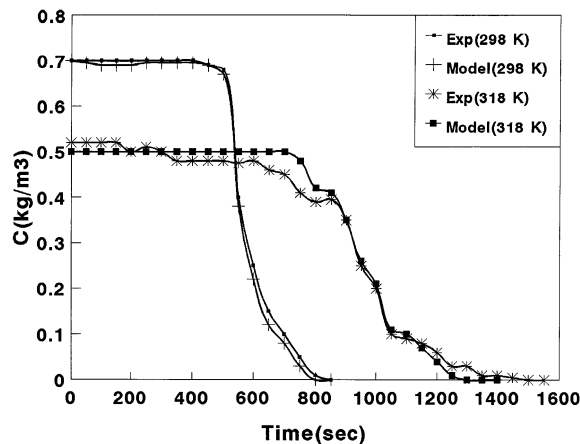


Fig. 11. Comparison of numerical and experimental desorption profiles of hexachlorobenzene from soil.

cause of the many advantages of using dimensionless parameters as it is common practice in the literature of chemical engineering to write the original partial differential equation and its boundary conditions in dimensionless form so that the number of variables can be reduced. Selection of the optimum operating conditions for the large-scale extraction unit must be made according to the aforementioned fundamental mass and momentum phenomena governing the entire process.

In order to investigate the applicability of the mathematical model, the theoretical results are compared with experimental results presented by Ghoreishi et al. [25] in Fig. 11 for the extraction of hexachlorobenzene from soil. As shown in Fig. 11, the mathematical model is able to predict the experimental data quite well within the range of error of the measurements.

Fig. 12 shows the results of the optimization of the configuration for the extraction column. For two known volumes of column, namely, 2500 and 25 000 gallons, the best ratio of height to diameter at pressures of 100–1200 psi are evaluated. The results indicate that the value of rule of thumb for $(H/D)_{opt} = 3$ can be in error by as much as $\pm 50\%$ from the actual optimum. Therefore, in order to minimize the fixed and operating costs, it is recommended to use the ratio of height to diameter predicted by the model in the actual extraction process.

8. Conclusions

In this study, the theoretical feasibility of supercritical carbon dioxide extraction of Mannitol from natural sources such as plane tree leaf was investigated. The results of this study demonstrated that supercritical fluid extraction can be a viable method with respect to the following limitations. The results indicated that the process conditions for a large-scale industrial extraction system do not require a high temperature to obtain a high extraction rate and efficiency. However, at low pressures the solubility of Mannitol in carbon dioxide would limit the successful extraction process and at very high pressures, the extraction process may not be economically feasible. An optimum value for the interstitial velocity of the extraction fluid is a function of the following momentum and mass transfer limitations. A low velocity results in a lower rate of dispersion and mass transfer and a high velocity increases the dispersion and mass transfer rate. Since a high rate of dispersion hinders the extraction rate and efficiency, therefore, it seems that a moderate flow rate would be the optimum value. Moreover, since the axial dispersion coefficient is solely a function of the characteristics of the extraction equipment, the optimum value for the interstitial velocity would be different for various extraction columns.

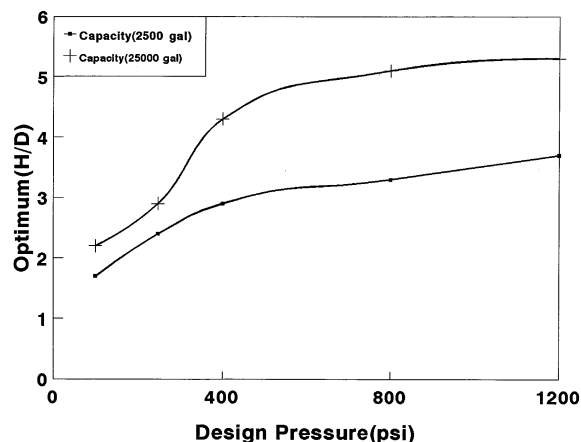


Fig. 12. Optimization of extraction column geometry at different operating pressures.

9. Notation

A	area of end of cylindrical vessel
A'	area of cylindrical surface of the vessel
AR	collocation matrix for gradient with Jacobi polynomials
AZ	collocation matrix for gradient with Legendre polynomials
BR	collocation matrix for Laplacian with Jacobi polynomials
BZ	collocation matrix for Laplacian with Legendre polynomials
c	Mannitol concentration in the shredded plane leaf pore
c_s	Mannitol concentration at the surface of the shredded plane leaf
C	Mannitol concentration in the supercritical phase
C_{sat}	saturation concentration in the supercritical phase
D	diameter of extraction column
D_1	axial dispersion coefficient
D_m	molecular diffusion coefficient
D_p	effective diffusivity in the shredded plane leaf pore
f	isotherm functionality, $q = f(c)$
f'	first derivative of the isotherm
H	length of extraction column
K	Freundlich constant
k_f	mass transfer coefficient
L	length of packed bed
n	exponent in the Freundlich isotherm
NR	number of interior collocation points in the ρ direction
NP	number of node interior collocation points in the z direction
of	optimization objective function
q	Mannitol concentration in the shredded plane leaf phase
r	axial coordinate in the shredded plane leaf
R_p	shredded plane leaf radius
S	price of metal per unit weight
t	time
t'	thickness of the cylindrical wall
u	vector concentration at node point
v	interstitial fluid velocity

x distance measured from bed inlet
 Z finite element frontier point

Dimensionless variables and parameters

s dimensionless axial coordinate in each finite element
 z dimensionless axial coordinate along the bed, x/L
 ρ dimensionless radial coordinate in the shredded plane leaf, r/R_p
 τ dimensionless time, $(tv)/L$
 Bi Biot number, $(k_f R_p)/D_p$
 Pe_b Peclet number for the bed, $(Lv)/D_1$
 Pe_p Peclet number for the shredded plane leaf, $(R_p v)/D_p$
 Sc Schmidt number, $\mu_f/(\rho_f D_m)$
 Re Reynold's number, $(2R_p v \rho_f)/\mu_f$
 Sh Sherwood number, $(2R_p k_f)/D_p$

Greek letters

ε void fraction of packed bed
 ε_p void fraction of shredded plane leaf
 τ_p tortuosity
 μ_f supercritical fluid viscosity
 ρ_f supercritical fluid density
 α, β ADE system matrices

Subscripts

0 time at $t = 0$
 el element
 o bed inlet
 s surface of the shredded plane leaf

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