ABSTRACT

The aim of this work was proposing a simple mathematical model to predict water loss and solute gain during osmotic process. The specific objective was the development of a correlation between dehydration/impregnation rates with effective diffusivity. The applicability of the model was evaluated using orange-fleshed muskmelons. Results from proposed model showed low dispersion (the mean relative error under 10% and $r^2$-values near 1.0), with a good fitting capability for kinetics of WL and SG. Diffusivity values were obtained as a function of temperature and solution concentration in the range of variables studied, varying from $1.11 \times 10^{-10}$ to $2.25 \times 10^{-10}$ m$^2$ s$^{-1}$ for WL and $1.10 \times 2.27 \times 10^{-10}$ m$^2$ s$^{-1}$ for SG, respectively. The values of the half-life were higher in higher mass transfer potential conditions (higher temperature and solution concentration), showing the relationship between dehydration and solid uptake rates and mass transfer potential. The half-life predicted values showed no significant differences for WL and mainly for SG. The proposed model allowed defining criteria for time process establishment for dehydration or impregnation. Also, it allows the establishment of a correlation between mass transfer rates and effective diffusivity and was more accurate than the diffusive model, mainly at the beginning of the process.

Keywords: water loss; solids gain; osmotic dehydration; diffusive and empirical model

INTRODUCTION

Osmotic dehydration (OD) is known as a partial dehydration process. It consists in water removal and solid uptake by food immersion in a hypertonic solution of sugar or salt for a specified period of time. The mass transfer rate during OD depends upon factors such as: temperature and concentration of solution, size and geometry of the solid, solution to solid mass ratio and degree of agitation. There is a lot of published information describing the influence of these variables on mass transfer rates. Considerable effort has been made toward developing models to predict the mass transfer kinetics of OD [1-4]. But it is difficult to developing mathematical models capable to consider adequately all variables involved in the process and their influence.

Due to the simplifications involved in solving the diffusion equation for a food subjected to osmotic process, the Fickian diffusion model becomes an empirical equation, despite its theoretical basis. Their analytical solutions for classical geometries allow obtaining diffusion coefficient, that should be used very carefully [2]. Therefore empirical models are important, notably for non-classical geometries, whose solutions of the diffusion coefficients involve numerical methods. Numerous empirical models without these restrictions have been reported for describing mass transfer during OD of food products [1,3-4].

Some authors have used statistical tools to study process variables, such as Response Surface Methodology (RSM) [5-6]. However, information about the process kinetics is omitted in this type of approach and moreover the process time could mask the effect of other process variables. Some efforts have been made to overcome these limitations [7-8]. Nevertheless, it is still difficult to define adequately the processing time.

The aim of this work was to propose a simple mathematical model to predict the water losses and solute gain during osmotic process. The specific objective was the development of a correlation between dehydration/impregnation rates with effective diffusivity. The applicability of the model was evaluated for orange-fleshed muskmelons osmotically dehydrated in corn syrup solutions.
MATERIAL & METHODS

Samples
Fresh muskmelons were obtained from a local market, sorted visually for size (14-16 cm diameter), weight (1800-2000 g), maturity level (9–11 °Brix) and physical damage. The product was sanitized and stored under refrigeration until used. After peeling, the fruits were cut into slices (30 x 40 and 5 mm) using an inox (AISI-306) cutter designed for this purpose.

Osmotic dehydration treatment
The samples were subjected to osmotic process for 30, 60, 90, 120, 180, 240, 360, 600 and 1440 minutes for each temperature (28–42°C) and solute concentration (38.7–61.3%w/w) conditions, given by central composite experimental design (Table 1), agitation (80 rpm) and weight ratio of sample to solution (1:10) kept constant. Water loss ($WL$) (g water/100g initial wet sample) and solids gain ($SG$) (g solids/100g initial wet sample) were determined by gravimetric method.

\[
WL = \frac{w_{w0} - (w_1 - w_s)}{w_0} \times 100
\]

\[
SG = \frac{w_{s} - w_{s0}}{w_0} \times 100
\]

Kinetic models
Data relative to mass transfer parameters were fitted using the equation proposed by Peleg [4] modified in the present work, in order to compare itself to the diffusion model.

Peleg’s model: Peleg [4] proposed a two-parameter, non-exponential, empirical equation to describe the kinetics of moisture sorption that approaches equilibrium asymptotically.

\[
x(t) = x_0 \pm \frac{t}{k_1 + k_2t}
\]

where $x(t)$ is amount (in grams) of solids or water at time $t$ and $x_0$ represents the initial amount. $k_1$ and $k_2$ are the original Peleg’s original parameters. In the Eq. (3), “±” becomes “−” if the process is impregnation and “+” if the process is dehydration. Relating Eq. (3) to equations (1) and (2), the Peleg’s model can be rewritten to describe $WL$ and $SG$ (Eq. 4).

\[
X(t) = \frac{t}{K_1 + K_2t}
\]

$X(t)$ represents $WL$ or $SG$. At $t\to\infty$, the reciprocal value of $K_2$ provides $X(t)$ at equilibrium ($X_\infty$) as follow.

\[
X_\infty = \lim_{t\to\infty} \left( \frac{t}{K_1 + K_2t} \right) = \frac{1}{K_2}
\]

The reciprocal value of Peleg rate constant ($K_i$) is related to the drying rate at the very beginning (i.e. $t=0$), according equation (6):

\[
\frac{dX(t)}{dt} \bigg|_{t=0} = \frac{1}{K_1}
\]

Thus a relationship between $K_1$ and the driving force of the process can be suggested. The half-life for dehydration/impregnation rate ($t_{1/2}$) can be expressed as follow:

\[
\frac{dX(t)}{dt} \bigg|_{t=t_{1/2}} = \frac{1}{2} \frac{dX(t)}{dt} \bigg|_{t=0}
\]

Thus, substituting equations (4) and (6) into equation (7), we obtain:

\[
t_{1/2} = \frac{K_1}{K_2} \left( \sqrt{2} - 1 \right)
\]

So, $t_{1/2}$ represents the ratio between $X_\infty$ and the initial rate, according to Eqs. (5-7). Based on Fick’s second law, Crank proposed an equation for diffusion in one dimension in a flat sheet in contact with an infinite amount of solution, considering transient regime and short periods of time, which can be expressed as a simplified equation of the type [9]:

\[
\frac{X(t)}{X_\infty} = 2 \sqrt{\frac{D(t) \pi L^2}{\pi L^2}}
\]
where \( D(t) \) is the instantaneous effective diffusion coefficient. Relating Eq. (8) with equations (4-5) and substituting into equation (9), a simple expression is obtained from which \( D(t) \) can be easily calculated at different times.

\[
D(t) = \frac{\pi}{4} \left( \frac{L}{t_{1/2}} \right)^2 \frac{1}{ \left( \frac{\sqrt{2}}{1} + t \right) }^2
\]  
(10)

This correlation gives to Peleg’s model a physical meaning since \( t_{1/2} \) represents the ratio between the constants of Peleg’s model. Finally, from Eq. (10) into Eq. (9):

\[
\frac{X(t)}{X_\infty} = \left[ \frac{t_{1/2}}{t(\sqrt{2} - 1)} + 1 \right]^{-1}
\]  
(11)

Diffusive model: For an infinite plane sheet (2L thickness) with uniform initial concentration, symmetry of concentration and constant concentration at the surface, the mathematical solution for the Fick’s second law of diffusion is given by Eq. (12) [9]:

\[
X(t) = X_0 \exp \left[ \frac{-(2n + 1)^2 \pi^2 D_{ef} t}{4L^2} \right]
\]  
(12)

where \( D_{ef} \) is the effective diffusion coefficient.

Statistical Analysis: A first-order central composite rotatable design was used for designing the experiments for osmotic dehydration of muskmelon slices using two factors: corn syrup concentration (38.7 to 61.3\% w/w) and temperature (28 to 42 °C), and seven triplicate combinations were performed, including three replications at the centre points (Table 1). Data from the central composite experimental design were subjected to the following first-order polynomial regression analysis using least square regression methodology to obtain the parameters of the mathematical models [10].

\[
Y = b_0 + b_1C + b_2T + b_{12}C \cdot T
\]  
(13)

Where: \( Y \) represents the response variables, \( b_0 \) is the intercept, \( b_1 \) and \( b_2 \) represent the salt concentration and temperature linear regression coefficients, respectively. And \( b_{12} \) represents the interaction effect. For statistical calculations, the variables \( C \) (corn syrup concentration) and \( T \) (temperature) were coded (Table 1) as \( x_i \) according the following equation.

\[
x_i = \frac{X_i - X_0}{\delta X}
\]  
(14)

where \( x_i \) is the dimensionless coded value of the variable \( X_i \) (C or T); \( X_0 \) the value of the \( X_i \) at the central point; \( \delta X \) is the step of unit level change at the centre point.

These coefficients, analysis of variance (ANOVA), test of lack of fit and the generation of two and three-dimensional graphs were calculated using the Statistica 5.0 software (Statsoft, 1997).

The criterion used to evaluate the best fitting model was their average relative error (\( P \)), defined as:

\[
P(\%) = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{Y - \bar{Y}}{Y} \right|
\]  
(15)

where \( Y \) and \( \bar{Y} \) are experimental and predicted values, respectively. \( n \) represents the number of experimental points. Values of \( P \) less than or equal to 10\% are considered to fit the experimental data satisfactorily.

RESULTS & DISCUSSION

Tables 1 and 2 show the kinetics parameter results for water loss and solids gain, respectively, for all experimental conditions predicted by Eqs. (5), (6), (8) and (12). Both models showed low dispersion (\( P \) values under 10\% and \( R^2 \)-values near 1.0), showing a good fitting capability for WL and SG (Fig. 1). The model also described mass transfer kinetics at different temperature and concentration conditions.

The observed difference between half-life for WL and SG was due to the fact that the upcoming solids during osmosis take place mostly between the extracellular space and not through the selective cell membrane as observed for water fluxes [11].

The data shown in Tables 1 and 2 into Eq. (10) provide \( D(t) \) values ranging 1.11-2.25x10^{-10} \text{ m}^2\text{s}^{-1} \) for WL and 1.10-2.27x10^{-10} \text{ m}^2\text{s}^{-1} \) for SG, respectively. Similar ranges were obtained for diffusion model.
In Figs. (2.a) and (2.b) is shown that the pattern of the curve changes with the variation of the $t_{1/2}$ for some experimental conditions of water loss (trials X2, X3 and X4, according Table 1). It can be observed that the proposed model is more accurate relative to diffusive model, mainly at the beginning of the process. Furthermore, it has the advantage of allowing the calculation of the equilibrium values satisfactorily. The lower fitting capacity of diffusive model relative to the other models has been reported by several authors [2-4]. It is possible that other phenomena besides diffusion are occurring during the osmotic process, or the assumptions made to obtain diffusive model are not fulfilled, especially in high viscosity solutions when high solids concentration was used.

**Table 1.** Experimental design matrix and mass transfer kinetics parameters for water loss (WL)

<table>
<thead>
<tr>
<th>Ind. Variables</th>
<th>Peleg modified model</th>
<th>Fickian model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
<td>C(%p/p)</td>
<td>T(ºC)</td>
</tr>
<tr>
<td>X1</td>
<td>38.7</td>
<td>28</td>
</tr>
<tr>
<td>X2</td>
<td>61.3</td>
<td>28</td>
</tr>
<tr>
<td>X3</td>
<td>38.7</td>
<td>42</td>
</tr>
<tr>
<td>X4</td>
<td>61.3</td>
<td>42</td>
</tr>
<tr>
<td>X5</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>X6</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>X7</td>
<td>50</td>
<td>35</td>
</tr>
</tbody>
</table>

*initial rate, $^a$at 1440 minutes of process, $^b$D$_{eff}$ x 10$^{-10}$

**Table 2.** Experimental design matrix and mass transfer kinetics parameters for solids gain (SG)

<table>
<thead>
<tr>
<th>Ind. Variables</th>
<th>Peleg modified model</th>
<th>Fickian model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
<td>C(%p/p)</td>
<td>T(ºC)</td>
</tr>
<tr>
<td>X1</td>
<td>38.7</td>
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</tr>
<tr>
<td>X2</td>
<td>61.3</td>
<td>28</td>
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<tr>
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<td>35</td>
</tr>
<tr>
<td>X6</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>X7</td>
<td>50</td>
<td>35</td>
</tr>
</tbody>
</table>

*initial rate, $^a$at 1440 minutes of process, $^b$D$_{eff}$ x 10$^{-10}$

**Figure 1.** Fitting capability of the diffusive (a) and proposed (b) models for WL(■) and SG(▲) kinetics.

Different experimental conditions (X3 and X4) exhibited similar values of $t_{1/2}$ (Table 1), as shown in Fig. (2b). The $t_{1/2}$ parameter gives a measure of the ratio of variable value at equilibrium ($X_\infty$) to its rate at beginning of the process ($dX(t)/dt|_{t=0}$). Consequently, it quantifies the relative importance of these two types of parameters for given experimental conditions. Above, X4 condition exhibited higher values of $t_{1/2}$, i.e. the higher driving force than X3 condition for WL.

For SG, at high corn syrup concentration (X4), higher values of $t_{1/2}$ were observed, while the initial rate was lower than the observed at low concentration and at the same temperature (X3), indicating that other variables have influenced on solid mass transfer, besides solution viscosity.
The values of the half-life were higher for highest mass transfer potential conditions (higher temperature and solution concentration), showing the relationship between dehydration and solid uptake rates and mass transfer potential. The predicted values at the half-life \(X(t_{1/2})\) showed no significant difference for WL and mainly for solids uptake (Table 3).

![Figure 2. Kinetics of water loss during osmotic dehydration of orange-fleshed muskmelons in corn syrup solutions.](image)

**Analysis of Variables Influence on** \(t_{1/2}\), \(dX(t)/dt|_{t=0}\) and \(X(t_{1/2})\) **for** WL and SG **Regression coefficients for the coded first order equations were tested by adequacy and fitness by analysis of variance (Table 3). For** WL, **all coefficients were significant (p<0.05) for all models, except for** WL\( (t_{1/2}) \). **High correlation coefficients were obtained for** WL’s models, whereas for SG, **a poor correlation for** \(t_{1/2}\) was obtained and the models for initial rate and solids gain at the half-life were not predictive. Therefore, temperature and solution concentration showed no significant influence on solid uptake rates at the beginning of the process. For WL at the half-life, the concentration was the only significant factor, providing a simple linear relationship. An interaction among variables for SG’s half-life was observed, meaning that concentration and solution temperature showed synergistic effect on this response.**

**Table 3.** Coded regression coefficients and analysis of variance (ANOVA) for half-life \( (t_{1/2}) \), initial rate \( (dX(t)/dt|_{t=0}) \) and \( X(t_{1/2}) \) for WL and SG kinetics during osmotic dehydration of orange-fleshed muskmelon

<table>
<thead>
<tr>
<th>Coded models</th>
<th>WL</th>
<th>SG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficients</td>
<td>(t_{1/2}(\text{min}))</td>
<td>(K_{1/2}^{-1}(\text{min}^{-1}))</td>
</tr>
<tr>
<td>(b_0)</td>
<td>43.73</td>
<td>0.618</td>
</tr>
<tr>
<td>(b_1)</td>
<td>6.55</td>
<td>0.106</td>
</tr>
<tr>
<td>(b_2)</td>
<td>-13.25</td>
<td>0.167</td>
</tr>
<tr>
<td>(b_{12})</td>
<td>-6.30</td>
<td>0.106</td>
</tr>
<tr>
<td>(F_{\text{calc}})</td>
<td>63.7</td>
<td>124.5</td>
</tr>
<tr>
<td>(F_{\text{tab}})</td>
<td>9.3</td>
<td>9.3</td>
</tr>
<tr>
<td>(P(%))</td>
<td>2.87</td>
<td>1.58</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.985</td>
<td>0.992</td>
</tr>
</tbody>
</table>

n.s non-significant (p>0.05). *Initial rate \( (dX(t)/dt|_{t=0}) \)

The variation in half-life values (higher for SG) occurred around a mean value, providing a range of processing time (30 to 70 minutes) in which the potential transfer reduction is similar, regardless the type (dehydration or impregnation) and conditions of process. In some researches, osmotic dehydration process times were higher than 120 minutes [8,12] and an important observation to be considered in these cases is solids amounts incorporated to the fruit during the osmotic dehydration. If for quality reasons, the fruits amount of sugars has to be enhanced, the period of time that the fruit should stay in the osmotic solution needs to be higher. Alternatively, if the process focus is on minimal solids uptake and cost reduction the period of time has to be as short as possible. Fig. 3 presents the models for \(t_{1/2}\) for WL (a) and SG (b) during osmotic dehydration of orange-fleshed muskmelons. It is important to remark that these models have a limited validity within the experimental range which their coefficients were obtained. For WL, higher process temperatures seemed to promote faster
water loss (i.e. low effect on $t_{1/2}$), causing swelling and plasticizing cell membranes and a faster water diffusion within the product and improved mass transfer characteristics on the surface can be observed, due to lower viscosity of the osmotic medium [2-3,11-12].

For SG, an increase in the $t_{1/2}$ was observed with increase on concentration, when higher temperatures were used. However at low temperature, $t_{1/2}$ values sharply decreased as concentration increased. It's important to highlight that SG and WL are countercurrent flows, and conditions that accelerate dehydration can slow down impregnation process, particularly at the beginning.

**Figure 3.** Response surfaces for $t_{1/2}$ for WL (a) and SG (b) as a function of temperature and concentration in corn syrup solutions during osmotic dehydration of orange-fleshed muskmelon.

**CONCLUSION**

The proposed model was able to predict the kinetics of osmotic dehydration and the WL and SG values at equilibrium. A correlation between rates of dehydration/impregnation process and effective diffusivities during osmotic dehydration of orange-fleshed muskmelon was obtained.

**REFERENCES**


