Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Kinetics and Mathematical Modeling of Anthocyanin Extraction with Carbon Dioxide and Methanol at High Pressure

C. Mantell[a]; M. Rodríguez[a]; E. Martínez de la Ossa[a]
[a] Department of Chemical Engineering, Food Technology, and Environmental Technologies, Science Faculty, University of Cadiz, Cadiz, Spain

To cite this Article Mantell, C. , Rodríguez, M. and de la Ossa, E. Martínez(2003) 'Kinetics and Mathematical Modeling of Anthocyanin Extraction with Carbon Dioxide and Methanol at High Pressure', Separation Science and Technology, 38: 15, 3689 — 3712

To link to this Article: DOI: 10.1081/SS-120024224

URL: http://dx.doi.org/10.1081/SS-120024224

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 15, pp. 3689–3712, 2003

Kinetics and Mathematical Modeling of Anthocyanin Extraction with Carbon Dioxide and Methanol at High Pressure

C. Mantell,* M. Rodríguez, and E. Martínez de la Ossa

Department of Chemical Engineering, Food Technology, and
Environmental Technologies, Science Faculty,
University of Cadiz, Puerto Real, Cadiz, Spain

ABSTRACT

In this work, the kinetics of the high-pressure extraction (HPE) of anthocyanins from red grape pomace using a packed bed was studied. The solvent used was carbon dioxide modified with methanol as a cosolvent. A penetration model was developed that due to the laminate form of the grape skin particles, was based on the application of the mass balance to an infinite planar particle. The model was completed with a study of the soaking time of the process and this concludes with an empirical equation describing the behavior of this variable vs pressure, temperature, solvent flow rate, and cosolvent percentage. The fit of the

---

*Correspondence: C. Mantell, Department of Chemical Engineering, Food Technology, and Environmental Technologies, Science Faculty, Box 40 University of Cadiz, 11510 Puerto Real, Cadiz, Spain; Fax: + 34-956-016-411; E-mail: casimiro.mantell@uca.es.

DOI: 10.1081/SS-120024224 0149-6395 (Print); 1520-5754 (Online)

www.dekker.com

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

model is satisfactory and it is able to predict in a reasonable way the extraction yield of the process. Finally, the model provides a value for the internal diffusion coefficient and this allows an analysis of the influence of the different variables in the extraction process.

Key Words: Penetration model; Anthocyanins; Grape pomace; Food dye; High-pressure extraction.

INTRODUCTION

The use of synthetic dyes is being increasingly rejected by the consumer. The current trend in the elaboration of foods and drinks is the use of dyes of natural origin, which are less harmful in terms of health. Most of the studies published to date describe diverse materials as potential sources of natural dyes: e.g. carotenoids, bixine, betaine, and anthocyanins.[1–4]

Anthocyanins are a group of phenolic compounds belonging to the flavonoid family. The main raw material that contains this dye is the red grape (*Vitis vinifera*) and, more specifically, the pomace produced in the red vinification process.[5,6] The commercial products obtained for food uses are denominated in different ways, e.g. enocyanin,[7] or enovit,[8] depending on the extraction technique used. Countries like The United States, Canada and Japan, as well as the EU, allow the use of this substance in the food industry.

The main problem associated with the use of these substances in food is related to the extraction process. The traditional techniques described in the bibliography use methanol, ethanol, acetone or water acidified with sulfur dioxide or hydrochloric acid, and require multiple purification stages and concentration of the extracted product.[9–15] Extraction with supercritical carbon dioxide is a viable alternative to the traditional techniques used to obtain products for human consumption.[16,17] As a result of the high polarity of anthocyanin compounds, it is necessary to add a small quantity of a substance that modifies the polarity of the carbon dioxide-usually a cosolvent (e.g. methanol, ethanol, water).[18] The modifying effect of a cosolvent is characterized by a marked increase in the solvent power and selectivity. This effect is caused by associations between the cosolvent molecules and solute by means of forces like hydrogen bonds. In cases where the extraction yield of the supercritical extraction + cosolvent is very low, some authors[19] have described the possibility of using mixtures of polar liquids with liquid carbon dioxide at high pressure-a system called an enhanced-fluidity-liquid. In all cases, however, the industrial application of these techniques is difficult due to two factors: 1) a lack of understanding of the behaviour of these solvent systems at high pressure and 2) the absence of thermodynamic data obtained for high-pressure systems and the lack of mass transfer models that describe the extraction process.

As far as the modelling is concerned, several different studies have been published that propose mass transfer models to describe the extraction process with supercritical carbon dioxide as solvent.[20] The most representative examples are based on the film model or the penetration model. The film model is preferred due to its conceptual and computational simplicity. On the other hand, a penetration model results in a better description of the process and allows values for the internal diffusion coefficient to be obtained. The studies presented by Reverchon et al.,[21] Brunner,[22] and Bartle et al.[23] are representative examples of this type of model. All of these models are based on the balance to a spherical particle; however, models applied to particles with other geometries, or to processes using cosolvents, are scarce.

In the work described here, we analysed the kinetics of the anthocyanin extraction process using carbon dioxide (as a solvent) modified with methanol (as a cosolvent) under different conditions of pressure, temperature, flow-rate and methanol percentage. Finally, assuming a planar structure for the skin particles, we propose a penetration model that describes the evolution of the yield of the extraction process versus time. Perhaps, a election of water or ethanol as cosolvent was more appropriate for their application in the food industries, but the extraction yields using methanol as cosolvent are higher than in the other systems and, considering the objectives of this work, we prefer the study with methanol for the analysis of the kinetic and the application of the penetration model. The validation of the model and the conclusion of the kinetics of the extraction process could be later extended to the extraction with other systems with more application in the food sector.

EXPERIMENTAL

Materials and Reagents

The raw material for the process was red grape pomace (Tempranillo variety) obtained in the Rioja region in the 1997 campaign, after the vinification process, and this was provided by Domecq S.A. (Jerez de la Frontera, Spain). Having received the samples, we proceeded to manually separate the skins from the rest of the seeds and other grape residues and the sample was homogenized to a uniform size (2 to 3 mm). Finally, the samples were stored in the absence of light at − 20°C until the extraction process was performed.

Carbon dioxide of high purity ($>99.99\%$) provided by Carburos Metálicos (Spain) was used as a solvent in the high-pressure extraction. Methanol, phosphoric acid, and acetonitrile were HPLC grade and provided by Merck (Germany).

HPE

A supercritical extractor (ISCO Lincoln, Nebraska, model SFX 220) with two extractors in parallel was used for the anthocyanin HPE. Each extractor consisted of a stainless steel chamber of 10-mL capacity and a filter (2 mm) at the outlet to avoid sample losses. The solvents were introduced into the extractor by two syringe pumps (models 100DX and 260D) of volumes 102.93 and 266.05 mL. These pumps provided maximum flow rates of 60 and 107 mL/min, respectively. The first pump was used for the addition of the cosolvent and the second for the addition of the carbon dioxide. The maximum working pressure was 560 bar (Figure 1).

The extraction cartridge was loaded with 3.0 g of sample. The cartridge was then introduced into the extractor for 15 minutes to attain the desired temperature uniformly throughout the sample. The pumps were loaded with the extraction solvents (CO_2 and methanol) and the system was allowed to reach its working pressure. Finally, the flow rate of the two pumps was balanced as a function of the desired percentage of cosolvent. At this time,

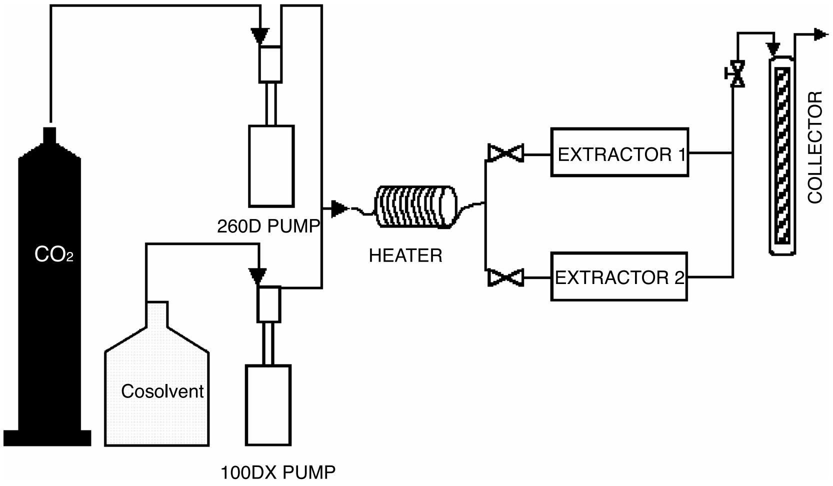

Figure 1. Schematic representation of the HPE equipment used in this work.

the extraction process was started and the flow rate of the solvent system was regulated with the thermostatic micrometric valve at 50°C.

Test samples were extracted into methanol after different intervals to study the kinetics of the process. The samples were dried under vacuum at 40°C in a rotavapor under an inert atmosphere. The extracts were weighed to obtain the value of the total extract and redissolved in 5 mL of the following solution: 10% acetonitrile, 4% formic acid, and 86% water, to give a pH in the sample that guaranteed the maximum color intensity for the anthocyanin solution.[6] The resulting solutions were filtered through a 0.45-μm Millipore filter and stored at 4°C in the absence of light until quantification of the anthocyanins.

Finally, the absorbance of each sample was measured against distilled water using a Shimadzu Multipurpose Spectrophotometer, model MPS-2000 (Kyoto, Japan), at 525 nm. The quantity of anthocyanins was calculated using malvin chloride as the standard (Symta, Madrid, Spain) [Conc (mg/l) $= 44.191\ A_{525} - 0.4923$; $R^2 = 0.9992$].

The variables studied were pressure (100 and 500 bar), temperature (40 and 60°C), solvent flow rate (0.52 and 0.97 g/min or the calculated values 12 and 22 mmol/min), and molar percentage of methanol (5 and 20%). The effect of these variables on the extraction yield was analyzed in a previous study.[24] The results indicate a negative effect on the yield for pressure but a positive effect of temperature, solvent flow rate, and cosolvent percentage.

THEORETICAL EXTRACTION MODEL

The mathematical description of the penetration model applied to an infinite plate of thickness 2 L begins with the equation of continuity in Cartesian coordinates:[25]

$$\frac{\partial C}{\partial t} + \left(\frac{\partial \aleph_x}{\partial x} + \frac{\partial \aleph_y}{\partial y} + \frac{\partial \aleph_z}{\partial z}\right) = 0 \tag{1}$$

where x, y, z are the Cartesian position coordinates; C is the solute concentration in the particle; and $\aleph$ describes the molar flux density of the solute. $\aleph$ can be considered as arising from Fick's law using the following expression:

$$\aleph = -\mathcal{D}_i\left(\frac{\partial C}{\partial x} + \frac{\partial C}{\partial y} + \frac{\partial C}{\partial z}\right) \tag{2}$$

Substituting Eq. (2) into Eq. (1), and considering that the concentration only depends on the coordinate x, the situation can be simplified in the following way:

$$\frac{\partial C}{\partial t} = \mathcal{D}_i \frac{\partial^2 C}{\partial x^2} \tag{3}$$

with the following boundary conditions:

$$\left.\frac{\partial C}{\partial x}\right|_{x=0} = 0 \tag{4}$$

$$-\mathcal{D}_i \left.\frac{\partial C}{\partial x}\right|_{x=L} = \mathcal{K}e\left(\frac{C|_{x=L}}{m} - C_f\right) \tag{5}$$

where C and C_f are the concentrations of the solute in the solid phase and in the supercritical phase, respectively, $\mathcal{K}_e$ and $\mathcal{D}_i$ are the mass-transfer coefficient and the internal diffusion coefficient, respectively, and m is the distribution coefficient considering a linear equilibrium in the solid–liquid interface. The value of this coefficient can be considered close to unity for low concentrations.[26] This situation is consistent with the works of Reverchon et al.,[21,27] who applied a similar model to a spherical particle in the extraction of essential oils from plants.

The proposed model is based on the following suppositions. The thickness (2 L) of all the particles in the bed is half the thickness of the raw material; the diffusion of the solute and the other compounds occur in parallel and there is no interaction between them; the diffusivity of the extracted compounds is independent of the position inside the particle; and finally, we consider that the controlling stage of the process is the internal diffusion on the basis that the interface concentration at the edge of the fluid, C_f, is considered similar to the concentration in the bulk of the fluid.

Eq. (3), with the boundary conditions, Eqs. (4) and (5), can be solved to establish an analogy with the heat transmission.[28] The solution is an equation that describes the profile of concentrations inside the solid as a function of the extraction time (t) and the position (x):

$$X(t,x) = \frac{C - C_f}{C_0 - C_f} = \sum_{k=1}^{\infty} \cdot \frac{2\sin\beta_k}{\beta_k + \sin\beta_k\cos\beta_k}\cos(\beta_k x/L) \times \exp\left[-\left(\frac{\beta_k}{L}\right)^2 \mathcal{D}_i t\right] \tag{6}$$

where C_0 is the initial concentration of the solute in the solid and β_k represents the k solutions in the following periodic equation:

$$\cot\beta_k = \frac{\beta_k}{\mathcal{K}e\dfrac{L}{\mathcal{D}_i}} \tag{7}$$

From expression 6, it is possible to obtain an equation for the molar flux density (ℵ), by substituting in Eq. (2) when x = L. The resulting equation is as follows:

$$\aleph = \frac{\mathcal{D}_i}{L}(C_0 - C_f)\sum_{k=1}^{\infty}\frac{2\beta_k \sin^2\beta_k}{\beta_h + \sin\beta_k\cos\beta_k}\exp\left[-\left(\frac{\beta_k}{L}\right)^2\mathcal{D}_i t\right] \tag{8}$$

The value of the external mass-transfer coefficient ($\mathcal{K}_e$), from Eq. (7), can be calculated using semiempirical equations that relate this coefficient with dimensionless numbers. The equation used for the solid–fluid transfer case in a supercritical extractor is that proposed by Tan et al.:[29]

$$Sh = 0.38\mathrm{Re}^{0.83}Sc^{1/3} \tag{9}$$

where Re, Sh, and Sc are the dimensionless numbers of Reynolds, Sherwood, and Schmidt, respectively:

$$\mathrm{Re} = \frac{\rho v d}{\mu} \quad Sh = \frac{2L\mathcal{K}e}{\mathcal{D}e} \quad Sc = \frac{\mu}{\rho\mathcal{D}e}$$

where ρ and μ are the density and viscosity of the solvent system, respectively, v is the linear velocity, d is the equivalent diameter of the particle, and $\mathcal{D}_e$ is the external diffusion coefficient. The values of density and viscosity were estimated by the modified Handinson–Brobst–Thomson method and the Chung method, respectively.[30] The value of the external diffusion coefficient was obtained using an empirical equation proposed in a previous study.[31] This equation relates the diffusion coefficient of anthocyanins with the density and composition of the CO_2 and methanol system as follows:

$$\begin{aligned} Ln\mathcal{D}e = {} & -10.125 + 0.1937 \cdot V_P + 0.0073 \\ & \cdot\rho - 0.2553 \cdot V_P \cdot \rho \end{aligned} \tag{10}$$

where V_P is the volumetric percentage of methanol in CO_2 and ρ is the density of the solvent system.

Table 1. Parameters for the determination of the mass transfer coefficient ($\mathcal{K}_e$) by the correlation proposed by Tan et al.,[29] values of the soaking times (t_{soak}) at the different operating conditions, and of internal diffusion coefficients ($\mathcal{D}_i$) obtained with the penetration model applied to a planar particle.

Solvent	Flow-rate (mmol/min)	Pressure (bar)	Temperature (°C)	Density (g/mL)	Viscosity (cP)	Velocity (10^5·m/s)	Re	Sc	$\mathcal{K}_e$ 10^5 (m/s)	t_{soak} (min)	$\mathcal{D}_i$ 10^{15} (m^2/s)	A.D. (%)
CO_2 + 5% methanol	12	100	40	0.781	0.074	6.19	43	0.024	1.33	55.9	426	0.04
			60	0.393	0.032	12.3	100	0.013	3.52	53.6	709	8.93
		500	40	0.997	0.145	4.88	22	0.049	0.735	91	3.77	20
			60	0.950	0.115	5.12	49	0.038	1.39	60.4	74.8	4.26
	22	100	40	0.781	0.074	11.7	82	0.024	2.25	31.1	654	9.83
			60	0.393	0.032	23.2	189	0.013	5.95	50	1910	27.37
		500	40	0.997	0.145	9.17	41	0.051	1.22	70.3	3.33	20.22
			60	0.950	0.115	9.65	51	0.040	1.44	90.1	1440	0.25
CO_2 + 20% methanol	12	100	40	0.854	0.131	5.30	23	0.062	0.677	29.6	3470	24.18
			60	0.811	0.099	5.53	30	0.039	0.91	29.6	11400	10.13
		500	40	0.980	0.175	4.63	0.02	0.137	0.012	60	168	21.33
			60	0.933	0.144	4.86	21	0.093	0.482	31.6	2820	10.89
	22	100	40	0.854	0.131	9.43	43	0.073	0.975	19.3	2850	12.72
			60	0.811	0.099	9.43	57	0.055	1.12	10.5	11500	16.11
		500	40	0.980	0.175	8.66	32	0.141	0.604	15	523	16.52
			60	0.933	0.144	9.19	39	0.092	0.824	36.6	16300	21.23

The values calculated from Eq. (9) for the external mass-transfer coefficient under the different operating conditions studied are shown in Table 1.

The model can be expanded to the whole bed by supposing that all the particles behave in the same way. This supposition takes into consideration that there is no axial dispersion in the bed and, therefore, the variation of the concentration in the fluid can be considered linear. In this way, modeling of the extraction process can be undertaken using averaged values for the time and the position in the extractor of concentration—represented by C_f in the fluid and C_0 in the solid. For this reason, the yield of the extraction process as a function of the extraction time y(t) is defined in the following way:

$$y(t) = \frac{\xi(t)M}{W} \tag{11}$$

where W is the total weight of red grape skin in the particle bed, M is the average molecular weight of the anthocyanin compounds, and ξ(t) is the total amount of extracted product as a function of time (calculated using the following expression):

$$\xi(t) = \aleph \cdot n_p \cdot 2H^2 \tag{12}$$

This expression depends on the molar flux density of one particle ($\aleph$), given by Eq. (8), on the surface of a particle $2H^2$ (where H is the length of the

Table 2. Parameters and characteristics of the anthocyanin extraction process.

Characteristics of the skins	
Average thickness of the particles (2 L)	$0.74 \cdot 10^{-3}$ m
Average length of the particle	$2.5 \cdot 10^{-3}$ m
Average width of the particles	$2.5 \cdot 10^{-3}$ m
Equivalent radii (to determine Re number)	$0.033 \cdot 10^{-3}$ m
Density	0.6815 g/mL
Initial content of anthocyanin	0.15%
Average molecular weight of anthocyanins	676 g/mol
Apparent density	0.31 g/mL
Characteristics of the extractor	
Length	0.0545 m
Diameter	0.015 m
Volume	9.631 mL

side of a planar particle taken to have a square geometry) and on the number of particles in the bed (n_p) calculated in the following way:

$$n_p = \frac{\textit{Volume occupied by the particles in the bed}}{\textit{Volume of one particle}} = \frac{V(1-\varepsilon)}{2L \cdot H^2} \qquad (13)$$

where V is the bed volume and ε is the porosity.

The parameters necessary for the development of the model are shown in Table 2.

The correlation of the experimental data with the model was carried out using the least-squares method. The adjustment parameter of the model is the internal diffusivity in the solid ($\mathcal{D}_i$), and the value selected for this coefficient is the one that showed the smallest deviation.

EXPERIMENTAL RESULTS AND DISCUSSION

The variation of the total extracted product versus time is shown in Figures 2 and 3 for the different operating conditions selected and in both solvent systems. These values are accumulated data from the amount of product extracted with time. The extraction yield is defined as the mass of product extracted per 100 g of skin. The error obtained in the experimental data is 18%, for a confidence level of 95%.

On the other hand, the values of the extraction yield of anthocyanins (symbols) vs time are shown in Figures 4 and 5 for the different operating conditions selected and for the two solvent systems used.

Finally, the variation of the concentration of anthocyanins in the total extracted product is presented vs time in Figures 6 and 7 for the different operating conditions selected and for the two solvent systems.

Kinetics of Extraction

The study of the kinetics for the extraction of anthocyanins shows two types of behavior, depending on the percentage of methanol in the carbon dioxide. When 5% methanol is added (supercritical fluid extraction with cosolvent), two periods are clearly observed that differ in the extraction kinetics. In the first period, which lasts approximately 45 minutes, anthocyanins are not extracted but, in the second period, the extraction yield increases in a linear way with time.

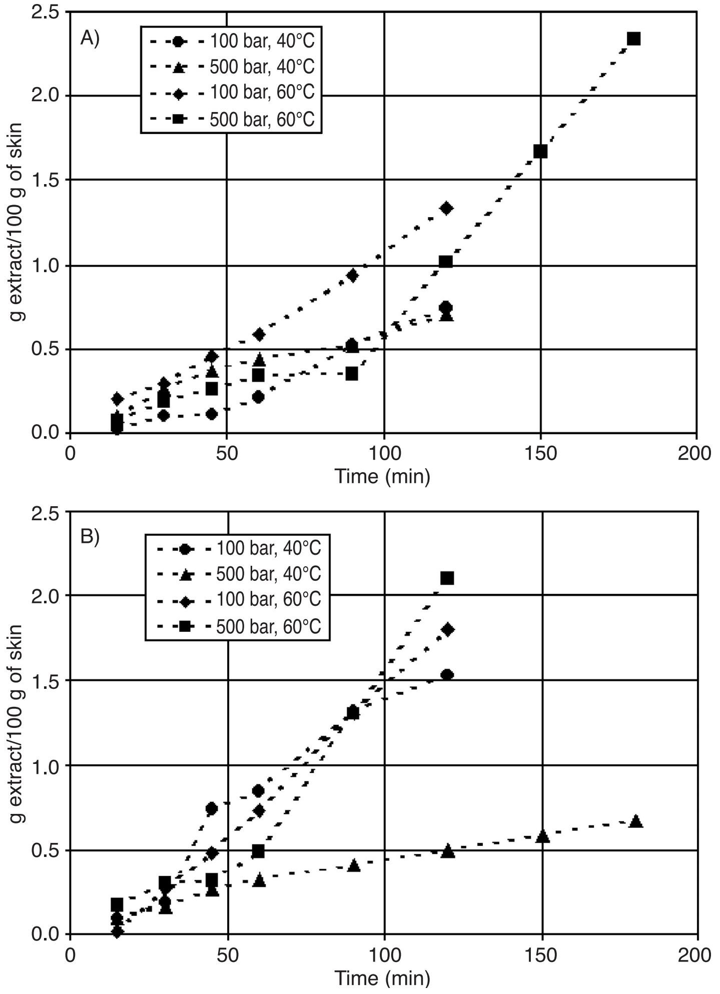

Figure 2. Yield of the total extract obtained with carbon dioxide and 5% of methanol. Flow-rate: (A) 12 mmol/min; (B) 22 mmol/min.

During the first period, which is denoted as the soaking period, the methanol is introduced into the extractor and impregnates the sample while the CO_2 leaves the extractor without cosolvent. In this period, we only extract those substances that are soluble in carbon dioxide, fundamentally, lipids. As can be observed in Figures 2 and 6, this period is characterized

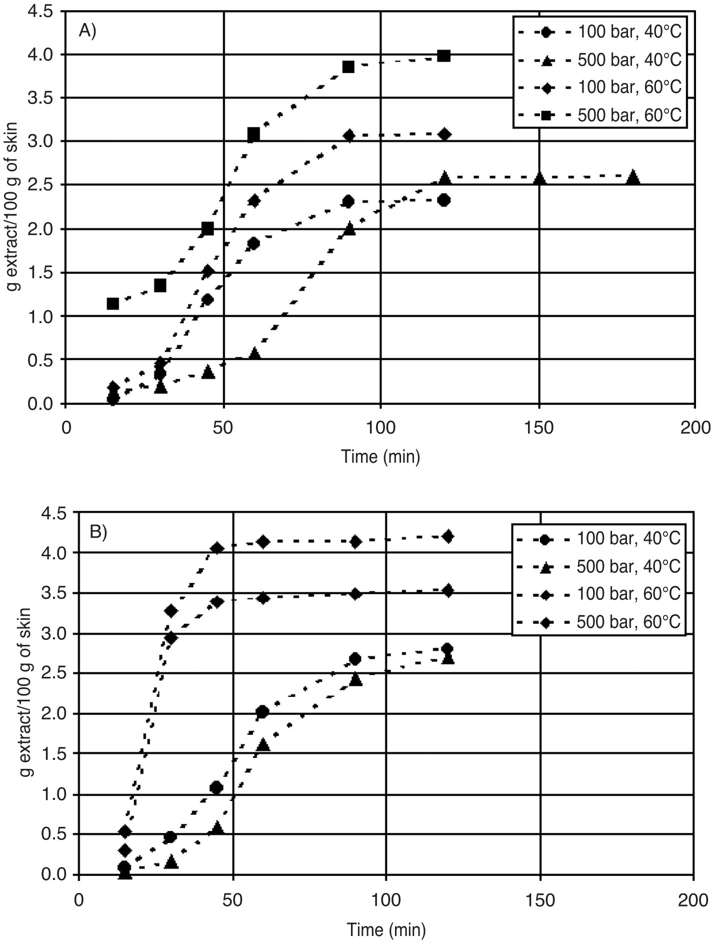

Figure 3. Yield of the total extract obtained with carbon dioxide and 20% methanol. Flow-rate: (A) 12 mmol/min; (B) 22 mmol/min.

by the production at a constant rate of a small amount of extract that does not contain any anthocyanins.

In the second period, or period of extraction at constant rate, the cosolvent begins to leave the extractor and this leads to the presence of anthocyanins in the extract, as can be clearly observed by the inflection points on the graphs in Figure 2. The best time for the extraction process would coincide with the appearance of a third period of extraction in which the extraction rate decreased with time.

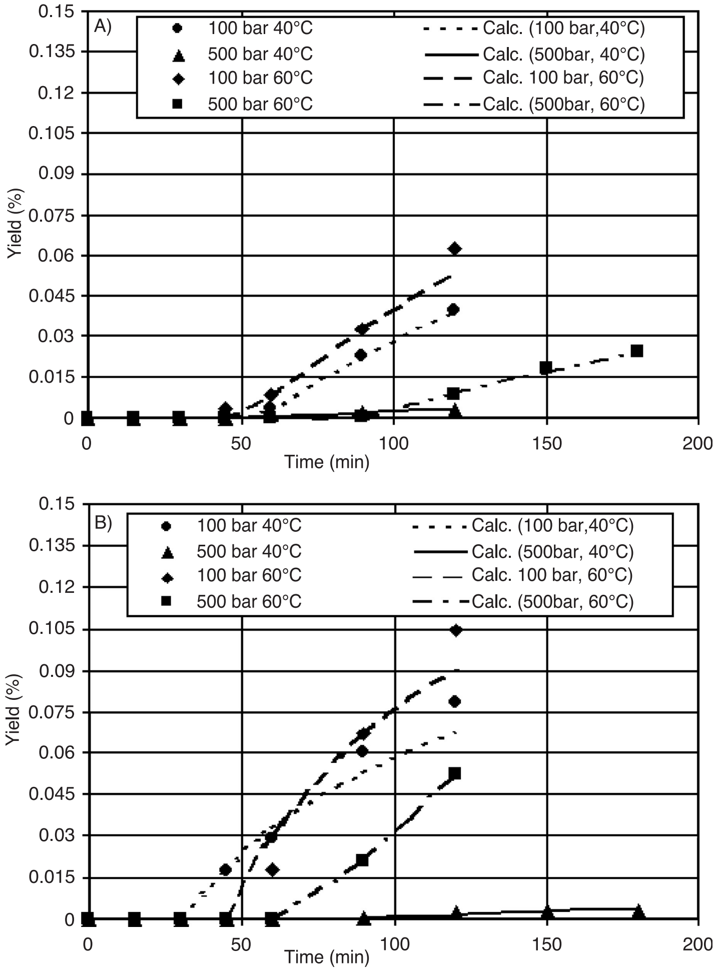

Figure 4. Experimental extraction yields (symbols) and calculated (lines) with the penetration model to a plane particle for the extraction process with carbon dioxide and 5% methanol. Flow-rate: (A) 12 mmol/min; (B) 22 mmol/min.

The next case concerns the addition of 20% methanol to the solvent system (extraction with an enhanced-fluidity-liquid) and here the kinetics of the anthocyanin extraction process give rise to three different periods. The first two are similar to those described for the 5% methanol case in that soaking and extraction lead to constant rate periods. The third period, however, is characterized by a decrease in the extraction rate with time. In

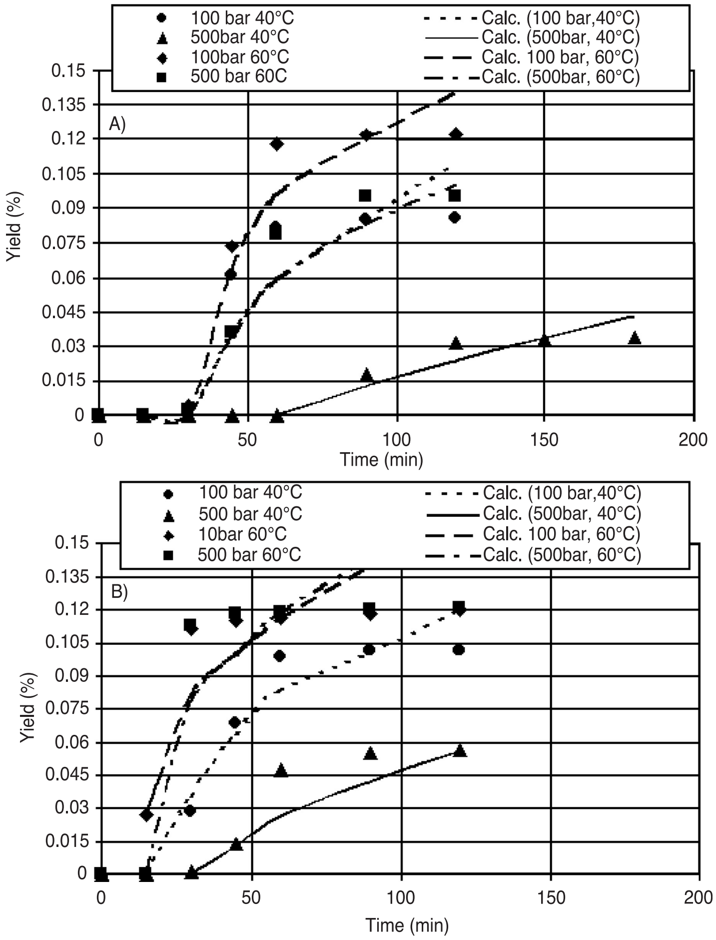

Figure 5. Experimental extraction yields (symbols) and calculated (lines) with the penetration model for a planar particle in the extraction process with carbon dioxide and 20% methanol. Flow-rate: (A) 12 mmol/min; (B) 22 mmol/min.

this period, the amount of anthocyanins obtained tends to a maximum of extraction asymptotically.

The duration of each period depends on the selected solvent flow rate in the period between the beginning of the extraction and is 15 to 30 minutes for the soaking stage, between 15 to 30 minutes to 45 to 60 minutes for the stage at constant rate, and from 60 to 120 minutes until the end of the extraction for the decreasing rate stage.

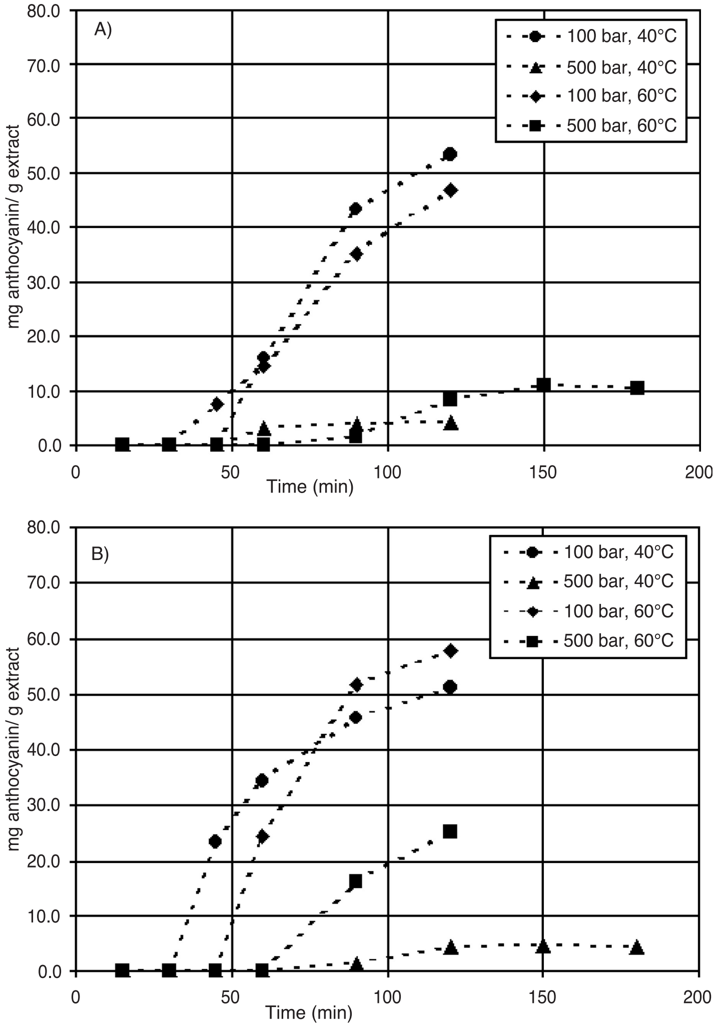

Figure 6. Content of the anthocyanin in the total extract produced with carbon dioxide and 5% methanol. Flow-rate: (A) 12 mmol/min; (B) 22 mmol/min.

In the period of constant extraction rate, the process is controlled by the solubility or by a constant resistance of the mass transfer. However, in the third period, the process is clearly controlled by the mass transfer. As the quantity of anthocyanins in the sample decreases, the used solvent system experiences greater difficulty in reaching the areas of the raw

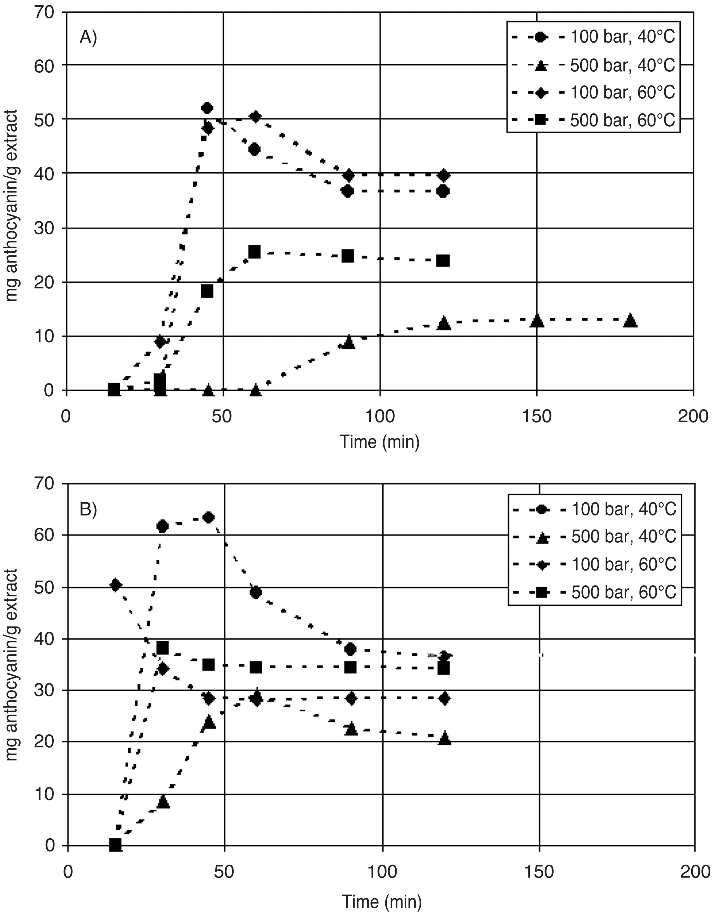

Figure 7. Content of the anthocyanin in the total extract produced with carbon dioxide and 20% methanol. Flow-rate: (A) 12 mmol/min; (B) 22 mmol/min.

material containing the solute. The result of this phenomenon is a decrease in the extraction yield of the process.

It can be seen from the results that the best extraction time to obtain the maximum anthocyanin concentration (with 20% cosolvent) is between 45 and 60 minutes, depending on the selected flow rate. Extraction times greater than this are not translated into appreciable increases in the yield. In addition, it can be seen from Figure 5 that in most cases, the maximum anthocyanin concentration is obtained within the aforementioned interval.

An increase in the extraction time would cause this concentration to decrease as the quantity of total extracted product continues to increase.

Soaking Time

As shown in the previous section, the anthocyanin extraction process at high pressure presents quite peculiar kinetics in which a period of retardation—denominated as soaking time—occurs. For this reason, in the penetration model applied here the expression for the molar flux density, Eq. (8), must be modified to include the soaking time (t_{soak}), in the extraction time:

$$\aleph = \frac{\mathcal{D}_i}{L}(C_0 - C_f)\sum_{k=1}^{\infty}\frac{2\beta_k \sin^2\beta_k}{\beta_h + \sin\beta_k\cos\beta_k} \times \exp\left[-\left(\frac{\beta_k}{L}\right)^2\mathcal{D}_i(t - t_{soak})\right] \quad (14)$$

To estimate the value of the soaking time, we carried out an extrapolation of the experimental results at zero yield. Figure 8 shows a representative example of the procedure followed. The range of values of the

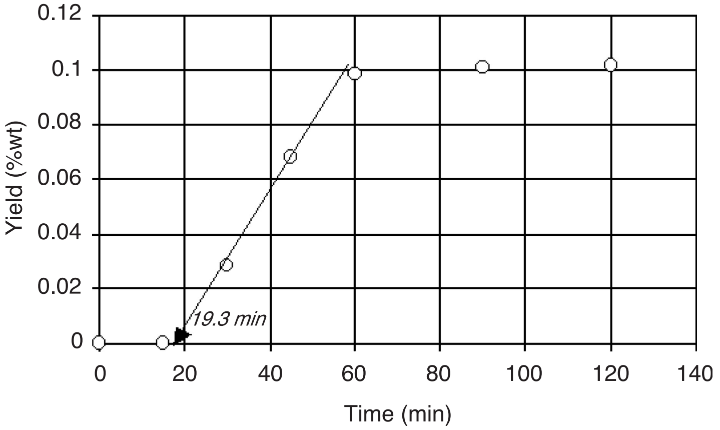

Figure 8. A representative example of the procedure for the soaking time estimation (extraction condition: 100 bar and 40°C, with CO_2 + 20% methanol, 22 mmol/min of solvent flow-rate).

Table 3. Effects of the different factors on the soaking time.

Factor	Effect
Temperature	−1.2 ± 6.97
Pressure	21.9 ± 6.97
Flow rate	−11.1 ± 6.97
Percentage cosolvent	−33.8 ± 6.97

soaking times are shown in Table 1 for the two solvent systems, studied as a function of the operating conditions.

From the experimental data, and with the aid of the program Statgraphics plus 4.0 (Statistical Graphics Corp. 1994–99), we developed the following correlation to estimate the soaking time as a function of the operating conditions:

$$t_{soak} = 78.8006 - 0.06125 \cdot T + 0.0548 \cdot P - 1.04717 \cdot Q - 2.23527 \cdot C \tag{15}$$

where t_{soak} is the soaking time (min), T is the temperature (°C), Q is the solvent flow rate (mmol/min), P is the pressure (bar), and C is the cosolvent percentage in the solvent system. The correlation coefficient is 0.91.

An estimation of the effects of these variables, together with the associated errors, are presented in Table 3. From the analysis of the results in this table, we can say that increases in temperature, flow rate, and cosolvent percentage are translated into decreases in the soaking time, while an increase in the operating pressure causes the opposite effect.

Mass Transfer Model Results

Starting from the mass transfer model applied to a plane particle, we were able to estimate the values of the internal diffusion coefficients of anthocyanins, $\mathcal{D}_i$, at the selected operating conditions. These values are shown in Table 1, together with the absolute deviations regarding the experimental values, defined as follows:

$$AD = 100 \cdot \sum_{1}^{n} \frac{|y(\exp) - y(calc)|}{y(\exp)} \tag{16}$$

The results show an increase in the values of the internal diffusion coefficients upon increasing the temperature from 40°C to 60°C and upon increasing the methanol percentage from 5 to 20% and, in general, a decrease of this coefficient when the pressure is increased from 100 to 500 bar. From the data obtained, as well as from the analysis of the values given by the Biot number, it is possible to select the most appropriate mass transfer model:

$$Bi = \frac{\mathcal{K}_e 2L}{\mathcal{D}_i} \tag{17}$$

If the Biot number is greater than 10, the internal diffusion is the controlling stage of the extraction process.[32] In these cases, the application of a penetration model is more appropriate. On the other hand, if $\mathrm{Bi} < 10$, the controlling stage is the mass transfer in the interstitial fluid. The most appropriate model is the film model. The calculated values of the Biot number range between $2.3 \cdot 10^4$ and $2.5 \cdot 10^6$ for the supercritical fluid extraction with 5% methanol as cosolvent, and between $4 \cdot 10^2$ and $2.5 \cdot 10^4$ for the enhanced-fluidity-liquids extraction ($CO_2 + 20\%$ methanol). These values are greater than 10 and, therefore, the internal diffusion controls the extraction process and the calculated values of the diffusion coefficient can be used in the design of the extraction process. In any case, it is noteworthy that the Biot number for the supercritical fluid extraction with 5% methanol is clearly greater than that for the enhanced-fluidity-liquids extraction. This behavior is indicative of a mode of control operating in the first case that is much more related to the internal diffusion.

Published data concerning the diffusion coefficients of anthocyanins for the studied solvent systems is lacking and so the estimated values obtained from the proposed model cannot be compared. However, there are values for the diffusion coefficients of different solutes in a vegetable matrix extracted with a supercritical carbon dioxide-like solvent. For example, Reverchon et al.[21,27] obtained values for the internal diffusion coefficient that are the same order of magnitude ($10^{-13} \mathrm{m}^2/\mathrm{s}$) in the extraction of essential oils with supercritical carbon dioxide, but smaller than ours for the extraction of cuticular waxes ($10^{-17} \mathrm{m}^2/\mathrm{s}$). These values are similar to those obtained by Nguyen et al.[33] in the extraction of vanilla but smaller than those obtained by Brunner[22] in the extraction of colza oil and by Molero et al.[34] in the extraction of wheat germ oil using supercritical carbon dioxide. These results are indicative of the different physical structures of the raw materials in the particular extraction processes; on the one hand, processes involving the extraction of essential oils from herbaceous matrixes such as rosemary, basil, etc.—which have a similar structure to the red grape

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

skins—and, on the other hand, the extraction of oil from vegetable seeds—which have a woodier structure that favors transport of the oil.

The absolute deviations obtained in the fit of the model are, in most of cases, lower than 10%. These results endorse the applicability of the model to predict the experimental values of extraction yields and for subsequent simulation studies.

The experimental data for the extraction yields can be compared with those calculated using the mass transfer model. It can be seen from Figures 4 and 5 that the model predicts in a satisfactory way the extraction yield when supercritical carbon dioxide and 5% methanol is used as compared to the case where 20% methanol is used. This behavior can be attributed to the larger degree of control shown by the internal mass transfer when the cosolvent percentage is low. This consideration is corroborated by the values obtained for the Biot number, which are much larger when the extraction process is carried out with carbon dioxide and 5% cosolvent. An increase in the content of methanol in carbon dioxide leads to a greater soaking of the herbaceous matrix, thus, favoring access of the solvent into the solid and the exit of the solute to the bulk of the fluid phase.

CONCLUSION

We developed a model for particles of planar geometry that is able to predict the behavior of the extraction process with carbon dioxide and methanol as cosolvent. The best fit for the model is obtained when the cosolvent percentage is 5%, a fact attributed to the greater influence of the mass transfer inside the solid on the control of the process in comparison to the case where the cosolvent percentage is 20%.

When designing plants working at high pressure using mixed solvents, it is of great importance to fix the percentage of the polarity modifier. This fact would imply the necessity of selecting a film model when the percentage is sufficiently high as opposed to a penetration model, which is more appropriate for processes with a small amount of modifier.

ACKNOWLEDGMENTS

This work was supported through a project sponsored by Plan Nacional de Investigación (Spain)—reference PPQ2000-0662. Thanks are due to Prof. Dr. Luis Pérez-Rodríguez, who provided the raw material used in this work.

NOTATION

Bi	Biot number
C	concentration of the solute in the particle, mol/m^3
d	equivalent particle diameter, m
$\mathcal{D}_e$	external diffusion coefficient, m^2/s
$\mathcal{D}_i$	internal diffusion coefficient, m^2/s
H	length of the particle side, m
$\mathcal{K}_e$	mass-transfer coefficient, m/s
$2L$	thickness of the particle, m
M	average molecular weight of the anthocyanins, g/mol
m	distribution coefficient
$\aleph$	density of molar flux of the solute, mol/m^2·s
P	pressure, bar
Q	molar flow rate, mmol/min
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
T	temperature, K
t	extraction time, s
v	linear velocity, m/s
V	volume of the bed, m^3
$\mathrm{V_P}$	percentage of methanol in the solvent system
W	weight of grape skin in the packed bed, Kg
y	extraction yield, mg of anthocyanins/100g of skin

Greek Symbols

β	solutions of Eq. (7)
ρ	density of the solvent, Kg/m^3
μ	viscosity of the solvent, Kg/m·s
ε	void fraction
$\xi(t)$	total amount of product extracted as a function of time, mol/s

Subscripts

k	vector index of the solution of Eq. (7)
f	in the fluid
0	initial

REFERENCES

1. Bath, M.M.; Zhou, C.; Kute, K.M.; Rosenthal, G.A. Determination of optimun conditions for supercritical fluid extraction of carotenoids from carrot (Daucus carota L.) tissue. J. Agric. Food Chem. **1995**, *43*, 2876–2878.
2. Elsharkawy, S.H.; Ali, A.M.; Mat, N. Supercritical fluid extraction of color from B. Orellana seeds alex. J. Pharm. Sci. **1995**, *9* (2), 155–158.
3. Ishida, T.; Rossky, P.J. Solvent effects on solute electronic structure and properties: theoretical study of a betaine dye molecule in polar solvents. J. Phys. Chem., A **2001**, *105* (3), 558–561.
4. Bridle, P.; Timberlake, C.F. Anthocyanins as natural food colours—selected aspects. Food Chem. **1997**, *58* (1–2), 103–109.
5. Francis, F.J. A new group of food colorants. Trends Food Sci. Technol. **1992**, *3*, 27–30.
6. Marakakis, P. *Anthocyanins as Food Colors*; Academic Press: New York, 1982.
7. Garoglio, P.G. *La Nuova Enologia*, 3ª Ed.; Inst. Ind. Firenze: Italy, 1965.
8. Fuleki, T.; Babjak, L.J. Natural food colorants from Ontario grapes. Highlights Agric. Res. Ont. **1988**, *9*, 6–9.
9. Dikmen, D.; Yildiz, F. Extraction of anthocyanins from red grape and red grape skin. Doga: Turk Tarim Ormancilik Derg **1988**, *14* (1), 57.
10. Yokotsuka, K.; Nishino, N. Extraction of anthocyanins from Muscat Bailey A grape skins. J. Ferment Bioeng. **1990**, *69*, 328–334.
11. Bonilla, F.; Barón, R.; Mérida, J.; Mayen, M.; Medina, M. Aprovechamiento de residuos de prensa de uva tinta para la obtención de pigmentos antociánicos. J. Vitic. Enol. Tierra de Barros (Spain) **1996**, XVIII, 237–244.
12. Bocevska, M.; Stevcesvska, V. Quality evaluation of anthocyanin extracts obtained from wine grape pomace. Food Technol. Biotechnol. **1997**, *35* (2), 139–143.
13. García-Viquera, C.; Zafrilla, P.; Tomás-Barberan, F.A. The use of acetone as an extraction solvent for anthocyanins from strawberry fruit. Phytochem. Anal. **1998**, *9*, 274–277.
14. Pérez-Munuera, I.; Antón, A.; Lluch, M.A. Extraction and characterization of the color in vinification residues from Valencia (Spain). Alimentaria **1998**, 295, 97–101, Sept.
15. Revilla, E.; Ryan, J.M.; Martín-Ortega, G. Comparison of several procedures used for the extraction of anthocyanins from red grapes. J. Agric. Food Chem. **1998**, *46*, 4592–4597.

16. Phelps, C.L.; Smart, N.G.; Wai, C.M. Past, present, and possible future applications of supercritical fluid extraction technology. J. Chem. Educ. **1996**, *73*, 1163–1168.
17. Subirats, S.; Millan, L.F.; Blasco, M. Aplicación de la extracción con fluidos supercríticos en la industria agroalimentaria. Alim. Equip. Technol. **1994**, 9, 61–67, Nov.
18. Luque De Castro, M.D.; Varcarcel, M.; Tena, M.T. *Extracción con Fluidos Supercríticos en el Proceso Analítico*; Reverté, S.A.: Barcelona, 1993.
19. Reighard, T.S.; Olesik, S.V. Comparison of the extraction of phenolic and nitroaromatic pollutants using supercritical and enhanced-fluidity liquid methanol-CO_2 mixtures. J. Chromatogr. **1996**, *737* (2), 233–242.
20. Brunner, G. *Gas Extraction*; Springer: New York, 1994.
21. Reverchon, E.; Donsi, G.; Osséo, L.S. Modeling of supercritical fluid extraction from herbaceous matrices. Ind. Eng. Chem. Res. **1993**, *32* (11), 2721–2726.
22. Brunner, G. Mass transfer from solid materia in gas extraction. Ver. Bunsen-Ges. Phys. Chem. **1984**, *88*, 887–890.
23. Bartle, K.D.; Clifford, A.A.; Hawthorne, S.B.; Langnfeld, J.J.; Miller, D.J.; Robinson, R.A. Model for dynamic extraction using a supercritical fluid. J. Supercrit. Fluids **1990**, *3*, 143–149.
24. Mantell, C.; Rodríguez, M.; Martínez de la Ossa, E. A screening analysis of the high-pressure extraction of anthocyanins from red grape pomace with carbon dioxide + cosolvent. Eng. Life Sci. **2003**, *3* (1), 38–42.
25. Bird, R.B.; Stewart, W.E.; Lightfoot, E.N. *Transport Phenomena*; Wiley and Sons: New York, 1960.
26. Simeonov, E.; Tsibranska, I.; Minchev, A. Solid-liquid extraction from plants—experimental kinetics and modelling. Chem. Eng. J. **1999**, *73*, 255–259.
27. Reverchon, E.; Sesti Osséo, L. Supercritical CO_2 extraction: model evaluation of the processing time. Chem. Biochem. Eng. **1994**, *8* (1), 31–34.
28. Mills, A.F. *Transferencia de Calor*; McGraw-Hill/Irwin: Colombia, 1999.
29. Tan, C.S.; Liang, S.K.; Liou, D.C. Fluid-solid mass transfer in a supercritical fluid extractor. Chem. Eng. J. **1988**, *38*, 17–22.
30. Reid, R.C.; Prausnitz, J.M.; Poling, B.E. *The Properties of Gases and Liquids*, 4th Ed.; McGraw-Hill: Boston, 1987.
31. Mantell, C.; Rodríguez, M.; Martínez de la Ossa, E. Measurement of the difusión coefficient of a model food due (malvidin 3,5-diglucoside) in a

high-pressure CO_2 + methanol system by the chromatographic peak-broadening technique. J. Supercrit. Fluids **2002**, *25*, 57–68.

32. Pérez Galindo, J.A.; López Miranda, J.; Martín Domínguez, I.R. Geometric and Reynolds number effects on oregano (Lippia Berlandieri Schauer) essential oil extraction. J. Food Eng. **2000**, *44*, 127–133.
33. Nguyen, K.; Barton, P.; Spencer, J.S. Supercritical carbon dioxide extraction of vanilla. J. Supercrit. Fluids **1991**, *4*, 40–43.
34. Molero, A.; Mantell, C.; Rodríguez, M.; Martínez de la Ossa, E. Modelling of supercritical CO_2 extraction of wheat germ oil. 8th Meeting On Supercritical Fluids, Bourdeau, France, 2002.

Received October 2002