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Dynamic model for mass transfer of solutes in cucumber fermentation ☆

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Abstract

A mathematical model for the mass transfer of solutes between whole cucumbers and brine in cucumber fermentation has been developed that takes into account permeation of solutes through stomata in the cucumber skin and through the epidermal cells in the skin, as well as film diffusion through the surrounding brine boundary layer. The model was used to fit experimental data for the time-dependent concentrations of solutes that permeate into the cucumbers (glucose and malate) and out of them (lactic acid, acetic acid, ethanol, and sodium chloride). The rate of lactic acid transport through the stomata was found to be three orders of magnitude greater than that through the epidermis, and the permeabilities of lactic and acetic acids were effectively independent of the brine circulation rate. These results indicate that the rate of permeation of solutes into and out of cucumbers was controlled by mass transfer through the stomata, with neither film diffusion nor epidermal diffusion having a significant effect. The model differential equation for solute transfer combined with a set of rate equations for microbial growth will provide a good basis to establish a complete mechanistic model for the cucumber fermentation process.

Keywords: Diffusion; Cucumber; Modeling; Acids; Sugar

1. Introduction

Cucumber fermentation involves transfer of various solutes between a brine and a porous solid phase, coupled with reaction within the liquid. Several authors have suggested that solute transport through micropores (stomata) in the skin may control the rate of diffusion of solute into and out of the cucumbers (Fasina, Fleming, & Thompson, 2002; Potts, Fleming, McFeeters, & Guinnup, 1986; Smith & Fleming, 1979).

The objectives of this study were to measure rates of solute movement into and out of non-fermenting, brined pickling cucumbers to formulate a transport model that accounts for solute passage through both the cucumber skin and the fluid boundary layer surrounding it, and to determine the controlling mechanism of solute transport. The resulting differential equation combined with rate equations for substrate consumption and metabolic production by microorganisms (Passos, Fleming, Ollis,

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Felder, & McFeeters, 1994) should serve to model the complete cucumber fermentation process.

2. Materials and methods

Calypso cv. cucumbers from a local farm were harvested manually and graded mechanically. Four grades based on cucumber diameter were examined: #1 (1.9–2.7 cm); #2 (2.7–3.8 cm); #3 (3.8–5.1 cm); and #4 (5.1–6.4 cm). Cucumbers free of disease and injury were selected and washed manually. Size #3 cucumbers were used in all experiments except those concerning the effect of fruit size. Cucumber surface area (A) was estimated from measured length (L) and maximum diameter (D) using the formula $A = \pi DL$ (Potts et al., 1986).

The fruits were brined in 1-gal (3.8-l) glass jars containing about 40% cucumbers and 60% brine by weight. The brine contained 8.6 wt.% sodium chloride, 78 mM acetic acid, 59 mM lactic acid, and 80 mM ethanol. Sodium metabisulfite from Sigma (Sigma Chemical Company, St. Louis, MO) was added to all jars in a concentration equivalent to 400 ppm of SO_2 in the brine to avoid growth of microorganisms. Brined cucumbers were held at 30 °C for 6 d. All jars were continuously purged with N_2 at a constant flow rate of 0.35 h^{-1} (liter of N_2/h × liter of jar) to simulate purging conditions in commercial fermentation of cucumber to prevent bloater formation.

To evaluate the influence of external mass transfer (film diffusion) on the overall solute permeation rate, brine circulation rates were varied. Flow rates used were no circulation (except for the movement caused by the N_2 purge), 0.63 h^{-1} (liter brine/h × liter of jar), 4.42 h^{-1}, and 26.3 h^{-1}. Four cucumber sizes were studied and the stomata area/total surface area ratio for sizes #1 and #3, as estimated by Smith and Fleming (1979), were used. Samples (2 ml) were taken periodically (3–12 h) from the brine. The jars were shaken before each sampling.

NaCl concentrations were determined by titration with standard $AgNO_3$ using dichlorofluorescein as an indicator (Fleming, McFeeters, & Daeschel, 1992), and concentrations of all other solutes were determined using HPLC. Brine samples were diluted twofold using distilled water, and 1.5-ml samples were centrifuged at 12,000 × g (Eppendorf centrifuge model 5415, Westburg, NY). Glucose, lactic acid, and acetic acid were analyzed with an Aminex HPX-87H column (Bio-Rad Laboratories, Richmond, CA) at 65 °C, a Waters differential refractometer (Waters Associates, Milford, MA) and a Shimadzu integrator (Shimadzu Corp., Columbia, MD). The column was eluted with 0.01 M H_2SO_4 at a flow rate of 0.7 ml/min. When malic acid and fructose were present in the sample, a Dionex (Sunnyvale, Ca) system was used with a conductivity detector for acid determination and a Dionex pulsed amperometric detector for sugar determination (McFeeters, 1993).

2.1. Transport model development

The principal model assumptions are that the brine is perfectly mixed and the vegetable skin is a flat membrane of uniform thickness h. If C_b is the concentration of the solute in the brine and C_c the concentration at the inner surface of the vegetable skin, then

$$\frac{dC_b}{dt} = \frac{KA_t}{V_b h}(C_c - C_b) \tag{1}$$

where K is the *overall permeability*, A_t is the total skin surface area, and V_b is the brine volume (Crank, 1975). The permeability is a function of various physical properties of the vegetable skin and of the surrounding brine, and may also depend on the rate of mixing and shear rate distribution in the fermentation vessel. Potts et al. (1986) showed that an expression of the form of Eq. (1) provided a good description of the permeation of lactic acid, acetic acid, and sodium chloride into brined cucumbers and of glucose and malic acid out of them.

Fasina et al. (2002) used the equation:

$$\frac{C - C_{eq}}{C_0 - C_{eq}} = \exp(-kt) \tag{2}$$

to represent the movement of solutes in brined cucumber. While this equation provided a good fit to their data, it has several limitations. The empirical parameter k depends on both transport parameters and physical dimensions of the cucumber in an unspecified manner, making it impossible to predict changes in permeation rates with varying system conditions. Moreover, unlike Eq. (1), the exponential expression cannot be combined with rate equations for microorganism growth and decay kinetics to provide a model for the total fermentation process.

To further develop the transport model, the following additional assumptions were made:

1. $C_{b,i}$ and $C_{c,i}$ are the concentrations of solute i in the brine and in the cucumber interior, respectively, at a point in time. Both concentrations are uniform, that is to say, the brine solution is perfectly mixed and diffusion within the cucumber interior is presumed to be extremely rapid relative to diffusion through the skin, an assumption consistent with conclusions of Potts et al. (1986). We will return to this point in the discussion section.
2. Permeation of solute from the brine to the cucumber interior involves convective mass transfer through a fluid boundary layer surrounding the cucumber (permeability k_f), followed by permeation through the skin by two parallel mechanisms: (i) diffusive

transport through pores (stomata) in the skin (permeability p_{st}), and (ii) Henry's law sorption into the epidermal cells of the skin followed by molecular (Fickian) diffusion through the cells into the cucumber interior (combined permeability p_{ec}).
3. All mass transfer coefficients and permeabilities are independent of both time and solute concentration.
4. The concentration profile from the brine to the cucumber interior achieves a quasi-steady-state; that is, it adjusts instantaneously to changes in C_b and C_c.
5. The skin thickness (h) is uniform and much smaller than the average cucumber radius, so that rectangular geometry can be used to describe the permeation, and the skin thickness and epidermal cell permeability do not change with cucumber size. A value of $h = 50$ μm was assumed, based on an electron microscopy image.
6. Stomatal pore areas were assumed as 0.118% and 0.062% of the surface of #1 and #3 fruits, corresponding to values determined by Smith and Fleming (1979).

If C_x is the solute concentration at the interface between the fluid boundary layer and the exterior cucumber surface, then the rate of solute permeation into or out of the cucumber, J_f (mol/s), is

$$J_f = k_f A_t (C_b - C_x) \tag{3}$$

where A_t is the external cucumber surface area. The flux through the skin is

$$J_s = \frac{(p_{st}A_s + p_{ec}A_e)}{h}(C_x - C_c) \tag{4}$$

where p_{st} and p_{ec} are the permeabilities of the solute through the stomata and the epidermal cells, respectively, and A_{st} and A_{ec} are the cross-sectional areas of these two diffusion channels. The permeability p_{ec} is the product of the Henry's law solubility of the solute and the diffusivity of the dissolved solute in the epidermis.

At steady-state $J_f = J_s = J$. Eliminating C_x between Eqs. (3) and (4) yields

$$J = KA_t(C_b - C_c) \tag{5}$$

where the overall permeability is given by the relation

$$\frac{1}{K} = \frac{1}{k_f} + \frac{hA_t}{A_s p_{st} + A_e p_{ec}} \tag{6}$$

Any one of the transport coefficients k_f, p_{st}, and p_{ec} could control the overall solute permeation rate, depending on the experimental conditions. The expectation, however, is that $p_{st} \gg p_{ec}$, so that diffusion through the epidermal cells should never be a significant factor.

A mass balance on solute i in the brine now becomes

$$V_b \frac{dC_{b,i}}{dt} = -KA_t(C_{b,i} - C_{c,i})$$

or

$$\frac{dC_{b,i}}{dt} = -\frac{KA_t}{V_b}(C_{b,i} - C_{c,i}) \tag{7}$$

where V_b is the brine volume. If the initial concentration in the brine is $C_{b0,i}$, the concentration in the cucumber is $C_{c0,i}$, the cucumber volume is V_c, and the solute is non-reactive, then at any time

$$V_c(C_{c0,i} - C_{c,i}) = V_b(C_{b,i} - C_{b0,i}) \tag{8}$$

or

$$C_{c,i} = C_{c0,i} - \left(\frac{V_b}{V_c}\right)(C_{b,i} - C_{b0,i}) \tag{9}$$

For lactic acid, acetic acid, and NaCl at $t = 0$, $C_b = C_{b0}$ and $C_{c0} = 0$. For malic acid, glucose, and fructose at $t = 0$, $C_b = 0$. Substituting Eq. (9) into Eq. (7) yields

$$\frac{dC_{b,i}}{dt} = -\frac{KA_t}{V_b}\left[\left(\frac{V_c + V_b}{V_c}\right)C_{b,i} - \left(C_{c0,i} + \frac{V_b}{V_c}C_{b0,i}\right)\right] \tag{10}$$

The time-dependent concentrations of different brine components may be predicted from Eq. (10) and the appropriate cucumber dimensions and initial concentrations.

3. Results and discussion

Runs were carried out at the experimental conditions described previously, and the measured solute concentration data were correlated using Eq. (10). The overall permeability (K) was estimated for each component based on the minimum predictive error, PE, defined as

$$\mathrm{PE} = \frac{\sum_{j=1}^{n}(Y_{mj} - Y_{pj})}{n} \tag{11}$$

where Y_{mj} and Y_{pj} are measured and predicted solute concentrations at each of n data points in a run. If the solute uptake rate is independent of the brine circulation rate, the external mass transfer resistance may be assumed negligible (an assumption supported by the data), and the k_f term may be dropped from Eq. (6). Values of the permeability K determined for different cucumber sizes should then enable the calculation of permeabilities p_{st} and p_{ec} from Eq. (6).

Table 1 summarizes cucumber dimension and packing ratios used in this study. Data represent the average of two jars for each treatment (24–50 cucumbers per jar). Fig. 1 shows the plot of the measured and predicted concentrations ($C_{b,i}/C_{b0,i}$) versus time for acetic acid (a) and lactic acid (b) at different brine circulation rates, and Fig. 2 shows the same plots for different cucumber sizes. Table 2 presents the calculated values of K for lactic and acetic acid for different brine circulation rates and cucumber sizes.

Table 1
Average cucumber dimensions

Brine circulation rates (h^{-1})	V_c[a] (m^3)	V_b (m^3)	D (m)	L (m)	m_c (g)	A_c (m^2)	A_t^1 (m^2)
External mass transfer study							
0.0	1.720	2.085	0.0445	0.1174	138.9	0.01641	0.1546
0.63	1.685	2.115	0.0442	0.1168	136.6	0.01622	0.1525
4.42	1.645	2.160	0.0427	0.1189	135.3	0.01595	0.1541
26.3	1.555	2.250	0.0408	0.1166	128.3	0.01495	0.1525
Cucumber size study							
Size no.							
1	1.555	2.250	0.0241	0.0776	30.1	0.00588	0.2581
2	1.580	2.225	0.0319	0.0926	58.9	0.00928	0.1981
3	1.720	2.085	0.0445	0.1174	138.9	0.01641	0.1546
4	1.780	2.025	0.0516	0.1227	188.2	0.01989	0.1380

Total surface area of all cucumber in jar=$(4 \times V_c)/D$.
[a] Values of the volume (V_c and V_b) were multiplied by 10^3.

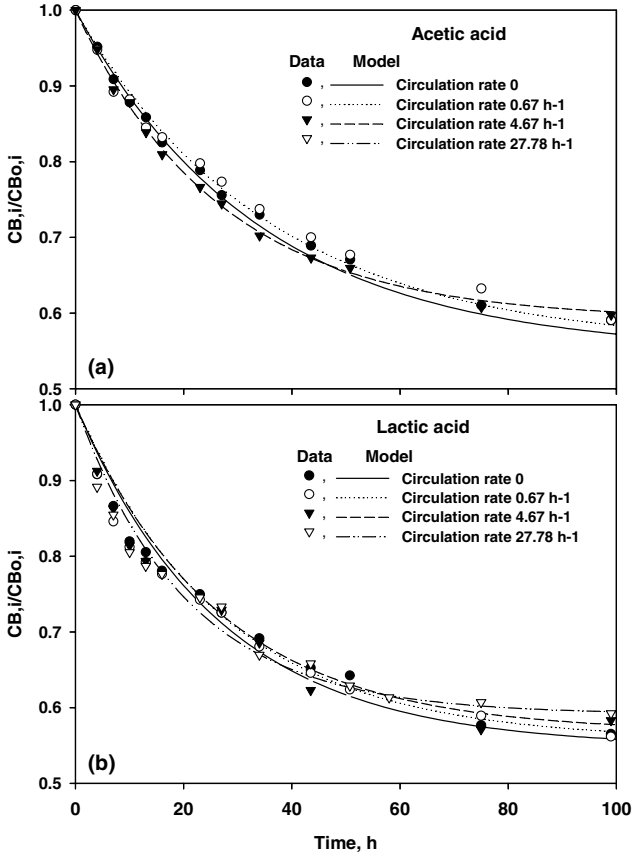

Fig. 1. Concentration of acetic (a) and lactic (b) acids in brine for different brine circulation ratios. Size no. 3 cucumbers were brined in 1-gal glass jars containing about 40% cucumbers and sodium chloride, acetic acid, lactic acid, and ethanol at room temperature. C_{A0} and C_{L0} are the initial concentrations.

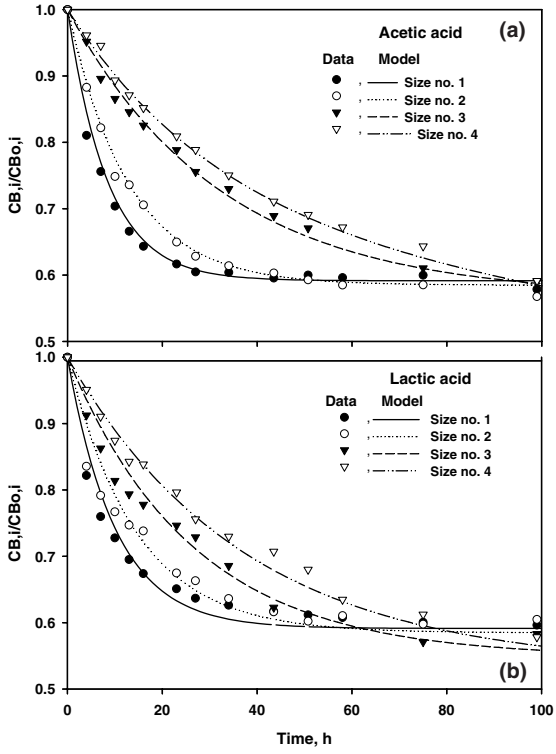

Fig. 2. Concentration of acetic (a) and lactic (b) acids in brine for different cucumber sizes. Size #1, #2, #3, and #4 cucumbers were brined in 1-gal glass jars containing about 40% cucumbers and sodium chloride, acetic acid, lactic acid, and ethanol at room temperature. C_{A0} and C_{L0} are the initial concentrations.

No significant effects ($p < 0.05$) of circulation rate on K values for lactic and acetic acids were observed, suggesting that film diffusion resistance to solute transport could be neglected. The same result is applied to all other solutes, an assumption that further experimentation would be needed to confirm.

To estimate the permeability coefficients for the stomata (p_{st}) and epidermal cells (p_{ec}), acetic acid permeation data for cucumber sizes #1 and #3 were used in Eq. (6). Neglecting film diffusion resistance ($1/k_f \approx 0$), Eq. (6) can be expressed as

Table 2
Effects of brine circulation rate and cucumber size on the permeabilities of lactic and acetic acid ($\times 10^8$ m/s)

	Brine circulation rates (h^{-1})				Size			
	0.0	0.63	4.42	26.3	1	2	3	4
Lactic acid	6.361	6.250	6.389	8.111	9.806	8.972	6.361	5.083
Acetic acid	4.944	4.778	–	6.222	11.750	11.750	4.944	4.472

$$\frac{1}{K} = \frac{hA_t}{A_s p_{st} + A_e p_{ec}}$$

or

$$K = \frac{A_s p_{st} + A_e p_{ec}}{hA_t} \quad (12)$$

As shown in Table 2, the values of K for lactic and acetic acids were, respectively 1.5 and 2.4 times greater for size #1 than for size #3 cucumbers. A scanning electron microscopy study carried out by Smith and Fleming (1979) estimated 130,000 and 105,000 stomata per fruit in the skin of "Chipper" and "GY14" cv. cucumbers, respectively. The stomatal pore areas were 33.6 and 59.9 μm^2 for sizes #1 and #3, corresponding respectively to 0.118% and 0.062% of the cucumber surface. Using these figures and assuming $h = 50$ μm, the values of the stomata and epidermal cell permeability coefficients for lactic acid may be estimated from Eq. (12) as $p_{st} = 3.411 \times 10^{-9}$ m^2/s and $p_{ec} \leqslant 1.4 \times 10^{-12}$ m^2/s, respectively, and the comparable figures for acetic acid were $p_{st} = 6.683 \times 10^{-9}$ m^2/s and $p_{ec} \leqslant 1.4 \times 10^{-12}$ m^2/s. These results confirm previous suggestions (e.g., by Potts et al., 1986) that the stomata constitute the principal route for mass transport through the skin during cucumber fermentation.

Fig. 3 shows plots of the experimental and predicted concentration ratios ($C_{b,i}/C_{b0,i}$) versus time for lactic acid, acetic acid, ethanol, NaCl, glucose, and malic acid,

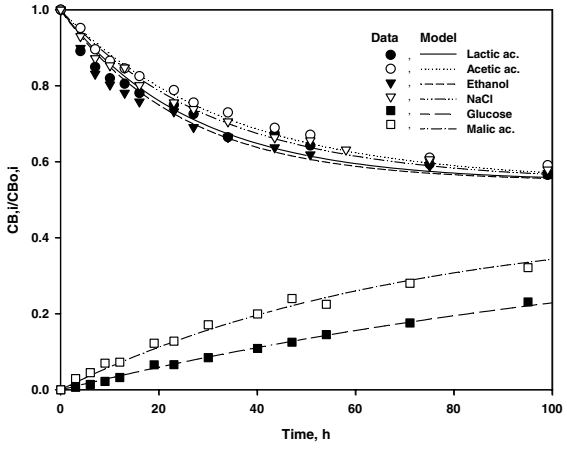

Fig. 3. Concentration of six different solutes. Size no. 3 cucumbers were brined in 1-gal glass jars containing about 40% cucumbers and sodium chloride, acetic acid, lactic acid, and ethanol at room temperature. $C_{i,0}$ are the initial concentrations.

Table 3
Values of the overall mass transfer coefficient, K, for glucose, acids, ethanol, and NaCl for size no. 3 cucumber ($\times 10^8$ m/s)

Parameters	Glucose	Malic	Acetic	Lactic	Ethanol	NaCl
K (cm/hr)	1.194	2.417	5.028	6.361	6.833	5.389

and Table 3 lists the overall permeabilities for these solutes. As seen in Table 3, the K values of the solutes that diffuse out of the cucumbers (glucose and malic acid) are small compared with the values for the solutes that diffuse in (lactic acid, acetic acid, ethanol, and NaCl). A possible reason for this difference was suggested by the study of Potts et al. (1986), who found that the diffusion coefficients of glucose and lactic acid were, respectively, 9.2 times higher and 5.2 times higher for peeled cucumber than for unpeeled cucumber. These results indicate the controlling importance of the skin in determining the overall mass transfer rate, but also show that diffusion resistance within the cucumber interior (which was neglected in the model development) contributes to the observed rate. However, the extent of the contribution was insufficient to justify the inordinate complexity that would result from including the time-dependent internal diffusion equation in the model formulation.

4. Conclusions

A model for mass transfer of solutes between whole fruit and brine in cucumber fermentation provides a good correlation of experimental data for several solutes and cucumber sizes. The model takes into account external film diffusion and parallel transfer through stomata and epidermal cells. The experimental results indicate that permeation through the stomata was the overall rate-determining step and that epidermal permeation and film diffusion resistance may be neglected. The model equation combined with a set of rate equations for microorganism growth (Passos et al., 1994) should provide a good basis for a complete mechanistic model of the cucumber fermentation process.

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