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Chemical Engineering Science 57 (2002) 3831–3838

Chemical
Engineering Science

www.elsevier.com/locate/ces

Semi-batch extraction of anthocyanins from red grape pomace in packed beds: experimental results and process modelling

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Received 17 December 2001; received in revised form 24 May 2002; accepted 19 July 2002

Abstract

A semi-batch extraction process of anthocyanins was studied in a packed bed. Methanol was used as solvent and the raw material studied consisted of skins of the tempranillo grape, which was obtained from the pomace from red wine vinification. The results show large diffusional effects due to strong control from the mass transfer. The best results were obtained using a high temperature and a high flow rate. A penetration model is proposed in terms of a bed of spherical particles. The model provides a value for the diffusion coefficient of the solute within the solid matrix. It can be seen that the adjustment of the model is satisfactory and that it is able to predict, to a reasonable extent, the yield of the extraction process.

Keywords: Anthocyanins; Extraction; Modelling; Grape pomace; Diffusion; Mass transfer

1. Introduction

In the design of industrial extraction processes, it is necessary to have a model that describes the process and to ascertain the values of the mass transfer parameters of the system. There are various types of model in the literature to predict the interfacial rates of mass transfer in the different stages. The most representative examples are based on the film model and the penetration model. The film model is preferred due to its conceptual and computational simplicity. However, the penetration model is a more real representation and allows the value of the internal diffusion coefficient to be obtained.

The work described here involves a study of the modelling of the semi-batch extraction process of anthocyanins in a packed bed using methanol as solvent. A penetration model is proposed that allows the estimation of the diffusional parameters of mass transfer in the extraction process. The influence of the temperature and the operation flow rate on the extraction yield have been analysed and the kinetics of the process investigated.

Anthocyanins are a group of phenolic compounds that belong to the flavonoid family. They are responsible for the coloration (orange, rose, red, violet and blue) of the petals of flowers and fruits of a great variety of plants (Strack & Wray, 1989), as well as of products that are made from vegetable materials, like wine (Mazza, 1995). The use of the anthocyanins as natural food dyes has been studied for many years due to their ready availability. Although there are numerous sources of these compounds, the main raw material is the grape (*Vitis vinifera*) and, more specifically, the pomace from the red wine vinification process (Francis, 1992; Marakakis, 1982). The first isolation of such a compound, which is commonly known as enocyanin, dates from 1879 (Marakakis, 1982, pp. 248–250). Since that time, many authors have developed patents for the production of concentrated aqueous solutions of anthocyanins for food use (Fuleki & Babjak, 1988). Numerous countries, like Canada, The United States, Japan and the European Union, allow the use of this type of substance as food dyes in drinks, marmalades, candies, ice creams, pastries, sweets, and even pharmaceutical products (US FDA, 1995; Council of EU, 1994).

In the last two decades, the majority of investigations on anthocyanins have centred on the study of diverse purification techniques. In particular, the use of different solvents has been studied, and these include methanol, acetone, ethanol,

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PII: S0009-2509(02)00320-2

and water, all of which are generally acidified with HCl or with SO_2 (Dikmen & Yildiz, 1988; Yokotsuka & Nishino, 1990; Bonilla, Barón, Mérida, Mayen, & Medina, (1996) Bocevska & Stevcesvska, 1997; García-Viquera, Zafrilla, & Tomás-Barberan, 1998; Pérez-Munuera, Antón & Lluch, 1998; Revilla, Ryan, & Martín-Ortega, 1998). However, the works to date that analyse the extraction process from an engineering point of view are not enough. Only Sriram, Surendranath, and Sureshkumar (1999) describe a two-interface mass transfer model that suppose a resistance across the two-film interface between the inert solid and the interstitial liquid and the two-film interface between the interstitial and bulk liquid. This film model is adequate in batch processes where the solvent has sufficient time to diffuse into the inert solid. When the extraction process is carried out in a packed bed with high flow rates of solvents, the more adequate model is the penetration one. At this moment, data of semi-batch extraction processes and report of the internal mass transfer parameters of the anthocyanins extraction are not available.

2. Experimental

2.1. Raw material

Grapes pomace of the tempranillo variety was used and these were obtained from the residue of the red wine vinification process. The residue was provided by Domecq S.A. (Spain) and corresponds to that obtained during the 1997 season in the Rioja region (Spain). The residue was stored at a temperature of −10°C until the extraction process was carried out.

Manual separation of the skin from the seed residues and other materials was performed prior to the extraction process. Finally, the skin obtained was crushed until an average particle size of 2.5 mm was attained.

2.2. Extraction apparatus and procedure

The extractions were carried out in an Isco extractor (model SFX220). The equipment included two extractors with a maximum capacity of 10 ml each and a 2 μm filter at the inlet and outlet to avoid haulage of the sample. The extractor also had a thermostatic system that allowed the extraction to be carried out at a constant temperature. The solvent was introduced with a syringe pump (Isco model 100DX) that allowed a constant flow of solvent.

The extracts were taken in glass tubes at different time intervals. These tubes were changed at different extraction times and the amount of anthocyanins extracted was analysed in order to study the kinetics of the extraction process. The extracts obtained in methanol were stored at 4°C, with the exclusion of light, until the analysis was performed.

2.3. Experimental design

A quadratic factorial design involving 3^2 experiments was created to study the effect of temperature and solvent flow rate on the yield of the extraction process. The order of the experiments was fully randomised to avoid the effects of lurking variables. The values of the variables studied were: temperature 40°C, 50°C, 60°C, and solvent flow rate 12, 17 and 22 mmol/min). The results obtained were analysed using an analysis of variance (ANOVA) with the aid of the program STATGRAPHICS Plus 4.0 (Statistical Graphics Corp. 1994–99).

2.4. Analytical methods

Samples were dried under vacuum in an inert atmosphere using a rotary evaporator, dissolved in 5 ml of a mixture containing 10% acetonitrile, 4% formic acid, and 86% water, and filtered through a 0.45 μm filter. Finally, the absorbance of the sample was measured in a Shimadzu Multipurpose Spectrophotometer (model MPS-2000). The amount of anthocyanins was calculated using a standard solution of malvidin 3,5-diglucoside for HPLC (Symta, Spain).

3. Theoretical extraction model

The mathematical description of the penetration model begins from the equation for the differential mass balance to a spherical particle of radius R when there is no reaction (Bird, Stewart & Lightfoot, 1980, pp. 18–25):

$$\frac{\partial c}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 N_r) + \frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}(N_\theta \sin\theta) + \frac{1}{r\sin\theta}\left(\frac{\partial N_\phi}{\partial \phi}\right) = 0, \tag{1}$$

where c is the concentration of the solute in the particle, and N describes the density of molar flux of the solute. N can be calculated using Fick's Law, in spherical coordinates, r, θ and ϕ, with the following expression (Costa, et al., 1991, p. 236):

$$N = -D_m\left(\frac{\partial c}{\partial r} + \frac{1}{r}\frac{\partial c}{\partial \theta} + \frac{1}{r\sin\theta}\frac{\partial c}{\partial \phi}\right). \tag{2}$$

Substituting Eq. (2) into Eq. (1), considering that the concentration of the solute is independent of ϕ and θ and the diffusivity does not depend on the radius r, the expression can be written as follows:

$$\frac{\partial c}{\partial t} = D_m\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right)\right) \tag{3}$$

with the following boundary conditions (Peev & Tzibranska, 1997):

$$\left.\frac{\partial c}{\partial r}\right|_{r=0} = 0, \tag{4}$$

$$-D_{mi}\left.\frac{\partial c}{\partial r}\right|_{r=R} = k_e\left(\frac{c|_{r=R}}{m} - c_f\right), \tag{5}$$

where c and c_f are the solute concentrations in the solid and liquid phases, respectively. k_e and D_m are the mass transfer coefficients and internal diffusion coefficient, respectively, and m is the distribution coefficient considering a linear equilibrium at the solid–liquid interface. If we consider the low concentration range, then the value of the coefficient is $m \approx 1$ (Simeonov, Tsibranska, & Minchev, 1999).

This model supposes that the bed is formed by spherical particles of uniform size. It could be considered that such assumption is inadequate for the extraction of grape skin because it has a laminate form. However, the grape pomace is a pressed grape skin pellet that can be considered as spherical.

Other considerations that must be kept in mind in the development of the model are the diameter of the particle corresponds to the average diameter of the sample; the diffusion of the solute and other compounds is carried out in parallel and there is no interaction between them; the diffusivity of the extracted compounds is independent of the particle radius; the controlling stage of the process is the internal diffusion, meaning that the solute concentration at the interstitial fluid, c_f, is similar to the concentration in the bulk of the solvent; and, finally, the family of anthocyanin solutes extracted is considered as a single compound.

Eq. (1), with the boundary conditions (4) and (5), can be solved using the heat transfer analogy (Mills, 1999, pp. 175–180). The solution is an expression that provides the concentration profile as a function of the time of extraction and the internal position:

$$X(t,r) = \frac{c - c_f}{c_0 - c_f} = \sum_k^{\infty} 2\,\frac{\sin\beta_k - \beta_k\cos\beta_k}{\beta_k - \sin\beta_k\cos\beta_k} \times \frac{\sin(\beta_k r/R)}{\beta_k r/R}\exp\left[-\left(\frac{\beta_k}{R}\right)^2 D_m t\right], \tag{6}$$

where c_0 is the initial concentration of the solute in the solid and the β_k values are the k solutions of the following periodic equation:

$$\beta_k\cot\beta_k = 1 - k_e\frac{R}{D_m}. \tag{7}$$

It is possible to obtain the equation for the density of molar flux N by substituting into Eq. (2) the concentration when $r = R$ from expression (6), as shown below

$$N = -\frac{2D_m C_f}{R} - 4\,\frac{D_m}{R}\,(C_0 - C_f) \times \sum_k^{\infty}\frac{2\sin\beta_k - \beta_k^2\cos^2\beta_k - \beta_k\sin\beta_k\cos\beta_k}{\beta_h^2 - \beta_k\sin\beta_k\cos\beta_k} \times\exp\left[-\left(\frac{\beta_k}{R}\right)^2 D_m t\right]. \tag{8}$$

The value of the external coefficient of mass transfer, k_e, from expression (7) can be calculated starting from semi-empirical correlations. These correlations relate the mass transfer with other parameters of the process with dimensionless numbers. The expression in the case of the flow of liquids on spherical particles when $2 < Re < 2000$ (Calleja, García, de Lucas, Prats, & Rodríguez, 1999, p. 306) is

$$Sh = 2 + 0.95Re^{0.50}Sc^{1/3}, \tag{9}$$

where Re, Sh and Sc are the Reynold, Sherwood and Schmidt numbers, respectively,

$$Re = \frac{\rho v d}{\mu}, \quad Sh = \frac{2Rk_e}{D_{12}}, \quad Sc = \frac{\mu}{\rho D_{12}},$$

where ρ and μ are the density and viscosity of the fluid, respectively, v is the linear rate, d is the particle diameter, and D_{12} is the external diffusion coefficient. To estimate this coefficient, we can use a correlation for liquids, such as the one proposed by Wilke and Chang (1949, 1955):

$$D_{12} = \frac{7{,}4\cdot 10^{-8}(\varphi M_2)^{0{,}5}T}{\mu v_1^{0{,}6}}, \tag{10}$$

where M_2 is the molecular weight of the solvent (g/mol), T is the temperature (K), φ is the association factor for the solvent, which is 1.9 for methanol (Treybal, 1980), and v_1 is the molar volume of the solute at the boiling point under normal conditions (cm^3/mol). This last variable can be estimated using the Le-Bas method described by Reid, Prausnitz, and Poling (1987). The values of the estimated diffusion coefficients for Eq. (10) appear in Table 1.

The values obtained for the different dimensionless numbers and the external mass transfer coefficient are indicated in Table 1.

The extension of the model to the bed can be made on the assumption that all the particles behave in the same way. The yield of the extraction process as a function of the extracting time $Y(t)$ is defined as follows:

$$Y(t) = \frac{E(t)M_1}{W}100, \tag{11}$$

where W is the total weight of grape skin in the packed bed, M_1 is the average molecular weight of the anthocyanins, and $E(t)$ is the total amount of product extracted as a function of time, calculated as follows:

$$E(t) = Nn_p 4\pi R^2. \tag{12}$$

This expression depends on the density of molar flux from a particle, N, obtained in Eq. (8), as well as on the area of a particle, $4\pi R^2$, and the number of particles calculated according to the following expression:

$$n_p = \frac{\text{Volume occupied by the particles in the bed}}{\text{Volume of one spherical particle}} = \frac{6V(1-\varepsilon)}{\pi d_p^3}, \tag{13}$$

where V is the volume of the bed and ε is the void fraction.

Table 1
Values of the dimensionless numbers, diffusion coefficient (D_{12}) estimated from the equation of Wilke and Chang, external coefficient of mass transfer, and internal diffusion coefficients, obtained with the spherical particle model for all the operation conditions studied

Temperature (°C)	Diffusion coefficient × 10^{10} (m^2/s)	Sc	Flow rate (mmol/min)	Re	Sh	k_e (m/s) × 10^5	Model parameters	
							$D_m \times 10^{10}$ (m^2/s)	AE (%)
40	7.86	774.6	12	198.8	125.0	3.93	3.53	7.8
			17	286.6	149.5	4.71		
			22	374.4	170.8	5.37		
			12	225.0	123.1	4.52		
50	9.18	614.0	17	324.3	147.4	5.41	3.85	5.4
			22	423.7	168.2	6.18		
			12	257.1	120.5	5.21		
60	10.8	471.1	17	370.7	144.3	6.23	5.02	8.6
			22	484.2	164.7	7.11		

Table 2
Some data form the extraction process of anthocyanins

Grape skins	Equivalent radius	0.00125 m
	Density	0.6815 g/ml
	Maximum yield	0.19%
	Average molecular weight	676 g/mol
	Apparent density	0.31 g/ml
Extractor	Height	0.0545 m
	Diameter	0.015 m
	Volume	9.631 ml

This model is based on the hypothesis that all the particles in the bed reach the same extraction level during the process. This hypothesis ignores the concentration profiles that appear along the bed as the solvent crosses it. To include in the model this fact, it is considered that there is no axial dispersion in the bed and therefore, a linear gradient of concentrations exists along the extraction vessel. In order to model the extraction process, values of average concentration in the liquid, c_f, and in the solid phase, c_0, are supposed. These average values are calculated for each interval of time, from the initial value at the inlet of the extractor vessel ($c_f = 0$) and the experimental value at the outlet, and from the initial concentration in the solid and the concentration after the extraction process, considering the experimental yield of extraction. This approach is consistent with the aim of providing a model more than a precise description of the system to which it is applied.

Model correlation with the experimental data was performed by using the least-squares method. The model adjustable parameter is the internal diffusivity in the solid (D_m). The diffusivity value that leads to the minimum error was selected. The parameters necessary for the development of the model are indicated in Table 2.

4. Experimental results and discussion

The extraction yield is defined as the mass of anthocyanins extracted per mass of grape skins (%wt). Fig. 1 shows the yield of the extraction process (symbols) of anthocyanins at different extraction times at the operating temperatures selected. These values are the accumulated data of anthocyanin amount extracted along the time. The error obtained in the experiments was 16% for a level of confidence of 95%.

4.1. Effect of working conditions

At high flow rates, the yield of the extraction process increases with temperature. However, the differences in the extraction yields at the temperatures selected are within the experimental error and are not significant at low flow rates.

This behaviour can be attributed to a high degree of control of the mass transfer stage. At low flow rates, the solvent has high residence times and has sufficient time to penetrate into the particle and dissolve the anthocyanin. The differences in the extraction yields are thus due to the different effective solubility of the anthocyanin in the methanol. Under these conditions, the effect of the selected temperatures on the solubility of the anthocyanins is not particularly significant—on the basis that an insignificant variation in the extraction yield is observed.

At a higher solvent flow rate, the residence time of the solvent in the extractor decreases. Nonetheless, an increase in the temperature causes a decrease in the viscosity and, therefore, an increase in the diffusivity of the solvent. These variations improve the solvent mass transfer stage within the vegetable matrix. The overall result is that the yield of the extraction process increases with temperature.

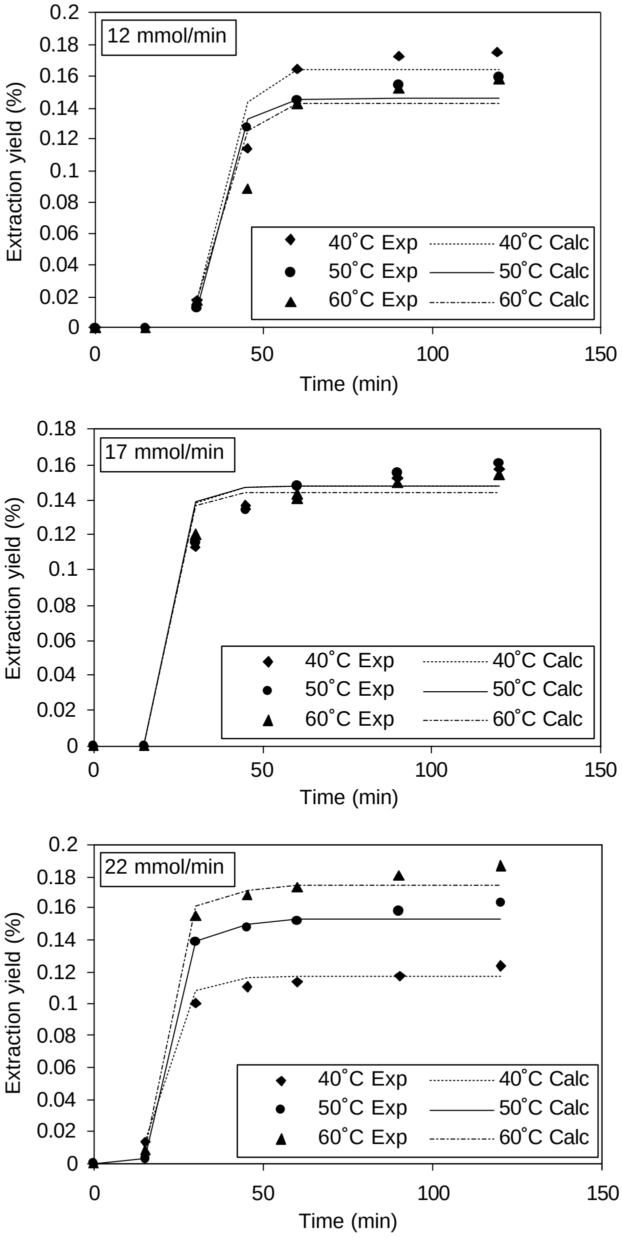

Fig. 1. Representation of the experimental data (symbols) and calculated data with the spherical particle model (lines) for the extraction processes of anthocyanins with methanol.

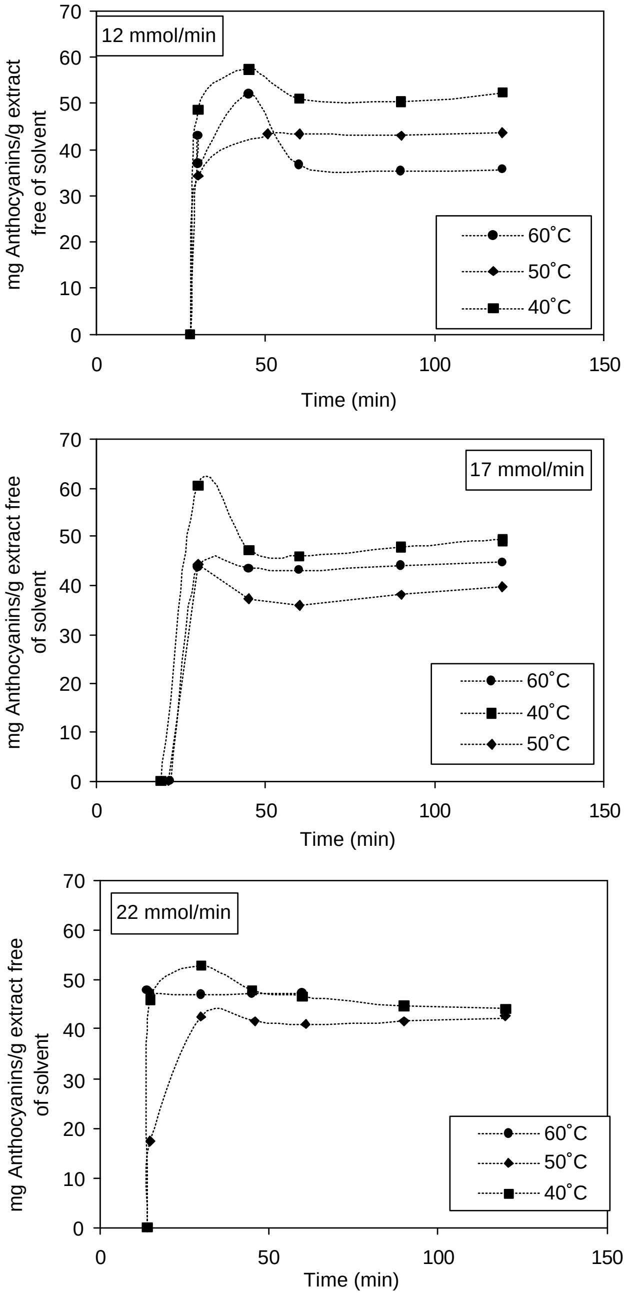

Fig. 2. Variation of the anthocyanin concentration in the extracted product during the extraction process.

4.2. *Kinetics of extraction*

The experimental results obtained indicate that the most appropriate extraction time is between 30 and 60 min according to the selected flow rate. Over this range, the increase in the yield of the extraction is not significant and, therefore, there is no advantage in going on with the extraction. There is a delay of approximately 15 min in the beginning of the extraction. This delay is attributed to the time required by the solvent to cross the vegetable matrix and the equipment.

Fig. 2 represents the variation of the anthocyanin concentration in the extract free of solvent. The maximum of the curve is observed between 30 and 60 min in each case. This indicates that the anthocyanins present extraction kinetics that is quicker than the rest of the substances present in the red grape skin. The result is a lower extraction time for the anthocyanins. In addition, the highest concentration obtained was found when the temperature was the lowest (i.e. 40°C). This behaviour is attributed to the small variation in the solubility over the range of temperatures studied. In contrast, the remainder of the substances experience a significant

Table 3
Effects estimated and ANOVA data for the extraction process of anthocyanins with methanol

Variable	Effects	p-value
Temperature (T)	10.1 ± 8.6	0.324
Flow rate (Q)	-9.7 ± 8.6	0.340
T	-0.8 ± 14.9	0.960
TQ	45.5 ± 10.5	0.023
QQ	9 ± 14.9	0.586

increase in their solubilities with temperature. This situation results in an increase in the extraction yield of the other substances as the temperature is increased and, subsequently, a decrease in the concentration of the extracted product. If the extraction is carried out at 40°C, the solubility of the anthocyanins does not vary significantly, but the solubility of the other substances decreases enormously, meaning that the extracted anthocyanin product is more concentrated.

In summary, if the objective of the process is to obtain the largest quantity of anthocyanins regardless of their concentration, the most appropriate procedure involves working for 2 h, at 22 mol/min and 60°C. Otherwise, when an extract is required with a high concentration of anthocyanins, the extraction should be carried out at 12 mmol/min and 40°C, and the process should be stopped when the maximum yield is reached (45 min), although 15% of the remaining anthocyanins are lost.

4.3. Optimum conditions

The statistical analysis carried out from the design of the experiments gave an expression that relates the variables with their influence on the process for the extraction of anthocyanins with methanol in the range of parameters studied:

$$Y = 558.6 \times 10^{-3} - 6.52 \times 10^{-3}(T - 273) - 27.97 \times 10^{-3}Q + 0.43 \times 10^{-3}(T - 273)Q + 0.16 \times 10^{-3}Q^2, \tag{14}$$

where Y is the extraction yield of the process (g of anthocyanins/100 g of skin), T the temperature (K) and Q the molar flow rate (mmol/min). The correlation coefficient is 0.88.

Correlation (14) allows the estimation of the effects and interactions between the ranges of operational variables studied. This effect is shown in the ANOVA data in Table 3, along with the associated errors.

The values obtained reflect that only the combined effect of temperature and solvent flow rate influence the process significantly (p-value < 0.05). This behaviour, as described in the previous sections, is attributed to strong control of the mass transfer step in the process at low operation temperatures.

The graphical representation of correlation (14) for the different conditions studied appears in Fig. 3. From this graph, we deduce that the highest extraction yields are obtained at the highest values of the studied variables, i.e. temperature of 60°C and solvent flow rate of 22 mmol/min.

4.4. Mass transfer model results

From the model for mass transfer in a spherical particle, we can estimate the values of the diffusion coefficient of anthocyanins, D_m, under different operation conditions, as

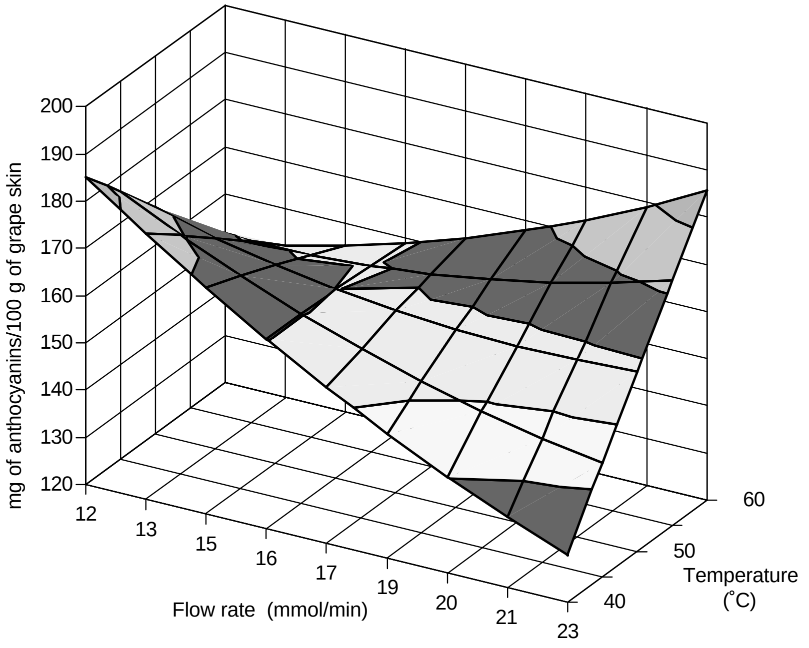

Fig. 3. Values of the extraction yields of anthocyanins estimated with the empirical correlation (1).

shown in Table 1 along with the absolute deviations from the experimental data. The results show an increase in the internal diffusion coefficient as we increase the temperature from 40°C to 60°C.

With these results, the selection of a penetration model is adequate if the value of the Biot number is analysed:

$$Bi = \frac{k_e R}{D_m}. \tag{15}$$

If the Biot number are greater than 10, diffusion is the controlling stage of the extraction process (Pérez Galindo, López Miranda, & Martín Domínguez, 2000). In these cases, a penetration model is more suitable. In contrast, the controlling stage is the mass transfer in the interstitial liquid or in the bulk liquid and a film model is more adequate. Calculations of the Biot number of the studied process result in values from 130 to 201. These values are higher than 10 and, therefore, diffusion controls the process and calculated diffusivity can be used in the design of process.

The value obtained for the internal diffusion coefficient is comparable to those obtained by other authors who have studied different systems of vegetable origin, such as the extraction of essential oils from oregano, between 5×10^{-10} and 20×10^{-10} m^2/s (Pérez Galindo et al., 2000), the drying of wheat, 2.8×10^{-10} m^2/s (Gekas, 1992), and alfalfa stems, between 2.6×10^{-10} and 26×10^{-10} m^2/s (Okos, Ganesan, Rakesh, & Weitnauer, 1992).

On the other hand, the average absolute deviations found in the fit of the experimental data for the extractions are below 10%. These results are indicative of the applicability of the model for the adjustment of the data.

The experimental data for the extraction yields can be compared with those calculated using the mass transfer model; the relevant data are shown in Fig. 1. From the data in this figure, we can see the perfect fit of the model for all the selected temperatures in the case of the highest flow rate of solvent (22 mmol/min). However, when the flow rate is decreased, the model loses some of its predictive capability, although the behavioural trend in the experimental data is predicted well in each case.

Notation

Bi	Biot number
c	concentration of the solute in the particle, mol/m^3
d	particle diameter, m
D_{12}	external diffusion coefficient, m^2/s
D_m	internal diffusion coefficient, m^2/s
$E(t)$	total amount of product extracted as a function of time, mol/s
k_e	mass transfer coefficient, m/s
M_1	average molecular weight of the anthocyanins, kg/mol
M_2	molecular weight of the solvent, g/mol
m	distribution coefficient
N	density of molar flux of the solute, mol/m^2 s
Q	molar flow rate, mmol/min
R	particle radius, m
Re	Reynold number
Sc	Schmidt number
Sh	Sherwood number
T	temperature, K
t	extraction time, s
v	linear rate, m/s
V	volume of the bed, m^3
W	weight of grape skin in the packed bed, kg
Y	extraction yield, mg of anthocyanins/100 g of skin

Greek letters

β	solutions of Eq. (7)
ε	void fraction
μ	viscosity of the solvent, Kg/m s
v_1	molar volume of the solute at the boiling point under normal conditions, cm^3/mol.
φ	association factor for the solvent
ρ	density of the solvent, kg/m^3

Subscripts

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

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