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

Kinetics of Anthocyanin Extraction from Fresh and Dried Grape Waste

G. Sriram[a]; C. Surendranath[a]; G. K. Sureshkumar[a]
[a] BIOCHEMICAL ENGINEERING GROUP, DEPARTMENT OF CHEMICAL ENGINEERING, INDIAN INSTITUTE OF TECHNOLOGY, MUMBAI, INDIA

Online publication date: 03 August 1999

To cite this Article Sriram, G. , Surendranath, C. and Sureshkumar, G. K.(1999) 'Kinetics of Anthocyanin Extraction from Fresh and Dried Grape Waste', Separation Science and Technology, 34: 4, 683 — 697
To link to this Article: DOI: 10.1081/SS-100100674
URL: http://dx.doi.org/10.1081/SS-100100674

SEPARATION SCIENCE AND TECHNOLOGY, **34**(4), pp. 683–697, 1999

Kinetics of Anthocyanin Extraction from Fresh and Dried Grape Waste

G. SRIRAM, C. SURENDRANATH and G. K. SURESHKUMAR*
BIOCHEMICAL ENGINEERING GROUP
DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY
BOMBAY, POWAI, MUMBAI 400 076, INDIA

ABSTRACT

Anthocyanins are *natural* pigments which can be extracted from grape waste. Anthocyanin extraction from fresh and dry grape waste was studied using various solvents. Six solvents were employed, and methanol with 0.1% (v/v) HCl provided the highest extraction of 1.18×10^{-3} g·g^{-1} for dry waste. The same solvent also exhibited the fastest kinetics and the shortest time (7 hours) required to attain equilibrium. The kinetics of extraction were well-described by a two-interface mass transfer model which considered the solvent diffusion effects on the mass transfer coefficients. Equilibrium and hold-up studies were also carried out using the safest solvent for human consumption from among the solvents used for extraction.

Key Words. Anthocyanin extraction kinetics; Grape waste; Two-interface model

INTRODUCTION

Many synthetic food colorants, particularly those with a red appearance, have been banned for use in food products in many countries around the world (1, 2), and hence there is renewed interest in natural pigments. Interestingly, grape waste can be a source of a natural red pigment (the red wine color) (3). Anthocyanins are the class of compounds responsible for the red color of

* To whom correspondence should be addressed. E-mail: gksuresh@che.iitb.ernet.in

grapes (4). They are either flavylium or 2-phenyl benzopyrylium salts and are part of the C15 group of compounds known collectively as flavonoids (5).

Although information on the chemical nature of anthocyanin from various grape varieties is abundant (3, 4, 6), information on the extraction (leaching) process from an engineering perspective, besides a time-variant analysis of unsteady-state extraction, is not available. In this work we present experimental data on anthocyanin extraction from fresh and dry grape waste, employing six different solvents. Anthocyanins are polar in nature (6), and the solvents employed in this study, [methanol with 0.1% HCl, ethanol with 0.1% HCl, 40% ethanol, 50% propylene glycol (PG), 75% PG, and 100% PG] differ in such properties as polarity and viscosity. Further, the kinetics of extraction has been modeled by using a two-interface mass transfer model.

MATERIALS AND METHODS

Waste (both fresh and dried) that remains from dark grapes (Bangalore, India) was used for the experiments. All experiments were performed using the same batch of either fresh or dried grape waste.

Anthocyanin concentrations were measured through absorbance at 532 nm, pH 1.0 (2), and comparison with a calibration plot. Separate calibration plots were prepared for each solvent. The calibration plots were prepared with solutions of pure, authenticated, anthocyanin powder (Jagdale Industries, Bangalore, India). The concentrations thus obtained in $g \cdot L^{-1}$ were converted to $g \cdot g^{-1}$ using solvent densities and solute (anthocyanin) mass fractions.

Anthocyanin extraction was performed using various solvents, and the concentrations were measured at required time intervals until equilibrium was achieved. The solvents used were 40% ethanol, ethanol with 0.1% HCl, methanol with 0.1% HCl, 50% propylene glycol (PG), 75% PG, and 100% PG. All solvents were diluted in water, and all percentages mentioned in this paper for extraction solutions are volume percentages. All extractions were carried out at 30°C and under mild agitation (100 rpm) in Erlenmeyer flasks placed in a shaker-incubator. The data for anthocyanin extraction from fresh waste using ethanol with 0.1% HCl are currently proprietary and hence not included in this article.

The above solvents, except propylene glycol, are commonly reported in the literature as extraction solvents for anthocyanin composition studies, and hence they were also used in this study. Propylene glycol is a known food additive in the fruit juices industry and hence it was employed in this study with a view to obviate the need for an additional solvent when used by the industry.

The equilibrium studies were carried out by contacting fresh and used slurries (which had already been used to attain equilibrium extraction) with fresh solvents. This was done to vary the initial amounts of anthocyanin in the solid

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

(*x*-axis) and hence to obtain data over a wide range of concentrations. To determine the total amount of anthocyanin present, extractions with fresh solvent were carried out until no measurable anthocyanin was obtained in the solution. Then the total amount of anthocyanin present initially was determined by using the anthocyanin concentrations in all previous extractions of the same solid and the corresponding volumes of solvent employed.

The holdup, *f*, which is the mass of solvent present in slurry per unit mass of inert solid, was determined from the difference in volumes of solvent added and bulk solution along with the concentrations in bulk solution. Also, a negligible volume change due to solute dissolution was assumed.

All experiments were at least duplicated to ensure confidence in the results presented. The maximum variation between data points in duplicate experiments was 5%, and the maximum variation in measured data from a triplicate analysis was 6%.

MASS TRANSFER MODEL FOR ANTHOCYANIN EXTRACTION

A two-interface mass transfer model was developed in this work to predict the kinetics of anthocyanin extraction. The model also considers the transport of solvent into the inert solid. This leads to a transient mass transfer coefficient across the solid–interstitial liquid interface. In addition, the variation of solvent holdup with anthocyanin concentration has also been included in the model. A simpler two-interface model was used earlier to describe oil extraction from peanuts (7).

Upon contacting the inert solid (grape waste) with the bulk liquid (solvent), a fraction of the bulk liquid is associated with the inert solid. We have modeled this holdup liquid as an "interstitial liquid" with an anthocyanin concentration significantly different from that in the bulk liquid (during the unsteady state existing before the attainment of equilibrium). This gives rise to two regions of interphase mass transfer: (1) the two-film interface between the inert solid and the interstitial liquid ($i1$), and (2) the two-film interface between the interstitial and bulk liquids ($i2$). This is schematically shown in Fig. 1.

We have designated the volumetric mass transfer coefficients in the respective films as $k_i a_i$, where a_i is the interfacial area per unit volume at the interface. Subscripts 1 and 2 on a indicate interfaces $i1$ and $i2$, respectively.

The concentration in the interstitial liquid at equilibrium is assumed to be the same as in the bulk liquid. This is a reasonable assumption since the interfacial and bulk liquids are composed of the same solvent. The slope of the equilibrium line representing the concentration in the inert solid against that in the interstitial liquid (and hence against the concentration in the bulk liquid) is represented as *m*.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

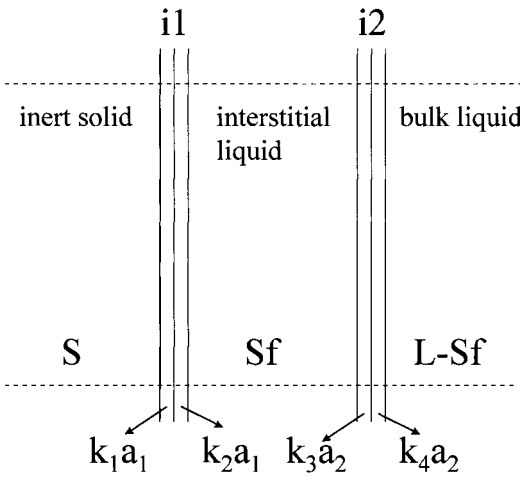

FIG. 1 Explanation of terms in the two-interface model.

The expressions for interphase fluxes and mass balances for the solute (anthocyanin) in each of the three phases can now be written, whence we obtain differential equations describing the transient behavior completely. Thus,

Rate of diffusion across $i1$:

$$R_1 = k_1a_1(z - z_i) = k_2a_1(x_{i1} - x) \tag{1}$$

Rate of diffusion across $i2$:

$$R_2 = k_3a_2(x - x_{i2}) = k_4a_2(y_i - y) \tag{2}$$

Equation (1) can be written as

$$\frac{R_1}{k_1a_1} = z - z_i \tag{3}$$

and

$$\frac{R_1}{k_2a_1} = x_{i1} - x = mz_i - x \tag{4}$$

since $z_i = x_{i1}/m$. Dividing Eq. (4) by m and adding with Eq. (3) gives

$$R_1 = \frac{z - \dfrac{x}{m}}{\dfrac{1}{k_1a_1} + \dfrac{1}{mk_2a_1}} \tag{5}$$

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Similarly,

$$R_2 = \frac{x - y}{\frac{1}{k_3 a_2} + \frac{1}{k_4 a_2}} \tag{6}$$

Further, the terms $1/[(1/k_1a_1) + (1/mk_2a_1)]$ and $1/[(1/k_3a_2) + (1/k_4a_2)]$ can be written as overall mass transfer coefficients K_1a_1 and K_2a_2.

Balances for anthocyanin in the inert solid, the bulk liquid, and the interstitial liquid can now be written from Eqs. (5) and (6), using the overall coefficients K_1a_1 and K_2a_2, as follows:

Mass balance in inert solid: Since the mass of solute on solid can be represented as Sz,

$$\frac{d(Sz)}{dt} = -R_1 = -K_1 a_1 \left(z - \frac{x}{m} \right) \tag{7}$$

Mass balance in interstitial liquid: Since the mass of solute in the interstitial liquid can be represented as Sfx,

$$\frac{d(Sfx)}{dt} = R_1 - R_2 = K_1 a_1 \left(z - \frac{x}{m} \right) - K_2 a_2 (x - y) \tag{8}$$

Mass balance in bulk liquid: Since the mass of solute in the bulk liquid can be represented as $(L - Sf)y$,

$$\frac{d[(L - Sf)y]}{dt} = R_2 = K_2 a_2 (x - y) \tag{9}$$

When the bulk liquid diffuses into the porous inert solid, the interfacial area a_1 can be expected to increase, which will result in a subsequent increase of the overall mass transfer coefficient, K_1a_1. Since the transport of solvent into the grape waste would be largely concentration-gradient-driven, it can be expected that the increase in K_1a_1 is large during the initial phases of solvent transport, and sluggish during the later phases. We have therefore approximated the increase in K_1a_1 by an exponential behavior, so that

$$K_1 a_1 = K_1 a_1^{\infty} \left[1 - \exp\left(\frac{-t}{t^*} \right) \right] \tag{10}$$

where t^* is a lumped parameter.

Besides, the holdup, f, which is the mass of interstitial liquid per unit mass of inert solid, can be empirically correlated with the concentration in the bulk liquid, y, as (8):

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

$$f(y) = \frac{1}{A + By} \tag{11}$$

The system of differential Eqs. (7), (8), and (9), coupled with Eqs. (10) and (11), was solved numerically by employing a fourth-order Runge–Kutta, with initial conditions $z = z_0$, $x = 0$, and $y = 0$ at $t = 0$. The parameters A and B were obtained from experiment. $K_1a_1^\infty$ and t^* were obtained from a least-squares fit. The slopes m of the equilibrium curves and K_2a_2 were obtained from equilibrium ($t \to \infty$) data. For K_2a_2 determination it was assumed that the equilibrium between the interstitial and bulk liquids was obtained faster than the equilibrium between the solid and the interstitial liquid, which is a reasonable assumption because the interstitial and bulk liquids are the same chemical species. The system parameters (S, L, m, z_0) for various solvents used in the simulations are presented in Table 1, while the mass transfer parameters (K_1a_1, $K_1a_1^\infty$, K_2a_2, t^*) are given in Table 2.

RESULTS, ANALYSIS, AND DISCUSSION

Extraction Extents with Various Solvents

Studies on anthocyanin characterization available in literature have reported many solvents for anthocyanin extraction from skins of fresh grapes.

TABLE 1
Parameters for Extraction of Anthocyanins from Dry and Fresh Grape Wastes Using Different Solvents. These Parameters Were Calculated from Experimental Data ($z_0 = 0.0137$)

Solvent	S (g)	L (g)	m
	Dry Waste		
MeOH + 0.1% HCl	25.0	138.6	0.194
EtOH + 0.1% HCl	5.1	39.1	0.022
40% EtOH	25.0	116.0	0.052
50% PG	25.0	112.1	0.039
75% PG	25.0	118.9	0.026
100% PG	25.0	163.2	0.023
	Fresh Waste		
MeOH + 0.1% HCl	25.0	99.0	0.261
40% EtOH	25.0	69.6	0.198
50% PG	60.0	201.8	0.048
75% PG	60.0	214.1	0.034
100% PG	60.0	226.0	0.031

TABLE 2
Parameters for Extraction of Anthocyanins from Dry and Fresh Grape Wastes Using Different Solvents. These Parameters Were Used in the Simulations and Were Determined by a Least-Squares Fit

Solvent	K_1a_1 at 8 hours $\times 10^4$ s^{-1}	K_1a_1 at 16 hours $\times 10^4$ s^{-1}	$K_1a_1^\infty$ $\times 10^4$ s^{-1}	K_2a_2 $\times 10^4$ s^{-1}	t^* (h)
		Dry Waste			
MeOH + 0.1% HCl	21.8	33.1	45.0	0.150	12.0
EtOH + 0.1% HCl	4.73	8.96	45.0	0.015	72.0
40% EtOH	2.67	4.05	5.50	0.025	12.0
50% PG	2.06	3.85	15.0	0.046	54.0
75% PG	1.32	2.26	4.50	0.025	22.9
100% PG	1.54	2.82	9.00	0.013	42.5
		Fresh Waste			
MeOH + 0.1% HCl	21.8	27.8	30.0	0.070	6.1
40% EtOH	11.5	18.4	29.0	0.017	15.9
50% PG	7.84	13.6	30.0	0.046	26.4
75% PG	8.41	14.0	25.0	0.028	19.5
100% PG	6.23	8.3	9.5	0.033	7.5

For example, 25% ethanol with varying SO_2 concentrations (4), water with 1200 ppm SO_2, ethanol–HCl, and methanol–HCl (6) have been reported. In this study, anthocyanins were extracted from fresh grape waste (used immediately after being employed for juice preparations) and dried grape waste (after being sun-dried for at least 15 days). Six different solvents, i.e., ethanol with 0.1% HCl (EtOH/HCl), 40% ethanol (40% EtOH), methanol with 0.1% HCl (MeOH/HCl), and propylene glycol (PG) at 50, 75, and 100% levels were used for the studies. The results presented in Fig. 1 (for dry waste) show that methanol with 0.1% HCl provided the highest extraction extent (1.18×10^{-3} g·g^{-1}) followed by ethanol with 0.1% HCl (6.2×10^{-4} g·g^{-1}), 40% ethanol (5×10^{-4} g·g^{-1}), 50% PG (4×10^{-4} g·g^{-1}), 75% PG (2.9×10^{-4} g·g^{-1}), and 100% PG (2.2×10^{-4} g·g^{-1}). Comparison with similar results presented for extraction from fresh waste (Fig. 2) shows that the extraction extent follows the same trend for different solvents (data were not available for extraction with ethanol with 0.1% HCl) as in the dry waste case. However, the extraction extents obtained for methanol with 0.1% HCl and 40% ethanol are nearly equal in the case of fresh waste, although the kinetics are different. Also, the amount of anthocyanin extracted (on a gram solute per gram solvent basis) was higher in the fresh waste case compared to the dry waste case for all solvents. For example, while extracting with 40% ethanol it was 68.8%

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

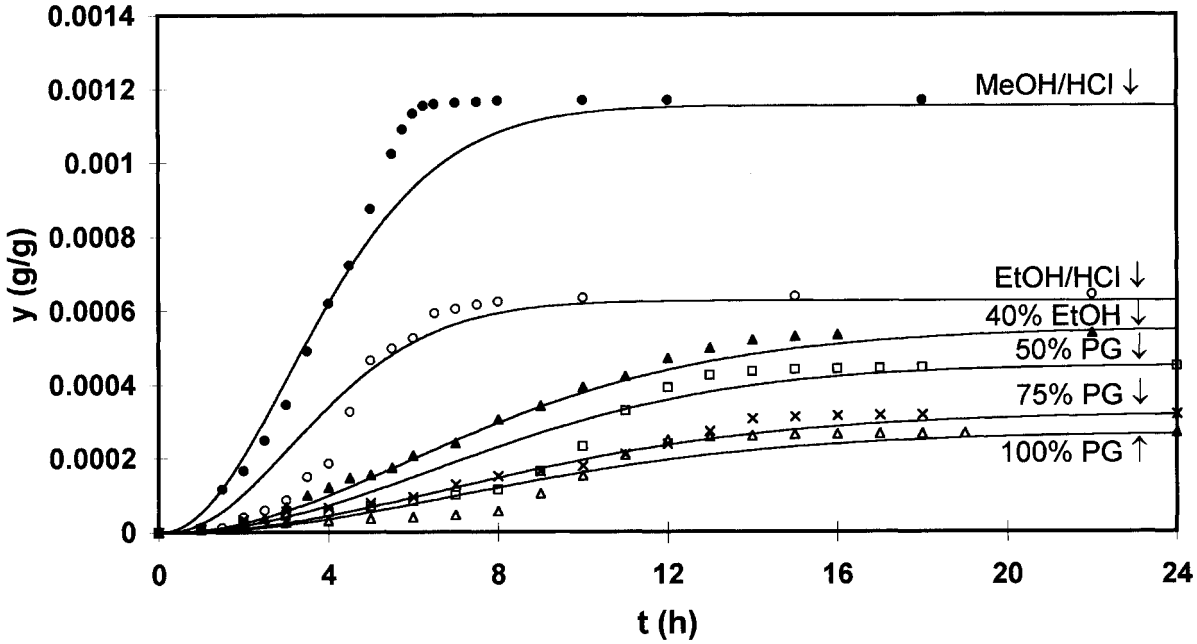

FIG. 2 Profiles of anthocyanin mass concentrations in bulk liquid (y) during extraction with different solvents from dry grape waste: experimental (symbol) and simulated (line) results.

higher and with methanol + 0.1% HCl it was 26.3% higher with fresh waste compared to dry waste.

The extraction extents obtained in this study for fresh waste compared favorably with the extraction extents estimated from literature data. For example, Yokotsuka et al. (4) obtained extraction extents of 1.29×10^{-4} g·g^{-1} with 5% ethanol, 2.32×10^{-4} g·g^{-1} with 10% ethanol and $2.36 \times 10-4$ g·g^{-1} with 25% ethanol (at the end of 24 hours of extraction with wine spirit diluted to the specified ethanol concentrations) compared with 8.44×10^{-4} g·g^{-1} obtained with 40% ethanol in this study. Also, Lamikarna (6) obtained an estimated 1.24×10^{-3} g·g^{-1} when methanol with 0.1% HCl was used as the solvent; the extraction extents obtained for water with 1200 ppm SO_2 and for ethanol with 0.1% HCl were 27.52 and 74.34%, respectively, of that obtained for methanol with 0.1% HCl in that study.

The extraction extents depend on solvent properties such as polarity and viscosity (9). Anthocyanins are polar molecules (6) and hence polarity of the solvent influenced extraction extents significantly. The dipole moments were estimated (10) to be 2.86 Debye (D) for methanol with 0.1% HCl, 1.65 D for ethanol with 0.1% HCl, 1.45 D for 40% ethanol, 1.3 D for 50% PG, 1.2 D for 75% PG, and 1 D for 100% PG. It can be seen that the order of solvent dipole moments corresponds to the order of extraction extents obtained with them. However, Yokotsuka et al. (4) reported a 72% increase in extraction extent

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

with 10% ethanol containing wine spirit when the temperature was raised from 15 to 25°C. Dipole moments are insensitive to temperature changes (10) and therefore solvent polarity may not be the only factor which influences anthocyanin extraction. Hence, the extraction extent must also depend on other properties of the solvent. Further, the viscosity of the solvent also influences extraction extents. The viscosities of the solvents at 25°C were estimated (10) to be 0.55 centipoise (cP) for methanol with 0.1% HCl, 1.04 cP for ethanol with 0.1% HCl, 0.96 cP for 40% ethanol, 10.15 cP for 50% PG, 14.78 cP for 75% PG, and 19.4 cP for 100% PG. Thus, the observed trend suggests that the lower the solvent viscosity, the higher is the extraction extent for anthocyanins. In addition, the wetting ability of the solvent could influence the kinetics of extraction, but it depends also on the nature of the solid in contact (9).

Extraction Kinetics

The simulated profiles for extraction with various solvents are shown in Figs. 2 and 3. As is evident, the simulation results fit the experimental data well. A comparison of the mass transfer coefficient values used in the simulations presented in Table 2 reveals that $K_1a_1^{\infty}$, the highest value of K_1a_1, is at least an order of magnitude lower than K_2a_2. This confirms the fact that trans-

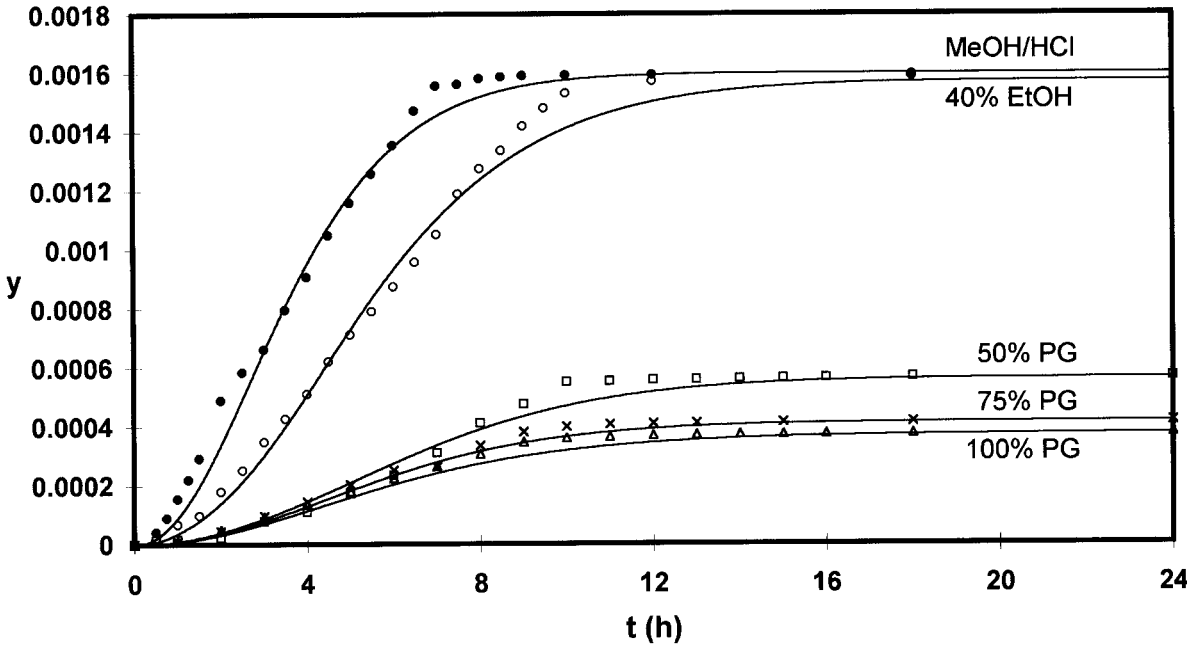

FIG. 3 Profiles of anthocyanin mass concentrations in bulk liquid (y) during extraction with different solvents from fresh grape waste: experimental (symbol) and simulated (line) results.

port across the interface between the solid and interstitial liquid controls the mass transport of anthocyanin and hence also the leaching process.

The data presented in Figs. 2 and 3 show three phases: an initial slow rise in the anthocyanin mass concentration in the bulk liquid, followed by a rapid rise and then a slow rise till saturation at the equilibrium concentration. It can be seen that the exponential profile for the increase in K_1a_1, postulated in Eq. (11), predicts the "lag" or the initial period of slow rise accurately. This implies that the initial phase of extraction is dominated by the diffusion of solvent into the inert solid. Also for the extractions with methanol + 0.1% HCl, the third phase of slow increase to the asymptotic value is almost absent, indicating that solvent diffusion may not have been completed by the time equilibrium was attained.

It can also be argued that solvent diffusion into fresh waste would be faster than in the case of dry waste, as the fresh waste may be more wettable. This leads to shorter periods of a slow increase of anthocyanin concentration in the case of fresh waste, which can be verified from the data in Figs. 2 and 3. Also, the values of t^* for each of the solvents is smaller in the case of extraction with fresh waste, which substantiates the fact that solvent diffusion (and hence an increase of K_1a_1) is faster in the case of fresh waste.

The parameter t^* is a first-order time constant for the increase in K_1a_1. As this parameter is different across various solvents, we have compared the mass transfer coefficients at $t = 8$ hours and $t = 16$ hours in Table 2. It can be seen that the mass transfer coefficients for methanol with 0.1% HCl are the highest, followed by ethanol with 0.1% HCl, the PGs, and 40% ethanol for extractions with both dry and fresh waste.

A comparison of various K_1a_1 values in Table 2 shows that K_1a_1 and K_2a_2 follow roughly the same trend across various solvents, being the highest in the case of methanol with 0.1% HCl and lowest for the PGs and 40% ethanol. The time taken to reach equilibrium varied with the type of solvent used in an inverse fashion as K_ia_i at 8 and 16 hours. For example, equilibrium with the dry waste was reached fastest (7 hours) for methanol with 0.1% HCl, followed by ethanol with 0.1% HCl (8 hours), PGs (14 hours), and 40% ethanol (15 hours). The same trend was also observed in the fresh waste case; however, equilibrium was reached faster compared to the dry waste case.

The simulated z (normalized) values are presented in Figs. 4 and 5. The normalized z values suggest that even in the case of methanol with 0.1% HCl, only about 45% of the extractable anthocyanin content has been extracted by using one extraction from both the dry and fresh wastes. Therefore, batch extraction may not be the preferred methodology for large-scale extractions of anthocyanins. Multiple contacting, either in a countercurrent or crosscurrent scheme, may be preferable.

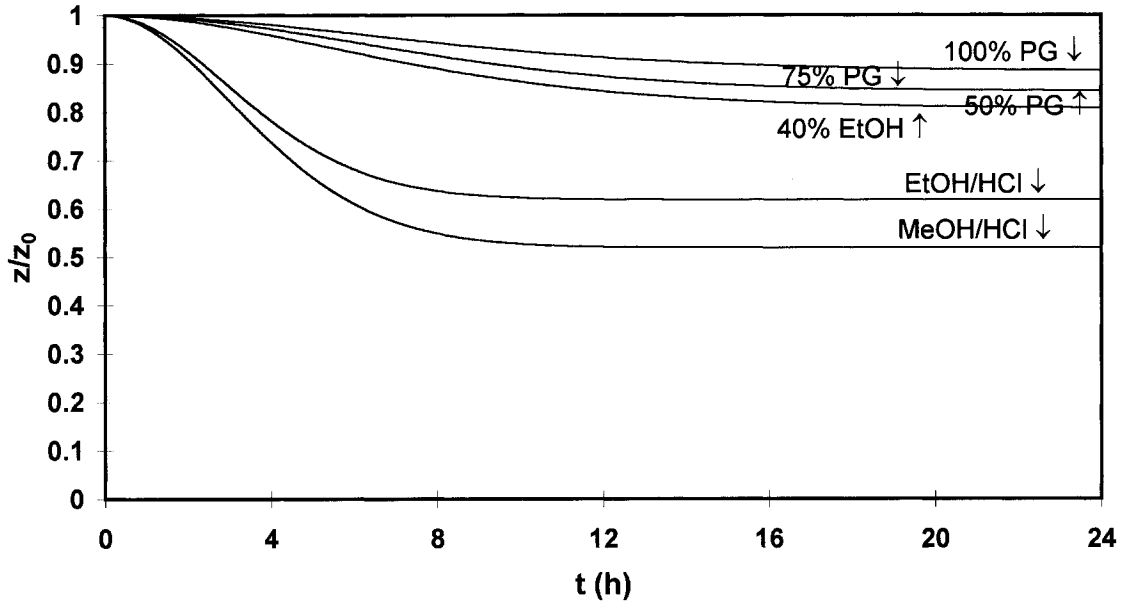

FIG. 4 Profiles of normalized anthocyanin mass concentrations in the solid (*z*, simulated results) during extraction with different solvents from dry grape waste.

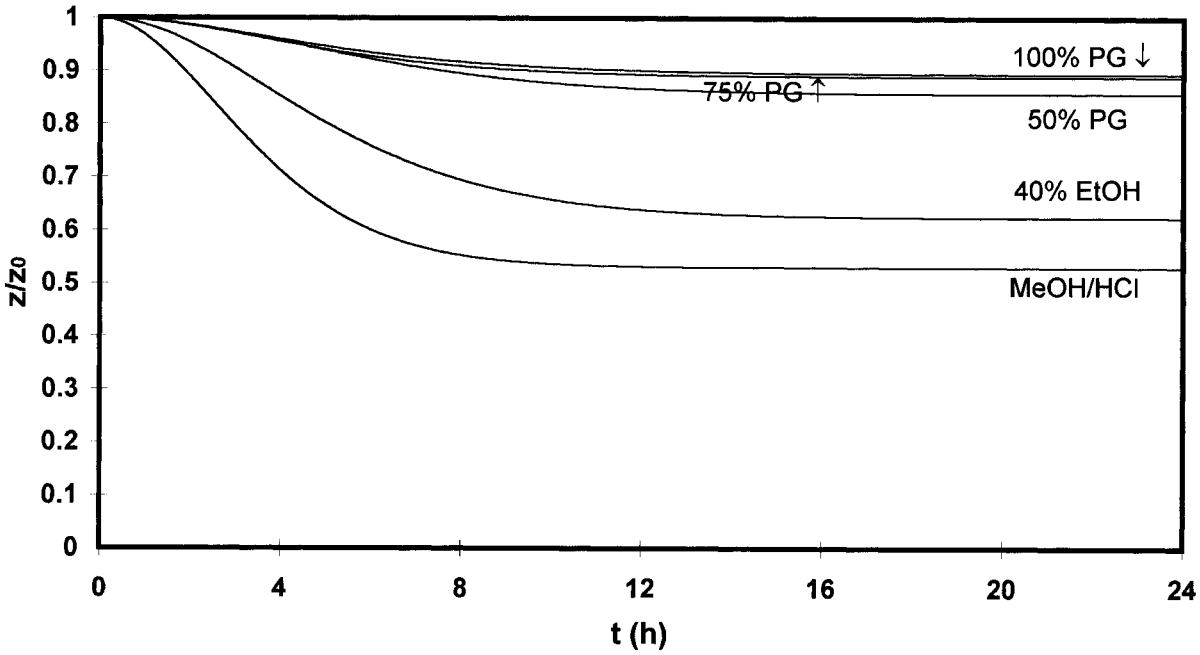

FIG. 5 Profiles of normalized anthocyanin mass concentrations in the solid (*z*, simulated results) during extraction with different solvents from fresh grape waste.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Holdup and Equilibrium Studies

From an industrial viewpoint, it is easier to work with dry waste than with fresh waste because of the ease in handling. Therefore, further studies have been carried out on dry waste. Further, since our aim is to use the extracted anthocyanins for human use, methanol was not considered further, although it was found to be the best solvent. A safe solvent which gave good extraction levels among the solvents used, ethanol with 0.1% HCl, was chosen for further studies.

The holdup, f (mass of solution associated with a unit mass of inert solid), was determined as described in the Materials and Methods Section by using the following empirical relationship (8):

$$f = \frac{1}{A + Bx} \tag{12}$$

The data showed a good fit to the empirical dependence of f on x. The empirical constants A and B were found to be 0.316 and 582.93, respectively, from a plot of $1/f$ vs x ($= y$ at equilibrium, see later paragraphs).

Equilibrium studies were carried out since any design for anthocyanin extraction would require equilibrium information. The equilibrium is expressed as a relationship between the mass concentration of anthocyanins in the slurry, q, to that in the bulk liquid, y. It should be noted that anthocyanin concentrations in the slurry, which includes the inert solid and the interstitial liquid, are used as the basis rather than the inert solid alone which is traditionally used as the basis. This is because measurements made at any time point will provide only the concentration in the slurry and not that in the inert solid. Therefore, any design based on an inert solid basis will require extensive measurements over various time periods to provide the necessary data.

Although the solute concentrations in the slurry, q, were used in the equilibrium relationship, it should be noted that at equilibrium it corresponds to the solute concentration in the solid. This is because, at equilibrium, it is reasonable to assume that the bulk liquid and the holdup liquid are at the same mass concentration ($y = x$). However, when equilibrium is yet to be achieved, solute mass transfer between the interstitial liquid and the bulk liquid takes place due to the concentration difference between the two phases.

The following relationship exists between the concentration of anthocyanin in the slurry, q, and the concentration in the bulk liquid, y (assuming $y = x$ and $z = x/m = y/m$).

$$q = \frac{Sz + Sfx}{S + Sf} = \frac{(y/m) + [y/(A + By)]}{1 + [1/(A + By)]} \tag{13}$$

Figure 6 shows the relationship between q and y, both as obtained from ex-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

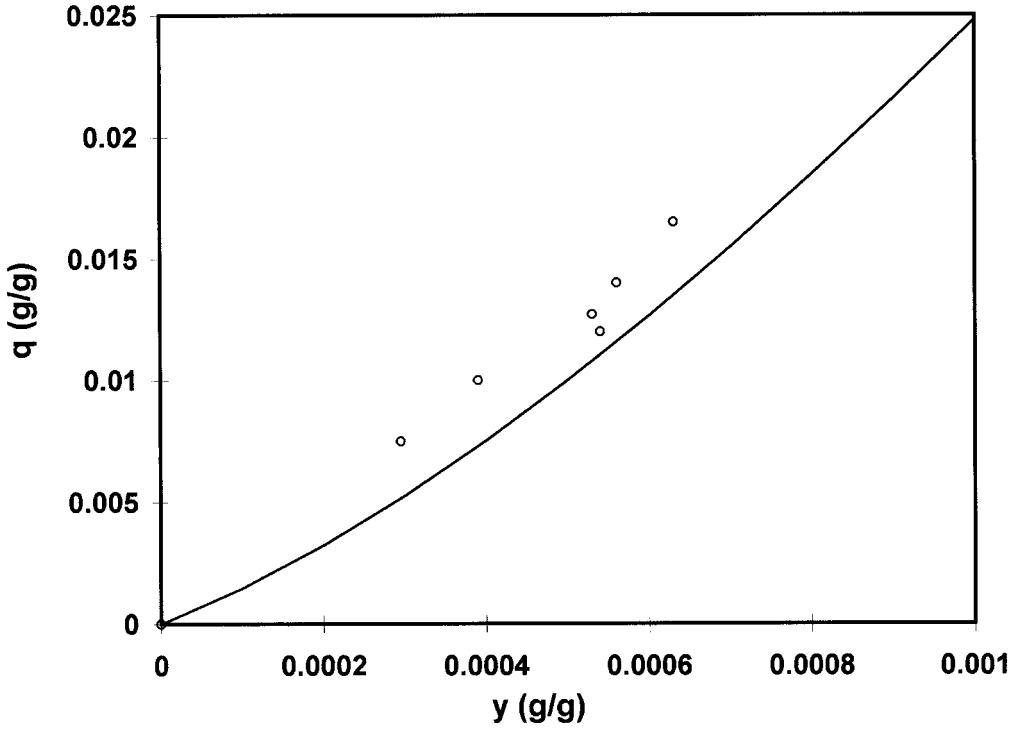

FIG. 6 Equilibrium relationship between anthocyanin concentration in slurry to that in the bulk liquid. The points are experimental data and the line represents the isotherm represented by Eq. (13).

periment and from the above isotherm. For the experiments, the initial slurry concentrations were varied by the method described in the Materials and Methods Section. As is evident, the isotherm is a good fit for the experimental data. This validates the holdup equation (Eq. 12), and also the assumption (made earlier in the formulation of the model) that the z–x equilibrium is linear with slope m^{-1}.

CONCLUSIONS

Anthocyanin extraction from grape waste using various solvents showed that among the six solvents employed, methanol with 0.1% HCl gave the highest extraction for dry waste. The extent of extraction was higher with fresh waste than with dry waste. A two-interface mass transfer model was able to predict the leaching data well. Inspection of the mass transfer coefficients showed that transport across the solid–interstitial liquid interface is at least an order of magnitude slower than that across the interstitial liquid–bulk liquid interface.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

The holdup data fitted well to its empirical relationship to the solute concentration in the interstitial liquid. The equilibrium relationship between anthocyanin concentrations in the slurry and the bulk liquid fitted the experimentally obtained equilibrium data well when written using this holdup relationship.

NOMENCLATURE

A, B	constants in Eq. (11)
f	holdup (= mass of interstitial liquid per unit mass of inert solid)
K_1a_1	overall mass transfer coefficient across the solid–interstitial liquid film (s^{-1})
K_2a_2	mass transfer coefficient across the interstitial liquid–bulk liquid film (s^{-1})
k_ia_i	mass transfer coefficients as shown in Fig. 1 (s^{-1})
L	mass of bulk liquid (g)
m	equilibrium constant at the solid–interstitial liquid interface
S	mass of inert solid (g)
q	mass concentration of solute in slurry (inert solid + interstitial liquid) (= mass of solute per unit mass of slurry)
R_1	rate of solute (anthocyanin) diffusion across interface $i1$ (s^{-1})
R_2	rate of solute (anthocyanin) diffusion across interface $i2$ (s^{-1})
t	time (s)
t^*	time constant for increase in K_1a_1 (s)
x	mass concentration of anthocyanin in interstitial liquid (= mass of solute per unit mass of interstitial liquid)
x_{i1}	mass concentration of anthocyanin at the inert solid–interstitial liquid interface (on the interstitial liquid side)
x_{i2}	mass concentration of anthocyanin at the interstitial liquid–bulk liquid interface (on the interstitial liquid side)
y	mass concentration of anthocyanin in bulk liquid (= mass of solute per unit mass of bulk liquid)
y_i	mass concentration of anthocyanin at the interstitial liquid–bulk liquid interface (on the bulk liquid side)
z	mass concentration of anthocyanin in inert solid (= mass of solute per unit mass of inert solid)
z_i	mass concentration of anthocyanin at the inert solid–interstitial liquid interface (on the inert solid side)

Subscripts

0	initial time

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Superscripts

∞ final time

ACKNOWLEDGMENT

The authors acknowledge Dr. K. L. K. Paranjyothi, Jagdale Industries Limited, Bangalore, India, for providing the raw materials.

REFERENCES

1. P. Knuthsen, "Investigations on Grape Skin Colours for Legislative Regulation," *Z. Lebensm.-Unters. Forsch., 184*, 204 (1987).
2. J. Zhong, T. Seki, S. Kinoshita, and T. Yoshida, "Effect of Light Irradiation on Anthocyanin Production by Suspended Culture of *Perilla frutescens," Biotechnol. Bioeng., 38*, 653 (1991).
3. K. Yokotsuka, K. Nozaki, and T. Kushida, "Comparison of Phenolic Compounds Including Anthocyanin Pigments between Koshu and Ryugan Grapes," *J. Ferment. Technol., 62*, 477 (1984).
4. K. Yokotsuka and N. Nishino, "Extraction of Anthocyanins from Muscat Bailey A Grape Skins," *J. Ferment. Bioeng., 69*, 328 (1990).
5. C. F. Timberlake and P. Bridle, *Food Colours from Natural Sources*, Chapman and Hall, London, 1978.
6. O. Lamikarna, "Anthocyanins from Grape Waste," *Cent. Enol. Agri. Elem., 11*, 31 (1987).
7. V. C. Belapurkar, K. C. Khilar, and H. S. Shankar, "A Note on a Mechanism for the Solvent Extraction of Oil from Peanut Cake," *Ind. Chem. Eng., 29*, 54 (1986).
8. R. N. Rickles, "Liquid–Solid Extraction," *Chem. Eng., 72*, 157 (1965).
9. Y. Marcus, "Principles of Solubility and Solutions," in *Principles and Practices of Solvent Extraction* (J. Rydberg, C. Musikas, and G. Choppin, Eds.), Dekker, New York, NY, 1992.
10. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York, NY, 1988.

Received by editor January 27, 1998
First revision received May 1998
Second revision received June 1998

PAGE 698 IS BLANK

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Request Permission or Order Reprints Instantly!