Mathematical modeling for the annatto (*Bixa orellana* L.) seed drying process

Dyego da Costa Santos1*, Alexandre José de Melo Queiroz1, Rossana Maria Feitosa de Figueirêdo1, and Emanuel Neto Alves de Oliveira1

The pigment extraction process using annatto (*Bixa orellana* L.) seed produces a large amount of seed waste. Although most of these seeds are discarded, a number of studies report promising results with their use in animal feed. The good fiber content also suggests human nutrition applications, with possible incorporation in dietary foods. In the present study, annatto seeds derived from color extraction were dried, with and without the layer of oil left over from the process. Seeds were dried at 40, 50, 60 and 70 °C. Drying data were fitted to the Diffusion Approximation, Two Term, Midilli, Page and Thompson models. Drying was carried out up to a moisture content of approximately 5% wet basis. All the models studied exhibited adequate fit to the drying kinetics data of the annatto seeds, with coefficients of determination above 0.98 and root mean squared error (RMSE) below 1.0. Seeds with oil had longer drying times at 40 and 50 °C and shorter times at 60 and 70 °C. The coefficients of diffusion showed values between $2.67 \times 10^{-11}$ and $9.50 \times 10^{-11}$ m$^2$ s$^{-1}$, while activation energies for liquid diffusions were 38.04 and 23.52 kJ mol$^{-1}$, for residual seed drying with and without oil, respectively.

**Key words:** Agricultural waste, *Bixa orellana*, drying.

**INTRODUCTION**

The *Bixa orellana* L. is a perennial tree of the family Bixaceae originally from tropical America. It is cultivated in several regions of Brazil and is popularly known as annatto. The fruits of this tree are abundant, with coloring ranging from yellow to dark red, in the form of capsules ovoid covered with long flexible spines and presenting 60-70 seeds inside (Kruppa et al., 2012). Annatto is very important for socioeconomic development in Northeastern Brazil, since 78.2% of its cultivation originates on family farms, under dryland conditions, with reduced costs compared to other cultivation methods (Anselmo et al., 2008).

The main product is the seed, whose coat is rich in bixin, a carotenoid coloring of wide interest in national and international markets. This interest, primarily in the food industry, is due to consumer demand for artificial coloring substitutes (Corlett et al., 2007; Santos et al., 2012). A large amount of seeds is produced by the pigment extraction process. Silva et al. (2006) report that annatto seed waste has a bright red color and an external layer of soy oil, used as a vehicle to dilute bixin. According to Rêgo et al. (2010), approximately 2500 t of annatto subproduct are obtained in Brazil every year, mainly in the Northeast, where almost 97% of the subproduct is not reused.

A number of studies have been conducted using annatto seeds in animal feed (Silva et al., 2006; Ofosu et al., 2010; Rêgo et al., 2010). However, future research should be directed towards better reuse of these seeds, such as incorporating them into human food.

Drying is the most widely used commercial process to preserve foods because, compared to other long-term preservation methods, it is less costly and easier to operate (Alexandre et al., 2009). According to Martinazzo et al. (2010), drying consists of removing a large portion of the water initially contained in the product immediately after maturity, up to the maximum moisture content in which it can be stored for long periods, without significant loss of quality. The literature contains a number of studies on drying fresh annatto seeds (Guedes and Faria, 2000; Faria and Rocha, 2000); however, there are none on drying seeds derived from the color extraction industry.

Thus, the aim of the present study was to dry annatto seeds, with and without oil from the pigment extraction process, fit different mathematical models to experimental data, and determine the coefficients of diffusion and activation energies, under experimental conditions.

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MATERIAL AND METHODS

Anatto seeds, donated by the Marata food company located in the state of Sergipe, Brazil, were used (bulk density of 725.6 kg m⁻³). Seeds were steeped in soy oil used in the pigment extraction process. Seeds were processed in two ways, as follows: in the first, seeds were maintained with a layer of oil (Treatment 1), and in the second, the oil layer was removed by washing the seeds with a mixture of water and commercial detergent (Treatment 2).

The drying experiments were carried out in a completely randomized design with four replicates, each replicate with approximately 15 g of sample. To determine drying kinetics in thin layer, samples were weighed and dried in a forced-air circulation (Fanem, model 330) oven at 40, 50, 60, and 70 °C and air drying speed of approximately 1 m s⁻¹, with drying air in the horizontal direction; moisture loss was monitored until moisture content of the samples reached approximately 5% wet basis (wb) (5.26% dry basis [db]).

Moisture ratios (MR) were calculated from weight loss data of the samples during drying. Equation [1] was used to calculate the moisture ratio:

\[
MR = \frac{X - X_e}{X_i - X_e}
\]

where \(MR\) is moisture ratio (dimensionless), \(X\) is moisture content at any time \(t\) (db), \(X_i\) is initial moisture content (db), and \(X_e\) is equilibrium moisture content (db).

The Diffusion Approximation, Two Terms, Midilli, Page and Thompson mathematical models were fit to experimental data obtained in the drying process. Where \(t\) is drying time (min), \(k\) is constant of drying (min⁻¹), \(a, b, n\) and \(q\) are models coefficients:

Diffusion Approach \(MR = a \exp(-k.t) + (1-a) \exp(-k.b.t)\) (Akpinar et al., 2008)

Two Term \(MR = a \exp(-k.t) + b \exp(-q.t)\) (Jittanit, 2011)

Midilli \(MR = a \exp(-k.t^n) + b.t\) (Midilli et al., 2002)

Page \(MR = \exp(-k.t^n)\) (Roberts et al., 2008)

Thompson \(MR = \exp((-a-(a^2 + 4.b.t)^{0.5})/2.b)\) (Botelho et al., 2011)

The coefficient of determination \(R^2\) and root mean squared error (RMSE) were used as criteria to assess the fit of mathematical models to experimental data, according to Equation [7]:

\[
RMSE = \left(\frac{1}{n} \sum_{i=1}^{n} (MR_{pred,i} - MR_{exp,i})^2\right)^{1/2}
\]

where RMSE is dimensionless, \(MR_{pred,i}\) is predicted moisture ratio (dimensionless), \(MR_{exp,i}\) is experimental moisture ratio (dimensionless), and \(n\) is number of observations.

Drying rates were calculated from moisture content data and drying times, according to Equation [8]:

\[
DR = \frac{X_{i,d} - X_t}{dt}
\]

where \(DR\) is drying rate (kg kg⁻³ min⁻¹), \(X_{i,d}\) is moisture content at \(t + dt\) (kg water kg⁻¹ DM), \(X_t\) is moisture content at a specific time, and \(t\) is drying time (min).

To determine the coefficient of diffusion, drying data of seeds with and without oil were fit to the mathematical model of liquid diffusion for the spherical geometric shape (Crank, 1975), with approximation of three terms (Equation [9]), maintaining the initial equivalent spherical diameter of seeds throughout the drying process. The model was used only with three terms, because for sufficiently long drying times the three terms (\(i = 3\)) in the series expansion gives a good estimate of the solution and with more three terms the resulted were the same.

\[
MR = \frac{X - X_e}{X_i - X_e} = \frac{6 \sum_{i=1}^{n} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D e t}{R_{eq}^2}\right)}{1}
\]

where \(MR\) is moisture ratio (dimensionless), \(D_e\) is effective moisture diffusivity (m² s⁻¹), \(n\) is number of terms, \(R_{eq}\) is radius of the equivalent sphere (m), and \(t\) is time (s).

To calculate the equivalent spherical diameter, the volume of 100 seeds (50 seeds with oil and 50 seeds without oil) was determined using the water displacement method (Mohsenin, 1986), and the equivalent diameter by the volume of a sphere (Equation [10]):

\[
V_e = \frac{4}{3} \pi r^3
\]

where \(V_e\) is grain volume (m³), and \(r\) is radius of the equivalent sphere (m).

The relationship between the diffusion coefficient and drying temperature was described using the Arrhenius-type equation (Equation [11]):

\[
D = D_o \exp\left(-\frac{E_a}{RT}\right)
\]

where \(D_o\) is pre-exponential factor (m² s⁻¹), \(E_a\) is activation energy (J mol⁻¹), \(R\) is universal gas constant (8.314 J mol⁻¹ °K⁻¹), and \(T\) is absolute temperature (°K).

The coefficients of the Arrhenius-type equation were obtained by linearizing Equation [11] with the application of the logarithm:

\[
\ln D = \ln D_o - \frac{E_a}{R} \cdot \frac{1}{T}
\]

where \(\ln D_o\) is logarithmic of pre-exponential factor (m² s⁻¹), \(E_a\) is activation energy (J mol⁻¹), \(R\) is universal gas constant (8.314 J mol⁻¹ °K⁻¹), and \(T\) is absolute temperature (°K).

The mathematical models were fit to the experimental data using Statistica software and non-linear regression, employing the Quasi-Newton method. The diffusion coefficients were submitted to ANOVA and means were compared by Tukey’s test at 5% probability, using Assistat software (Silva and Azevedo, 2002).
RESULTS AND DISCUSSION

Figure 1 shows the experimental drying kinetics data of Treatment 1 and Treatment 2 samples at 40, 50, 60 and 70 °C, expressed by moisture ratio as a function of drying time. The times required for Treatment 1 samples to reach the desired moisture content (approximately 5.0% wb) were 5460 min at 40 °C, 3660 min at 50 °C, 780 min at 60 °C and 270 min at 70 °C. Mean initial moisture content was 16.95 ± 0.74% wb (20.41% db) and the final content was 4.94 ± 0.04% wb (5.20% db). With respect to Treatment 2 samples, times spent in drying kinetics were 4020, 2580, 1380 and 660 min, for drying at 40, 50, 60 and 70 °C, respectively, with mean initial moisture content of 19.48 ± 1.30% wb (24.19% db) and final moisture content of 4.88 ± 0.07% wb (5.13% db).

The results maintain the expected dependence of drying velocity with the temperature used and corroborate several authors working with agricultural products, who reported the influence of temperature on drying velocity (Koyuncu et al., 2004; Doymaz, 2005; Corrêa et al., 2010; Costa et al., 2011; Reis et al., 2011; Tavakolipour, 2011; Jittanit, 2011; Ferreira et al., 2012; Diógenes et al., 2013; Santos et al., 2013).

Was performed a comparison between drying times of annatto seed samples with and without oil. Two contrasting behaviors are observed depending on whether high or low temperatures were used. At 40 and 50 °C the oilless seeds dried nearly 30% faster than those with oil; at 60 and 70 °C, the opposite occurred, as samples with oil dried 77 and 144% faster than their oilless counterparts. One hypothesis to explain such behavior is that at lower temperatures the physical barrier represented by the film of oil hinders the release of water from the seeds into the environment. At higher temperatures, when shrinking in the surface layers of the seed becomes more important, the oil coating would prevent excessively rapid drying of the outer layers, reducing contraction and maintaining cell interstices for water migrating from inside the seed.

Lower drying times were reported by Tavakolipour (2011) when drying pistachio at 40, 50, 60 and 70 °C and by Roberts et al. (2008), drying grape seeds 40, 50 and 60 °C and drying speed of 1.5 m s⁻¹. Longer drying times were recorded by Koyuncu et al. (2004) when drying walnuts at 40, 50, 60 and 70 °C and drying speed of 0.5 and 1.0 m s⁻¹, while Corrêa et al. (2010) obtained similar drying times with coffee beans at temperatures of 35, 45, and 55 °C.

Figure 2 shows the drying rates of Treatment 1 and Treatment 2 samples dried at 40, 50, 60 and 70 °C. No constant drying rate was found for either sample, given that drying occurred during periods of falling speed. These data corroborate the results obtained by Doymaz (2005), Lema et al. (2007), Doymaz (2009), and Ferreira et al.
(2012), in a study on drying green beans, parsley, spinach leaves and grape bagasse, respectively. The drying rate decreases as the process continues, justified by the greater energy demand in products with lower moisture content and in the final drying stages. The Treatment 1 samples exhibited the lowest drying rates, possibly related to the presence of the oil layer, which can form a physical barrier on the seed surface, hindering moisture loss. With respect to drying temperatures, the highest rates were recorded at 70 °C (0.659 kg kg^{-1} min^{-1} for Treatment 1 and 0.782 kg kg^{-1} min^{-1} for Treatment 2), whereas the lowest drying rates were found at a temperature of 40 °C (0.445 kg kg^{-1} min^{-1} for Treatment 1 and 0.582 kg kg^{-1} min^{-1} for Treatment 2).

Tables 1 and 2 depict the fit parameters of Diffusion Approximation, Two Terms, Midilli, Page and Thompson mathematical models, drying kinetics data of Treatment 1 and Treatment 2 samples in the temperatures between 40 and 70 °C and their respective R^2 and RMSE.

All the models assessed fit well to the drying data of Treatment 1 and Treatment 2 samples for the temperature range studied, with R^2 above 0.98 and RMSE values below 0.1. The Diffusion Approximation and Two Terms models were used to estimate the drying kinetics curve of the samples, given that they display the highest R^2 and lowest RMSE values.

Several authors also demonstrated good fit to the mathematical modeling when studying the drying kinetics of agricultural products, such as apples (Menges and Ertekin, 2006), rice grains (Hacihafizoglu et al., 2008), green beans (Doymaz, 2005), spinach leaves (Doymaz, 2009), chili peppers (Pontes et al., 2009), peas (Doymaz and Kocayigit, 2011), coffee beans (Resende et al., 2009; 2010; Corrêa et al., 2010), parsley (Lema et al., 2007), salvia (Radünz et al., 2010), pumpkin seeds (Jittanit, 2011), yellow lantern chili (Reis et al., 2011) and grape bagasse (Ferreira et al., 2012).

For the Treatment 1 samples (Table 1) the increase of the drying temperature caused an increase in the constants “k” of Diffusion Approximation model, “n” of Midilli and Page models and “b” of Diffusion Approximation and Thompson models. For the parameter “a” of Diffusion Approach and Midilli models, it was observed decrease with the increase of the drying air temperature. These data corroborate with Santos et al. (2013), that in studying the drying kinetics of the annato flour showed increases in the constants “k”, “n” and “b” and a reduction in the constant “a” of drying models fitted to the experimental values.

For Treatment 2 samples (Table 2) was observed behavior similar to that detected in the Treatment 1 samples, with increases in the constants “k” of the Diffusion Approach model, “n” of the Midilli model and “b” of the Diffusion Approach and Thompson models. The constant “a” of Midilli model decreased with increasing of the drying air temperature. Jittanit (2011) reported of the drying kinetics of pumpkin seeds an increase of the constant “k” and reducing of the constant “a” in the models surveyed with increasing drying temperature. Diógenes et al. (2013) observed reductions in constant “n” models fitted to experimental data, being opposite to that found in this work.

Corrêa et al. (2010) reported that the constant of drying “k” tends to increase because higher temperatures cause greater drying rates coming to an equilibrium moisture content in less time of submission of the sample to air

<table>
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^1In quadruplicate for each temperature.
drying. The parameter “n” has a moderating effect of time and corrects the errors likely due to the neglect of the internal resistance to moisture transfer (Guedes and Faria, 2000).

ANOVA showed a significant effect at 1% probability using the F test for diffusion coefficients of Treatment 1 and Treatment 2 samples obtained for drying at 40, 50, 60 and 70 °C. Tukey’s test exhibited a significant difference between all the means at 5% probability.

Diffusion coefficient values increased with a rise in drying temperature, a phenomenon observed by other authors (Corrêa et al., 2010; Sousa et al., 2011; Costa et al., 2011; Faria et al., 2012; Ferreira et al., 2012). According to Corrêa et al. (2010), an increase in temperature promotes a decrease in water viscosity, which directly influences fluid outflow resistance. As such, its decline facilitates water molecule diffusion in the capillaries of the product.

The Treatment 1 samples exhibited diffusion coefficients with magnitudes of $2.67 \times 10^{-11}$, $3.37 \times 10^{-11}$, $5.43 \times 10^{-11}$ and $9.50 \times 10^{-11}$ m$^2$s$^{-1}$, for drying at 40, 50, 60 and 70 °C, respectively. The Treatment 2 samples had diffusion coefficients of $2.7 \times 10^{-11}$, $3.57 \times 10^{-11}$, $4.13 \times 10^{-11}$ and $6.21 \times 10^{-11}$ m$^2$s$^{-1}$, for drying at 40, 50, 60 and 70 °C, respectively. Similar diffusion coefficient values were reported by Sousa et al. (2011), who studied turnip seed drying in the temperatures between 30 and 70 °C, and Faria et al. (2012), who investigated crambe seed drying in the temperatures between 30 and 70 °C. Both had coefficients of $10^{-11}$ m$^2$s$^{-1}$.

Diffusion coefficients increased linearly and their dependence on drying temperature was described by the Arrhenius equation (Figure 3). According to Faria et al. (2012), declining linearity demonstrates the uniform variation in drying rate within the temperature range under study.

![Figure 3. Arrhenius plot for the diffusion coefficient, as a function of drying temperature for Treatment 1 (A) and Treatment 2 (B) samples.](image)
Activation energies for liquid diffusion in the drying of Treatment 1 and Treatment 2 samples were 38.04 and 23.52 kJ mol⁻¹, respectively. In accordance with Costa et al. (2011), in drying processes, the lower the activation energy the higher the moisture diffusiveness in the product. Therefore, Treatment 2 samples showed greater moisture diffusion with increased drying time, corroborating drying rate data. Corrêa et al. (2010) and Costa et al. (2011) reported similar activation energy to those of Treatment 1 samples, when drying coffee and crambe seeds, corresponding to 38.34 and 37.07 kJ mol⁻¹, respectively. Sousa et al. (2011) and Ferreira et al. (2012) obtained similar activation energy to that of Treatment 2 samples, corresponding to 24.78 and 26.44 kJ mol⁻¹ when studying turnip seed drying and grape bagasse, respectively.

CONCLUSIONS

All the models studied represented satisfactorily the drying kinetics of annatto seeds with and without oil at a temperature range 40-70 °C of drying air; within the models tested, the Diffusion Approximation and Two Terms drying models exhibited the best fit parameters with an $R^2 \geq 0.99$ and RMSE $\leq 0.0145$. At lower temperatures (40 and 50 °C), annatto seed samples with oil showed slower drying; at higher temperatures (60 and 70 °C) seeds with oil dried in a shorter period of time.

Diffusion coefficients increased with a rise in drying temperature, showed values with magnitudes of $10^{-11}$ m² s⁻¹. Samples without oil (Treatment 1) showed the greatest diffusivity in the temperatures of 40 and 50 °C, while the samples with oil (Treatment 2) showed higher diffusivity at 60 and 70 °C. The relationship between the diffusion coefficient and temperature can be described by the Arrhenius equation, which displays activation energies of 38.04 and 23.52 kJ mol⁻¹ for samples of annatto seeds with and without oil, respectively.

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LITERATURE CITED


