

Mathematical modelling of mass transfer during osmotic dehydration of seedless guava (*Pisidium guajava* L.) cubes

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Abstract: The present work aimed to study kinetics of osmotic dehydration of seedless guava in terms of solid gain and water loss, which was evaluated at three sucrose concentration levels (30, 40 and 50% w/w), three temperature levels of osmotic solution (30, 40 and 50°C) for 240 min. The experimental data was fitted to different empirical kinetic models including Peleg, Page and Azuara. Determination of coefficient (R^2), root mean square error (RMSE) and mean relative deviation modulus (E) were used for determination of the best suitable model. The present work shows that the Peleg empirical model satisfactorily described the dehydration kinetics with the highest R^2 (>0.95) and the lowest RMSE (<0.003) and E ($<5.20\%$). Moreover, the effect of solution concentration and temperature was also studied and it was found that initial water loss and solid gain are related to solution concentration and temperature whereas equilibrium contents are related to sucrose concentration. From the experimental data it is possible to estimate the equilibrium content of water and solid.

Keywords: Mathematical modelling, osmotic dehydration, seedless guava, solid gain, water loss

Introduction

Guava, *Pisidium guajava* L., is originated in the Caribbean and common in Malaysia which has great amount of vitamins C (>3 of an orange vitamin C content), A and B. Guava fruit, as other tropical fruits, is highly perishable which needs preservation methods to increase its shelf-life (Andrade *et al.*, 2007). In recent years, considerable amount of attention has been paid to osmotic dehydration technique for preservation of fruits and vegetables due to its potential to keep sensorial and nutritional properties similar to the fresh fruits (García-Martínez *et al.*, 2002). Osmotic treatment has been carried out to partially remove water of fresh foods by immersing pieces of the food in a highly concentrated solution. This solution is referred to as a hypertonic solution in the literature. The potential difference between osmotic pressure of fresh material and surrounding solution provides a driving force for remove of water from cells (Corzo and Bracho, 2005). Mass transfer during osmosis process consists of two major simultaneous counter-current fluxes of water and solutes due to the fact that the complex cell wall structure is not perfectly selective (Madamba, 2003). Leakage of neglectable amount of natural solutes presents in the cells into osmotic solution has considered as third minor flux (Rastogi and Raghavarao, 2004). The effect of several factors like solution concentration,

temperature, immersion time, sample size and shape, solution to sample ratio and applied pretreatments on kinetics of mass transportation have been extensively investigated (Rastogi *et al.*, 2002; Panades *et al.*, 2008). Mathematical modelling of mass fluxes during the process gives invaluable information to have clearer understanding of dehydrated material composition and operational design. In this regard, several equations based on Fick's second law have been proposed which are not useful practically due to the fact that some of the assumptions are unrealistic and complexity of the equations (Chausi *et al.*, 2001). Peleg (1988), Azuara (1992) and Page (1949) recommended simpler empirical equations including parameters with physical meaning. These empirical equations have been used to model the rate of dehydration of different plant-based materials (García-Pascual *et al.*, 2006; Schmidt *et al.*, 2009; Khin *et al.*, 2006; Mercali *et al.*, 2010; Kaymak-Ertekin and Sultanoglu, 2000; Singh *et al.*, 2007). However, in literature, the suitability of these equations to model the dehydration rate of seedless guava is scarce. The aim of current study were to evaluate the effect of temperature and sucrose solution concentration on mass transfer during osmosis process and to assess the predictive capacity of Peleg, Azuara and Page's equations during osmotic dehydration of seedless guava.

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Materials and Methods

Preparation of seedless guava samples

Fresh seedless guava (*Psidium guajava* L.) fruits were obtained daily from a local market (Serdang, Malaysia). Guavas selected at commercial maturity according to their similarity of color, size, absence of surface defects and ripening grade (around 8 °Brix). Before each experiment fruits were washed and peeled. Cube-shaped guavas (20 ± 2 mm³) were obtained manually by very sharp stainless steel knife, and then gently blotted with tissue paper to remove the excess of surface humidity. Guava cubes with the same size were selected to minimize the effect of sample size on the collected data. The dimensions of fruit cubes were measured by Mitutoyo digital caliper (± 0.02 mm) (Mitutoyo, Waterbury, CT, USA).

Osmotic dehydration procedure

Commercial grade sucrose mixed with required amount of distilled water to give desired concentration of osmotic solution. The sucrose solution concentrations were 30, 40 and 50% (w/w). The sucrose solution concentration was checked by refractometer (Atago-Master-20 M, Japan). Osmotic treatments were performed in temperature range of 30-50°C using a circulating water bath (Memmert, WNE14, Memmert GmbH Co. KG, Germany). The temperature verification was done using a digital thermometer (Ellab CTD-85, Ellab, Denmark) equipped with type T constantan needle thermocouple (1.2 mm diameter). The ratio of sample to sucrose solution was always set at 1:10 (w/w). At determined times (15, 30, 45, 60, 90, 120, 150, 180 and 240 min), the guava cubes were removed from the osmotic solutions, rinsed quickly with distilled water (below 30s) to eliminate the solution adhered to the surface and carefully blotted with tissue paper to remove the excess surface water. The experiments were repeated thrice and the average (\pm SD) values are reported.

Kinetics parameters Determination

The fresh and dehydrated seedless guava cubes after each contact times were placed in oven (Heraeus Vacutherm VT6025, Germany) at 105°C until constant weight (24 h) in order to measure the moisture and solids content according to AOAC method No. 931.04 (AOAC, 1990). In order to determine mass change, all samples were weighed with accuracy of ± 0.0001 g before and after treatment using an analytical balance (Mettler AJ 150, Switzerland). The following equations were applied to evaluate solid gain (SG) and water loss (WL) (Panagiotou *et al.*, 1999).

$$WL \left(\frac{g}{g} \right) = \frac{(M_0 - m_0) - (M_t - m_t)}{M_0} \quad (1)$$

$$SG \left(\frac{g}{g} \right) = \frac{m_t - m_0}{M_0} \quad (2)$$

Where M is sample mass (g) and m is sample dry mass (g). Subscripts 0 and t represent values at initial and each sampling time, respectively.

Peleg's equation

Peleg (1988) suggested a two parameter equation to explain moisture sorption kinetics which approaches equilibrium asymptotically. Eq. (3) presents the adaptation of this equation for this study:

$$X = X_0 \pm \frac{t}{K_1 + K_2 t} \quad (3)$$

Where X is dependent variable at time t, X₀ is initial dependent variable.

Dehydration rate at the very beginning of the process ($t = t_0$) explained by Peleg rate constant or K₁:

$$\frac{dX}{dt} = \pm \frac{1}{K_1} \quad (4)$$

The relationship between equilibrium content (X_e) as $t \rightarrow \infty$ and the Peleg capacity constant or K₂ is given by Eq. (5):

$$X_e = X_0 \pm \frac{1}{K_2} \quad (5)$$

Azuara's equation

Azuara (1992) proposed a mass balance-based equation as Eq. (6):

$$XG = XG^\infty - XG^* \quad (6)$$

Where XG* is the mass of solid or water that did not enter (or leave) the sample after an elapsed time t, XG[∞] is the concentration after long immersion times. As XG increases and XG* decreases during the immersion time, these variables can be interrelated by a parameter K, i.e. $XG = KXG^*$. The K parameter depends on the immersion time (t) and on the rate of mass transfer (water or solid), as given by Eq. (7).

$$XG^* = \frac{XG}{Kt} \quad (7)$$

The substitution of Eq. (6) into the Eq. (7) leads to an equation that could be used for predicting the mass transfer during immersion time (Eq. (8)).

$$XG = (8) \frac{K.tXG^\infty}{(1 + K.t)} \quad (8)$$

Page's equation

Page (1949) suggested a useful modified empirical equation (Eq. (9)) based on simple exponential model which was used to fit the experimental dehydration data.

$$W_{W or s} = \frac{MC(t) - MC_{eq}}{MC_0 - MC_{eq}} = \exp(-Kt^n) \quad (9)$$

In which, K is the dehydration constant, n is the Page's parameters and t is the process time (min).

Experimental design and statistical analysis

The experimental design applied was a 3 × 3 × 9 factorial design in a frame of Complete Randomized Design (CRD), corresponding to the three solution concentrations, three temperatures and nine immersion time intervals. Statistical significance (p<0.05) was analysed through analysis of variance (ANOVA) using Minitab v.14 (Minitab Inc. State College, PA, USA). Non-Linear regression using Levenberg-Marquardt method was used to fitting database to different models by using the STATISTICA 6.0 software (StatSoft, Inc., USA). The criteria for characterizing the fitting to the model were the determination coefficient (R²), the root mean square error (RMSE) and the mean relative percentage deviation modulus (E). These parameters can be calculated as follows:

$$RMSE = \frac{1}{n} \left[\sum_{i=1}^n (V_{exp} - V_{pre})^2 \right]^{0.5} \quad (10)$$

$$E(\%) = \frac{100}{n} \sum_{i=1}^n \frac{|V_{exp} - V_{pre}|}{V_{exp}} \quad (11)$$

Where V_{exp} and V_{pre} are the experimental and predicted values, respectively, n is the number of experimental data. According to Deng and Zhao (2008) a model with E value below than 10% is considered acceptable. Therefore, the best model should follow the highest coefficient of correlation (R²), the least RMSE and E values as criteria.

Results and Discussions

Figures 1–2 show the evolution of solid and water contents during osmotic treatments. As expected, SG and WL increased with immersion time. From the data in figures 1-2, a clear trend of a high initial rate of SG and WL, and subsequent slower gain/loss is apparent. Similar curves for different osmotically dehydrated foods have been published (Eren and Kaymak-Ertekin, 2007; Schmidt *et al.*, 2009; Corrêa *et al.*, 2010). Previous research findings revealed

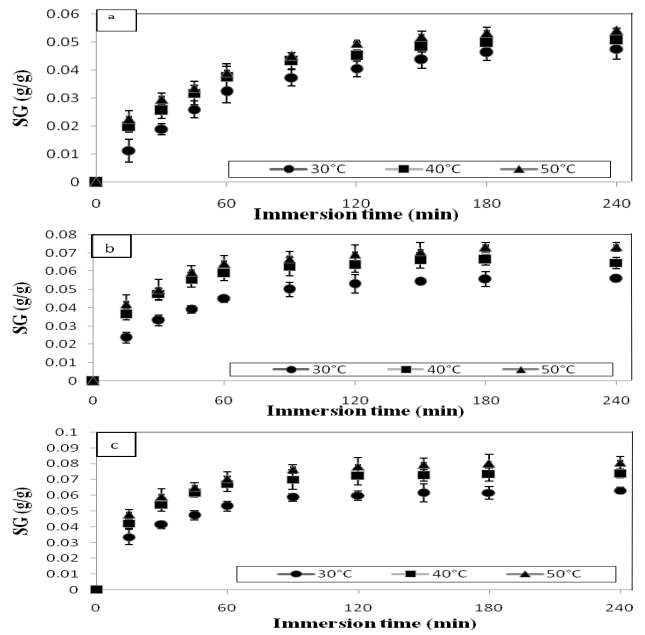


Figure 1. Experimental SG during osmotic dehydration of seedless guava at different sucrose concentrations: 30% (a), 40% (b), 50% (c) and temperatures

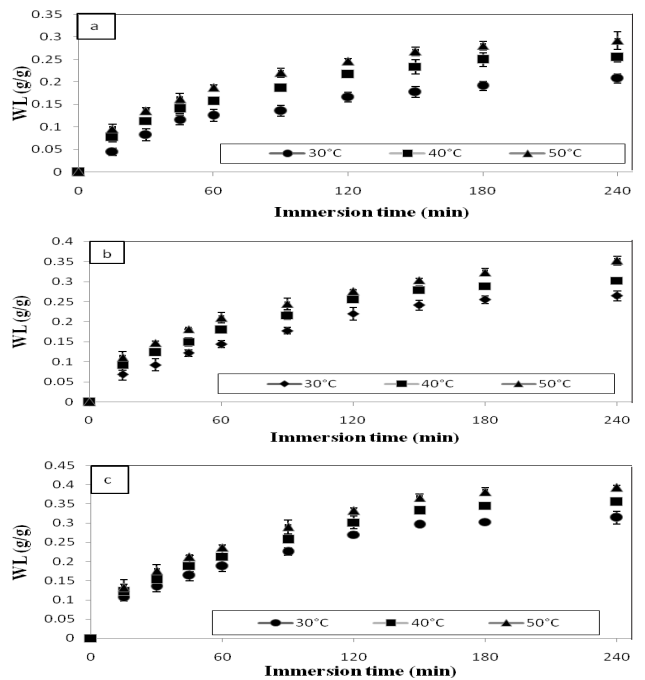


Figure 2. Experimental WL during osmotic dehydration of seedless guava at different sucrose concentrations: 30% (a), 40% (b), 50% (c) and temperatures

higher amount of WL and SG in more concentrated solutions due to the greater osmotic pressure gradients (Ito *et al.*, 2007; Ispir and Togrul, 2009). According to Antonio *et al.* (2008), a relationship exists between great gradient of osmotic pressure and loss of plasmatic cell membrane functionality which allows easier entrance of solute into the cells. High temperatures of osmotic media also cause accelerated mass transfer as shown in Figures 1–2. This behavior was more pronounced in the most concentrated

solutions. Increase in kinetics of mass transfer at high temperatures can be attributed to diffusion rate enhancement due to swelling and plasticizing of cell membranes and better water transfer characteristics on the product surface as a result of lower viscosity of the osmotic solution (Uddin *et al.*, 2004; Singh *et al.*, 2007). In several studies, it has been concluded that cells membrane destruction at higher temperature lead to higher solid uptake by plant-based materials during osmosis treatment (Le Maguer, 1988; Sachetti *et al.*, 2001; Corzo and Bracho, 2006; Tortoe *et al.*, 2007; Corrêa *et al.*, 2010).

Peleg, Azuara and Page's equations were used to evaluate osmotic dehydration kinetics of seedless guava cubes. Table 1 presents Peleg parameters under different experimental conditions. The k_1 parameter of the Peleg's model decreased with solution concentration and temperature elevation suggesting that initial rate of mass transfer increased. ANOVA results revealed that the value of initial mass transfer coefficients for SG and WL rely on the solution concentration and temperature significantly ($p < 0.05$). The parameter k_2 describes the rate of SG and WL at the equilibrium stage of osmotic dehydration process. A significant ($p < 0.05$) relationship between k_2 and solution concentration observed, i.e., the higher osmotic concentration caused lower values of k_2 for SG and WL.

Azuara's equation parameter obtained for SG and WL are shown in Table 2. In Eq. (8), K represents the required time for diffusion of half of water or solid out/into the product, respectively. Similar trend was observed for Azuara's equation parameter (K) for SG as the k_1 parameter which decreased with the increase of concentration and temperature ($p < 0.05$) whereas for WL the K parameter did not follow a clear pattern with sucrose concentration and temperature ($p > 0.05$).

Table 3 presents Page's parameters calculated for SG and WL under different experimental conditions. Its results of SG revealed that parameter K decreased with solution concentration and temperature whereas parameter n did not show a clear pattern with temperature. In the case of WL, parameter K did not show any trend with solution concentration and temperature, while parameter n increased at higher concentrations and temperature. Similar findings were published on page model by Azoubel and Murr (2004) and Vega-Gálvez *et al.* (2009).

The criteria which were used for qualification of the goodness of fit (R^2 , RMSE and E) revealed the adequacy of Peleg model to predict the values of SG and WL under different experimental conditions due to high values of R^2 and small values of RMSE and E (Table 1-3).

Table 1. Peleg's parameters and goodness of fit for mass transfer during osmotic dehydration

Conc. (% w/w)	Temp. (°C)	SG					WL				
		k_1	k_2	R^2	RMSE	E (%)	k_1	k_2	R^2	RMSE	E (%)
30	30	939.09±78.39	16.32±0.43	0.99	0.0003	2.91	257.49±43.08	3.85±0.22	0.97	0.002	3.96
	40	612.48±55.74	17.06±0.44	0.99	0.0002	2.50	187.09±20.62	3.17±0.11	0.98	0.001	3.12
	50	549.78±61.67	16.23±0.52	0.99	0.0004	3.21	148.96±20.92	2.87±0.12	0.98	0.001	3.03
40	30	412.23±78.88	15.74±0.84	0.96	0.0002	1.71	255.53±29.61	2.67±0.13	0.98	0.002	4.87
	40	191.58±53.63	14.06±1.05	0.99	0.0003	1.76	183.64±19.35	2.56±0.09	0.98	0.002	4.33
	50	180.86±29.94	12.89±0.57	0.97	0.0004	1.81	154.24±14.90	2.37±0.07	0.99	0.003	3.88
50	30	258.09±53.49	14.73±0.84	0.95	0.0004	2.25	166.55±18.42	2.53±0.42	0.98	0.003	5.20
	40	162.56±26.39	12.61±0.54	0.97	0.0003	1.25	145.27±15.22	2.26±0.07	0.98	0.003	4.84
	50	148.43±27.85	11.67±0.58	0.96	0.0003	1.35	125.27±15.88	2.06±0.08	0.98	0.003	4.42

Table 2. Azuara's parameters and goodness of fit for mass transfer during osmotic dehydration

Conc. (% w/w)	Temp. (°C)	SG				WL			
		K	R^2	RMSE	E (%)	K	R^2	RMSE	E (%)
30	30	0.016±0.001	0.98	0.0003	3.19	0.015±0.001	0.97	0.0020	3.94
	40	0.028±0.002	0.99	0.0003	3.10	0.017±0.001	0.98	0.0019	3.39
	50	0.030±0.002	0.97	0.0004	3.34	0.020±0.001	0.96	0.0020	3.36
40	30	0.038±0.001	0.99	0.0002	1.72	0.011±0.001	0.96	0.0025	5.19
	40	0.073±0.005	0.99	0.0004	1.76	0.015±0.001	0.97	0.0029	4.77
	50	0.071±0.005	0.98	0.0004	1.81	0.012±0.002	0.90	0.0044	6.12
50	30	0.057±0.004	0.97	0.0004	2.26	0.016±0.002	0.96	0.0039	5.69
	40	0.077±0.004	0.98	0.0003	1.26	0.017±0.003	0.95	0.0036	4.33
	50	0.078±0.004	0.97	0.0003	1.36	0.016±0.001	0.96	0.0034	5.23

Table 3. Page's parameters and goodness of fit for mass transfer during osmotic dehydration

Conc. (% w/w)	Temp. (°C)	SG					WL				
		K	n	R^2	RMSE	E (%)	K	n	R^2	RMSE	E (%)
30	30	5.92±0.31	0.12±0.01	0.97	0.0003	8.35	5.34±0.31	0.22±0.01	0.95	0.0021	5.62
	40	5.02±0.18	0.09±0.00	0.98	0.0005	4.72	4.83±0.20	0.23±0.00	0.96	0.0007	2.08
	50	4.86±0.14	0.09±0.00	0.98	0.0004	3.57	4.52±0.14	0.24±0.00	0.95	0.0006	1.45
40	30	4.56±0.19	0.08±0.00	0.96	0.0007	5.55	6.10±0.42	0.28±0.01	0.96	0.0019	5.29
	40	3.75±0.16	0.06±0.00	0.93	0.0009	5.37	5.25±0.31	0.27±0.01	0.96	0.0019	4.08
	50	3.70±0.12	0.06±0.00	0.96	0.0007	3.91	4.93±0.16	0.28±0.00	0.99	0.0014	2.29
50	30	4.03±0.13	0.07±0.00	0.96	0.0006	4.19	4.93±0.35	0.27±0.01	0.97	0.0024	4.78
	40	3.60±0.14	0.06±0.00	0.94	0.0010	4.81	4.93±0.35	0.29±0.01	0.97	0.0026	4.65
	50	3.52±0.11	0.06±0.00	0.96	0.0007	3.44	4.93±0.32	0.30±0.01	0.95	0.0024	3.79

Conclusion

The effects of concentration and temperature on mass transfer kinetics were investigated in terms of SG and WL. The results of this investigation revealed the existence of a relationship between the rate of SG and WL and independent process variables (concentration and temperature). Among different applied equations, Peleg's model showed the best adjustment of the experimental data. Peleg's parameters k_1 and k_2 for SG were from 939.09 ± 78.39 to 148.43 ± 27.85 and from 16.32 ± 0.43 to 11.67 ± 0.58 , respectively, and for WL varied from 257.49 ± 43.08 to 125.27 ± 15.88 and 3.85 ± 0.22 to 2.06 ± 0.08 , respectively. Therefore, the SG and WL of seedless guava at any sucrose solution concentration and temperature could be estimated sufficiently using the Peleg equation and consequently it can be used as a useful tool in the design and control of the corresponding industrial operation.

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