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Statistical evaluation of models for sorption and desorption isotherms for barleys

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ABSTRACT. This study presents a novel approach to evaluate water sorption and desorption isotherm modeling consisting in statistical evaluation of the fit followed by the ranking of the models. Water sorption and desorption isotherms for BRS Elis and BRS Cauê barley cultivars were evaluated at 40, 50, and 60°C. Data were analyzed by the GAB, Freundlich, Halsey, Henderson, Langmuir, Oswin, and Smith models. The BET model was also fitted to determine the moisture content. All models were submitted to five tests to determine whether the model was statistically significant. Then, the models were ranked using corrected Akaike information criterion. At all temperatures, the equilibrium moisture content increases as water activity increases and temperature decreases. Data showed no hysteresis in both cultivars. The statistical parameters evaluated indicate the goodness of the fit for all models except for the GAB model for BRS Elis cultivar at 60°C. The analysis with the corrected Akaike information criterion revealed that the Oswin and Henderson models showed best results at 40 and 50°C for both cultivars studied. At 60°C, the Freundlich model was the best for both cultivars. For both cultivars, the value of isosteric heat decreases with an increase in moisture content.

Keywords: Akaike information criterion; equilibrium moisture content; mathematical models; barley cultivar.

Avaliação estatística de modelos de isotermas de sorção e dessorção em cultivares de cevada

RESUMO. Este trabalho apresenta uma nova abordagem para avaliar modelos de sorção e dessorção de umidade, que consiste em avaliar estatisticamente a classificação dos modelos ajustados. Isotermas de sorção e dessorção para as cultivares de cevada BRS Elis e BRS Cauê foram determinadas a 40, 50 e 60°C. Os dados foram analisados pelos modelos GAB, Freundlich, Halsey, Henderson, Langmuir, Oswin e Smith. O modelo BET também foi ajustado para determinar o teor de umidade. Os modelos foram submetidos a cinco testes estatísticos para determinação da significância estatística; para fins de classificação, foi utilizado o Critério de Informação de Akaike corrigido (AICc). Em todas as temperaturas, a umidade de equilíbrio aumenta com o aumento da atividade da água e com a diminuição da temperatura. Os parâmetros estatísticos avaliados indicaram um bom ajuste dos modelos, com exceção do modelo GAB para a BRS Elis a 60°C. A análise com a utilização do AICc mostrou que os modelos Oswin e Henderson possuem melhores resultados a 40 e a 50°C para as duas cultivares. A 60°C, o modelo de Freundlich foi o melhor para as duas cultivares. Para ambas as cultivares, o calor isostérico diminuiu com o aumento do conteúdo de umidade.

Palavras-chave: critério de informação de Akaike; teor de umidade de equilíbrio; modelos matemáticos; cultivares de cevada.

Introduction

Barley (*Hordeum vulgare* ssp. *vulgare*) is a small grain cereal that constitutes one of the world's most important sources of food (Food and Agriculture Organization of the United Nations [Faostat], 2015). Barley is commonly used in industry for malting and as animal feed. However, its high fiber content has motivated interest in increasing human consumption of it, for example in bakery products (Ghosh, Jayas, & Gruwel, 2009; Sharma, Singh, & Rosell, 2011). Different cultivars may influence the barley's chemical composition and hydration thermodynamic properties (Montanuci, Jorge, & Jorge, 2013). Åman and Newman (1986) and Oscarsson, Andersson, Salomonsson, and Åman (1996) reported that these differences may be influenced by dry weather and crop management.

The moisture content of barley is important for costs and quality, since a high moisture content increases the risk of deterioration during storage and decreases the shelf life. In order to avoid this, barley with high moisture content should be submitted to drying processes, which will increase costs (Briggs, Houge, Stevens, & Young, 1981; Santos, 1999). More than 200 isotherm models developed theoretically, semi-theoretically, or empirically in order to describe the relation between equilibrium moisture content (X_{eq}) and water activity (U_r) are reported in the literature (Basunia & Abe 2005). However, choosing the best model to describe this relation is difficult, and should be done considering different statistical parameters, which is often not the case in studies found in the literature. Water sorption isotherms are unique for each material and must be evaluated experimentally. For these reasons, many authors have studied equations for sorption isotherms by applying several different biological materials over the years (Al-Muhtaseb, McMinn, & Magee, 2002).

A thermodynamic study is one way to understand water sorption into biological systems and to estimate the energy requirements, such as the heat of sorption, differential enthalpy, and differential entropy, which are estimated by modeling sorption isotherms (Thys, Noreña, Marczak, Aires, & Cladera-Olivera, 2010). So, it is essential to determine the best model with the highest possible accuracy.

Due to the technical and economic importance of water sorption isotherms and the importance of an accurate and reliable choice of mathematical model, the objectives of the present study were: (i) to determine the adsorption equilibrium moisture content for two different barley cultivars (BRS Cauê and BRS Elis) from the 2013/2014 crop at temperatures of 40, 50, and 60ºC; (ii) to determine which mathematical model best fits the experimental data, along with its parameters and errors, using a series of statistical tests; (iii) to determine the solid surface specific area; and (iv) to calculate the net isosteric heat of sorption.

Material and methods

Materials

Samples of barley of BRS Cauê and BRS Elis cultivars from the 2013/2014 crop were used in this study. It was determined that both cultivars were suitable for malting, according to a grading analysis by Ordinance 691/1996 of Brazil's Ministry of Agriculture.

Selected salts were used to obtain a water activity ranging from 0.110 to 0.818 (Perry & Chilton, 1973), namely LiCl, CH_3CO_2K, K_2CO_3, NaCl, $NaNO_2$ (Neon, Brazil, degree of purity > 99.0%), $MgCl_2$ (Biotec, Brazil, degree of purity = 99.0%), and KCl (Vetec, Brazil, degree of purity = 99.0%).

Experimental procedures

Equilibrium moisture content analysis

Adsorption and desorption isotherms were determined using the static gravimetric method. The arrangement of the experiment consisted in using BRS Cauê and BRS Elis cultivars and seven saturated salt solutions at 40, 50, and 60ºC. All assays were performed in triplicate to ensure the reproducibility of the data.

To ensure that the adsorption process would occur, samples were first dried in an oven at 102ºC for five days. After dried the samples were placed in the reservoirs and back in the oven, which was set to heat up until it reached the equilibrium temperature of 40, 50, or 60°C.

To ensure that the desorption process would occur, samples were placed in contact with an atmosphere provided by potassium chloride (which provides a higher humidity condition of 83%) at 20ºC. The samples had to be left in this atmosphere for approximately 24 hours to obtain a moisture content of 28% (d.b.), a value that is higher than the estimated value of X_{eq} in higher relative humidity, for testing at the desorption temperatures of 40, 50, and 60ºC. Then, as for the adsorption process, samples were placed in the reservoirs and placed back in the oven, which was set to heat up to the temperature chosen for the experiment, until equilibrium was reached. This procedure was done for 40, 50, and 60ºC.

Data analysis

Influence of temperature and cultivar on equilibrium moisture content

In order to verify the influence of temperature and cultivar on the equilibrium moisture content for adsorption and desorption, the software Statistica 10.0 (StatSoft, USA) was used. The average values of X_{eq} were analyzed by analysis of variance (ANOVA) with Tukey's *post hoc* test, with the significance defined at $p < 0.05$, between different temperatures (40, 50, and 60°C) and different cultivars. All experiments were performed in triplicate.

Isotherm models

Seven different models (Equation 2 to 9) presented in the literature (Table 1) were used to fit

the sorption and desorption data for both BRS Cauê and BRS Elis barley cultivars in the whole water activity range evaluated (0.11 to 0.82). The BET model was also applied to the data in order to determine the moisture content (U_m) in the water activity range of 0.11 to 0.50. The data were submitted to a nonlinear regression routine developed in MATLAB (MathWorks, USA), where the minimized error function was the mean absolute error (Equation 1).

$$EM_{abs} = \frac{\sum_{i=1}^{n}\left|(X)_{exp} - (X)_{cal}\right|}{n} \quad (1)$$

where:
$(X)_{exp}$ is the experimental data, $(X)_{cal}$ is the predicted data and n is the number of experimental points. The parameter estimation and parameter deviation were calculated as described by Gomes, Araújo, Lenzi, Silva, and Lenzi (2013).

Table 1. Models used to fit the water sorption onto BRS Cauê and BRS Elis barley cultivars.

Model	Equation		Reference
BET	$X_e = \frac{U_m.c.U_r}{(1-U_r).(1+(c-1).U_r)}$	(2)	Brunauer, Emmett, and Teller (1938)
Freundlich	$X_e = A.U_r^B$	(3)	Togrul and Arslan (2007)
Halsey	$X_e = \left(\frac{-A}{T.\log(U_r)}\right)^{1/B}$	(4)	Halsey (1948)
Henderson	$X_e = \left(-\left(\frac{1}{T.A}\right).\log(1-U_r)\right)^{1/B}$	(5)	Henderson (1952)
Langmuir	$X_e = \frac{A.B.U_r}{1+B.U_r}$	(6)	Langmuir (1918)
Oswin	$X_e = A.\left(\frac{U_r}{1-U_r}\right)^B$	(7)	Oswin (1946)
Smith	$X_e = A - B.\log(1-U_r)$	(8)	Smith (1947)
GAB	$X_e = \frac{X_m.c.k.U_r}{(1-k.U_r).(1+(c-1).k.U_r)}$	(9)	Van den Berg and Bruin (1981)

Note: X_e, equilibrium moisture content (kg water kg^{-1} dry solids); U_r, water activity; X_m, monolayer moisture content (kg water kg^{-1} dry solids); A, B, c and k, are parameters of the Equations.

In order to decide which model has statistical significance in the water sorption onto barley, five tests were proposed. For the model to be considered statistically significant, it should pass all five tests. Model data were subjected to these tests after the regressions were performed.

Test 1: The R^2 test. For the model to pass this test, the coefficient of determination (Equation 10) should be higher than 0.9 ($R^2 > 0.9$).

$$R^2 = 1 - \frac{\sum\left((X)_{exp} - (X)_{cal}\right)}{\sum\left((X)_{exp} - \bar{X}\right)} \quad (10)$$

where:
$\bar{X}$ is the average of the experimental data.

Test 2: The second test indicates whether or not the average of the residues was equal to zero with a 95% confidence level.

Test 3: The third test indicates whether the residues had a normal distribution (95% confidence level). This test applied the Kolmogorov–Smirnov normality test (Massey, 1951), where the hypotheses were:

H_0: the data come from a standard normal distribution;

H_1: the data do not come from a standard normal distribution.

If the p-value was higher than 0.05, there was insufficient evidence to reject the null hypothesis and the residues could be considered to have a normal distribution.

Test 4: The fourth test performed to evaluate the data was the parameter deviation test. This test indicates whether the absolute value of the parameter was higher than its deviation.

Test 5: The last test indicates if the nonlinear regression was significant, using the chi-square (χ^2) hypothesis test. If the calculated value (Equation 11) was lower than the tabulated one ($\alpha = 5\%$), the nonlinear regression was considered significant for the proposed model.

$$\chi^2 = \sum_{i=1}^{n}\frac{\left[(X)_{exp} - (X)_{cal}\right]^2}{(X)_{cal}} \quad (11)$$

In order to determine which model best describes the experimental data between the models which passed through the statistical analysis, the Akaike information criterion (AIC) was calculated (Akaike, 1974). This criterion provides a relative measure of information lost by a model when compared to the perfect model (experimental data). This criterion penalizes models with a higher number of parameters and was developed with statistical basis (Kullback–Leibler information) (Burnham & Anderson, 2004), which provides a reliable response. The general form of the AIC (Equation 12) is given as (Akaike, 1974):

$$AIC = -2\ln(L) + 2j \quad (12)$$

where:
j is the number of parameters of the model and L is the maximum value of the likelihood function. If the model errors are normally and independently distributed, the Equation 15 can be rewritten as Equation 13:

$$AIC = n\ln(\sigma^2) + 2j \quad (13)$$

where:
n is the number of experimental data points and σ^2 is the estimated variance of the model. A second order correction was proposed when the relationship of n and j is small ($n/j < 40$) (Burnham & Anderson, 2004). The corrected Akaike information criterion (AIC_C) is given by Equation 14:

$$AIC_C = n\ln(\sigma^2) + 2j + \frac{2(j-1)}{n-j-1} \quad (14)$$

The AIC_C number for a model by itself is useless and should be compared with other AIC_C calculated with other models. In order to compare the proposed models, a new scale (Δ_i) can be calculated as (Equation 15):

$$\Delta_i = AIC_{Ci} - AIC_{Cmin} \quad (15)$$

where:
AIC_{Ci} is the AIC_C value for the model i and AIC_{Cmin} is the minimum AIC_C value among the models proposed. This transformation allows a meaningful interpretation without considering problems with unknown constants in the models and distinct sample sizes (Burnham & Anderson, 2004). Models with $\Delta_i \leq 2$ have good evidence to be considered the best model; $4 \leq \Delta_i \leq 7$ have little evidence of being the best model and; $\Delta_i > 10$ have essentially no evidence to be considered the best model. The best model was that showed a lower AIC_C.

Specific area

The solid surface specific area can be estimated by assuming the water surface area (A_m) to be 1.06×10^{-19} (m^2 $molecule^{-1}$) using Equation 16 (Mazza & LeMaguer, 1978).

$$Area = \frac{X_m N_A A_m}{M_{wat}} \quad (16)$$

where:
Area is the solid surface area (m^2 g_{solids}^{-1}), X_m is the monolayer moisture content (% d.b.) calculated from the BET equation, M_{wat} is the water molecular weight (18 kg $kmol^{-1}$) and N_A is Avogadro's number (6×10^{26} molecules kg mol^{-1}).

Determination of the net isosteric heat of sorption

The net isosteric heat was calculated following the procedure described by Arslan and Toğrul (2006). The isosteric heat can be estimated through sorption equilibrium data with a relation derived from the Clausius-Clapeyron equation. The slope obtained from a linear regression of the sorption data as $\log(U_r)$ versus $1/T$ for a specific and constant moisture content provides a measure of the net isosteric heat of sorption, q_{st} (Equation 17). The heat of sorption, Q_{st}, can be estimated through Equation 18.

$$q_{st} = -R\left[\frac{d(\log U_r)}{d\left(\frac{1}{T}\right)}\right]_{X_e} \quad (17)$$

$$Q_{st} = q_{st} + H_L \quad (18)$$

where:
H_L is the latent heat of vaporization of pure water at 50°C (the average temperature studied in this work) and R is the universal gas constant. U_r data were calculated using the best-fitting model at constant X_e for all temperatures evaluated.

Results and discussion

Equilibrium moisture content

Figure 1 shows the experimental results obtained in this study, showing the equilibrium moisture content for adsorption and desorption at 40, 50 and 60°C for BRS Cauê and BRS Elis barley cultivars. The same behavior was found in adsorption and desorption for both cultivars. According to this figure, it is possible to see that the X_e values of BRS Elis were higher than those of BRS Cauê in all conditions, with a significant difference ($p < 0.05$). They showed sigmoidal S-shaped curves for both cultivars at 40, 50, and 60°C, reflecting the Type II isotherm characteristics according to the classification of Brunauer et al. (1938). In all curves, X_e increases as water activity (U_r) increases and temperature decreases, with a significant difference ($p < 0.05$). This phenomenon was also observed for cassava bagasse by Polachini, Betiol, Lopes-Filho, and Telis-Romero (2016), extruded snacks by Wani and Kumar (2016), prickly pear seeds by Hassini, Bettaieb, Desmorieux, Torres, and Touil (2015), and rice by Torres and Seijo (2016). The decrease of X_e with temperature could be caused by the reduction of active sites for binding water, as the energy levels of the water increase with temperature and the water breaks away from the water binding sites of the barley, thereby decreasing the moisture content (Palipane & Driscoll, 1993). This behavior indicates that barley becomes less hygroscopic at higher temperatures. In addition, the Tukey mean test indicated no significant difference ($p < 0.05$) between adsorption and desorption, indicating that the hysteresis phenomenon does not occur in the two barley cultivars. This behavior can be easily seen in Figure 1.

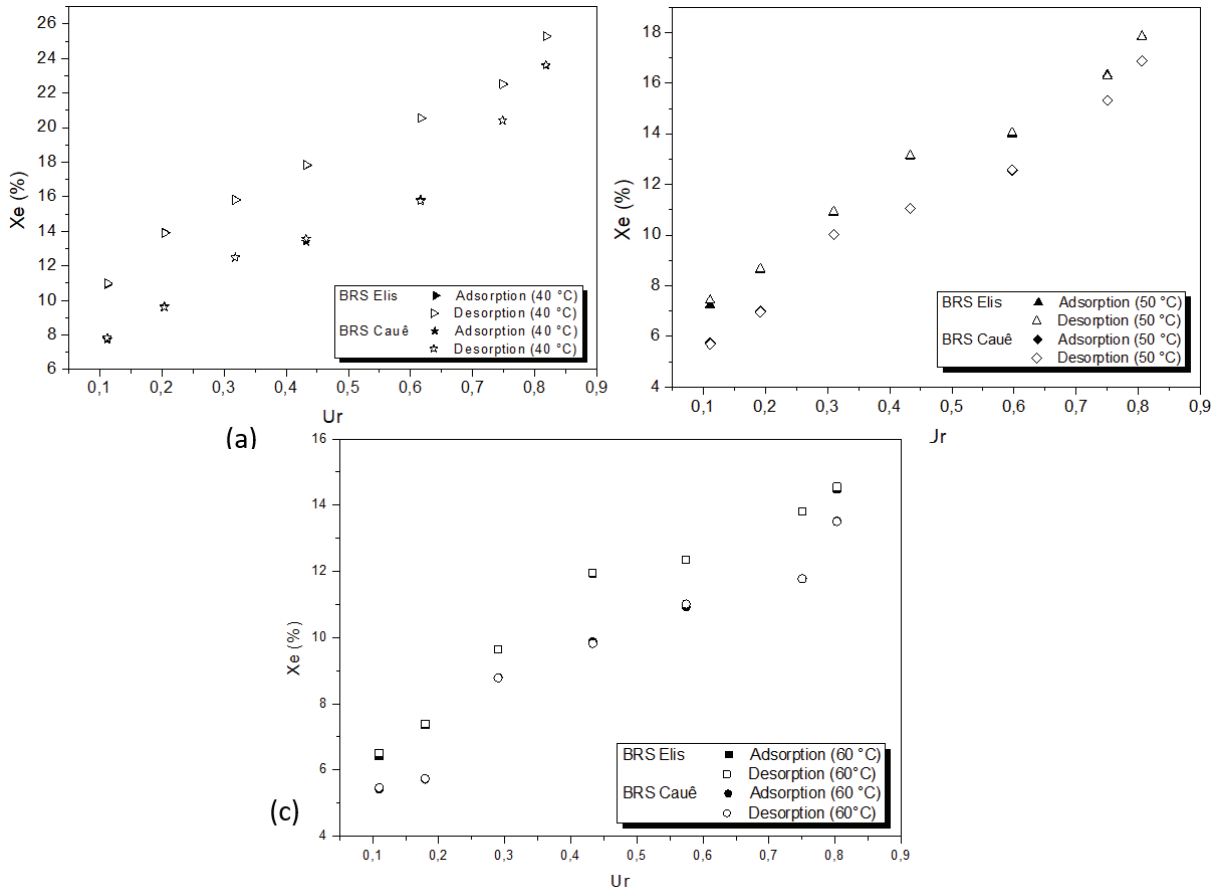

Figure 1. Experimental data for water adsorption and desorption onto barley BRS Elis and BRS Cauê cultivars at: (a) 40, (b) 50 and (c) 60°C.

Adsorption modeling

Statistical analyses used to model sorption isotherms are important to determine which mathematical model best fits the experimental data. Since there is no standard statistical parameter to determine which model should be chosen, researchers have used different statistical analyses to make this decision easier and more accurate. By far, the most commonly used parameter is the R^2, which may not be adequate to compare experimental data shaped as an exponential function (such as moisture isotherm). Currently, the literature shows that the R^2 is an unfavorable measure to validate the nonlinear regression (Spiess & Neumeyer, 2010). In addition, the sum of squared errors is widely used to evaluate the fit, which, although technically more accurate than R^2, is not good enough to tell if one model is better than another, especially if the compared models have a different number of parameters. Chi-square is also used, but it is a statistical tool that must be compared to a theoretical number, a rare approach in the literature.

Sorption and desorption data obtained for both BRS Cauê and BRS Elis barley cultivars were subjected to nonlinear regression using a routine developed in MATLAB in the whole water activity range evaluated. All data sets were then subjected to five tests in order to determine whether the data had statistical significance. For BRS Cauê, all seven models passed the five tests. For BRS Elis, only the GAB model (at 60°C) failed one test, while the other six models passed all tests. The coefficient of determination (R^2) was higher than 0.90, indicating high correlation between moisture content and water activity for all models. The average of the residues was considered equal to 0 (at the 95% confidence level) for all models evaluated for the data for both types of barley. Also, the Kolmogorov-Smirnov normality test showed no evidence that the null hypothesis could be accepted. Therefore, the residues were considered to have a normal distribution for all data sets (at the 95% confidence level). The parameter deviations were also calculated and only one parameter of the GAB model was found to be higher than its absolute value (parameter *c*, for adsorption onto BRS Elis cultivar at 60°C). For all models, the chi-square values are

lower than the tabulated ones at the 95% confidence level, which indicates the goodness of the fit for all models. Chi-square indicates that the models were adequate to predict the phenomenon. With this evidence, it was considered that all data sets had statistical significance for water sorption and desorption onto BRS Cauê. For BRS Elis, the GAB model was the only one that showed no statistical significance for water sorption onto barley at 60°C.

In the moisture sorption onto BRS Cauê cultivar (Table 2) at 40°C, the Oswin model showed the lowest AICc along with the Halsey model; at 50°C, the Henderson model was the best; at 60°C, the best model was Freundlich, followed by the Henderson and Langmuir models. As expected considering the statistical data, the same results were found for desorption. In general, the Henderson and Oswin models presented the best results for describing the water sorption and desorption onto BRS Cauê cultivar at different temperatures.

In the moisture sorption onto BRS Elis cultivar (Table 2), at 40 and 50°C, the best model was Henderson. At 60°C, Freundlich was the best model. As happened for BRS Cauê cultivar, no significant difference (α = 5%) was found between results of adsorption and desorption trials, and therefore the same models were considered with high evidences to be a good representation of the experimental data.

In general, the Henderson model was ranked as the best model in most cases (mean ranking equal to 2.0) followed by the Oswin and Freundlich models (mean ranking equal to 2.8) for adsorption and desorption at 40, 50 and 60°C, for both cultivars. The parameters calculated for the best model at each temperature are summarized in Table 3. In addition, Figure 2 shows the experimental data and the best model for each cultivar at 40, 50 and 60°C.

Specific area

The surface areas of the two barley varieties were estimated through Equation 16 using the moisture content calculated from the BET equation. The average surface area was 249.5 m^2 g_{solids}^{-1} for BRS Cauê cultivar, and 293.8 m^2 g_{solids}^{-1} for BRS Elis cultivar. The value found for BRS Cauê was in accordance as that to be expected for foods, between 100 and 260 m^2 g_{solids}^{-1} (Cassini & Marczak, 2006). The surface area found for BRS Elis cultivar was higher than the value found in the literature for food products. This variation in the surface area can be attributed to the presence of several intrinsic micro and mesoporous in the barley structure. This result shows that the BRS Elis cultivar has more sites than the BRS Cauê cultivar does for water binding.

Table 2. Classification of the tested models for the adsorption and desorption moisture content for BRS Cauê and BRS Elis cultivar using the corrected Akaike information criterion.

	Freundlich	GAB	Halsey	Henderson	Langmuir	Oswin	Smith
K	2	3	2	2	2	2	2
BRS CAUÊ							
Adsorption at 40°C							
EM_{abs}	1.07	0.44	0.49	0.70	1.40	0.36	0.54
AICc	11.26	6.22	0.18	5.06	14.66	-1.30	2.07
Δ_i	12.56	7.52	1.48	6.36	15.96	0.00	3.37
Rank	6	5	2	4	7	1	3
Adsorption at 50°C							
EM_{abs}	0.50	0.35	0.68	0.36	0.68	0.43	0.72
AICc	-0.51	1.73	3.71	-4.84	4.57	-2.16	4.64
Δ_i	4.33	6.57	8.55	0.00	9.41	2.68	9.48
Rank	3	4	5	1	6	2	7
Adsorption at 60°C							
EM_{abs}	0.47	0.47	0.86	0.52	0.58	0.65	0.94
AICc	-1.57	5.35	5.85	-0.12	0.39	2.52	6.90
Δ_i	0.00	6.92	7.42	1.45	1.95	4.09	8.46
Rank	1	5	6	2	3	4	7
Desorption at 40°C							
EM_{abs}	1.06	0.48	0.52	0.70	1.40	0.38	0.57
AICc	11.49	6.86	0.38	5.47	14.84	-0.65	2.29
Δ_i	12.14	7.51	1.03	6.12	15.49	0.00	2.93
Rank	6	5	2	4	7	1	3
Desorption at 50°C							
EM_{abs}	0.49	0.35	0.71	0.37	0.67	0.44	0.75
AICc	-0.75	1.82	4.09	-4.70	4.29	-1.71	4.96
Δ_i	3.96	6.53	8.80	0.00	8.99	3.00	9.66
Rank	3	4	5	1	6	2	7
Desorption at 60°C							
EM_{abs}	0.45	0.45	0.86	0.52	0.57	0.65	0.94
AICc	-1.73	5.28	5.77	-0.26	0.38	2.42	6.82
Δ_i	0.00	7.01	7.50	1.47	2.11	4.15	8.55
Rank	1	5	6	2	3	4	7
BRS ELIS							
Adsorption at 40°C							
EM_{abs}	0.63	0.28	0.71	0.31	1.09	0.40	0.87
AICc	2.14	-0.19	4.93	-6.34	10.21	-3.54	7.46
Δ_i	8.48	6.15	11.27	0.00	16.55	2.80	13.80
Rank	4	3	5	1	7	2	6
Adsorption at 50°C							
EM_{abs}	0.40	0.34	0.68	0.33	0.66	0.41	0.77
AICc	-2.94	0.92	4.07	-6.26	4.27	-1.98	5.64
Δ_i	3.31	7.17	10.32	0.00	10.53	4.28	11.90
Rank	2	4	5	1	6	3	7
Adsorption at 60°C							
EM_{abs}	0.26	0.30	0.87	0.44	0.37	0.65	0.97
AICc	-7.68	-0.91	6.81	-1.87	-4.97	2.71	8.16
Δ_i	0.00	6.77	14.49	5.81	2.71	10.39	15.84
Rank	1	4	6	3	2	5	7
Desorption at 40°C							
EM_{abs}	0.633	0.28	0.69	0.29	1.09	0.39	0.85
AICc	2.22	-0.30	4.69	-6.54	10.32	-3.97	7.25
Δ_i	8.75	6.24	11.22	0.00	16.86	2.56	13.79
Rank	4	3	5	1	7	2	6
Desorption at 50°C							
EM_{abs}	0.42	0.35	0.67	0.32	0.68	0.40	0.76
AICc	-2.76	1.22	3.71	-6.28	4.55	-2.30	5.35
Δ_i	3.53	7.50	9.99	0.00	10.83	3.98	11.64
Rank	2	4	5	1	6	3	7
Desorption at 60°C							
EM_{abs}	0.28	0.31	0.85	0.41	0.40	0.63	0.95
AICc	-7.57	-0.30	6.46	-2.26	-4.01	2.30	7.85
Δ_i	0.00	7.27	14.02	5.31	3.55	9.87	15.41

Table 3. Best model for BRS Cauê and BRS Elis cultivar for adsorption and desorption at 40, 50 and 60°C.

	BRS Cauê cultivar			BRS Elis cultivar		
	Best fit	A	B	Best fit	A	B
			Adsorption			
40°C	Oswin	14.65 ± 0.07	0.30 ± 0.07	Henderson	3.64E-04 ± 3.04E-07	3.35 ± 0.01
50°C	Henderson	1.33E-03 ± 1.04E-03	2.53 ± 0.32	Henderson	2.94E-04 ± 3.98E-06	3.01 ± 0.01
60°C	Freundlich	14.26 ± 0.29	0.46 ± 0.02	Freundlich	15.80 ± 0.15	0.41 ± 0.02
			Desorption			
40°C	Oswin	14.68 ± 0.06	0.30 ± 0.00	Henderson	3.65E-05 ± 2.98E-07	3.36 ± 0.01
50°C	Henderson	1.38E-03 ± 5.99E-05	2.52 ± 0.02	Henderson	2.94E-04 ± 5.48E-06	3.07 ± 0.01
60°C	Freundlich	14.25 ± 0.14	0.45 ± 0.01	Freundlich	15.81 ± 0.12	0.41 ± 0.01

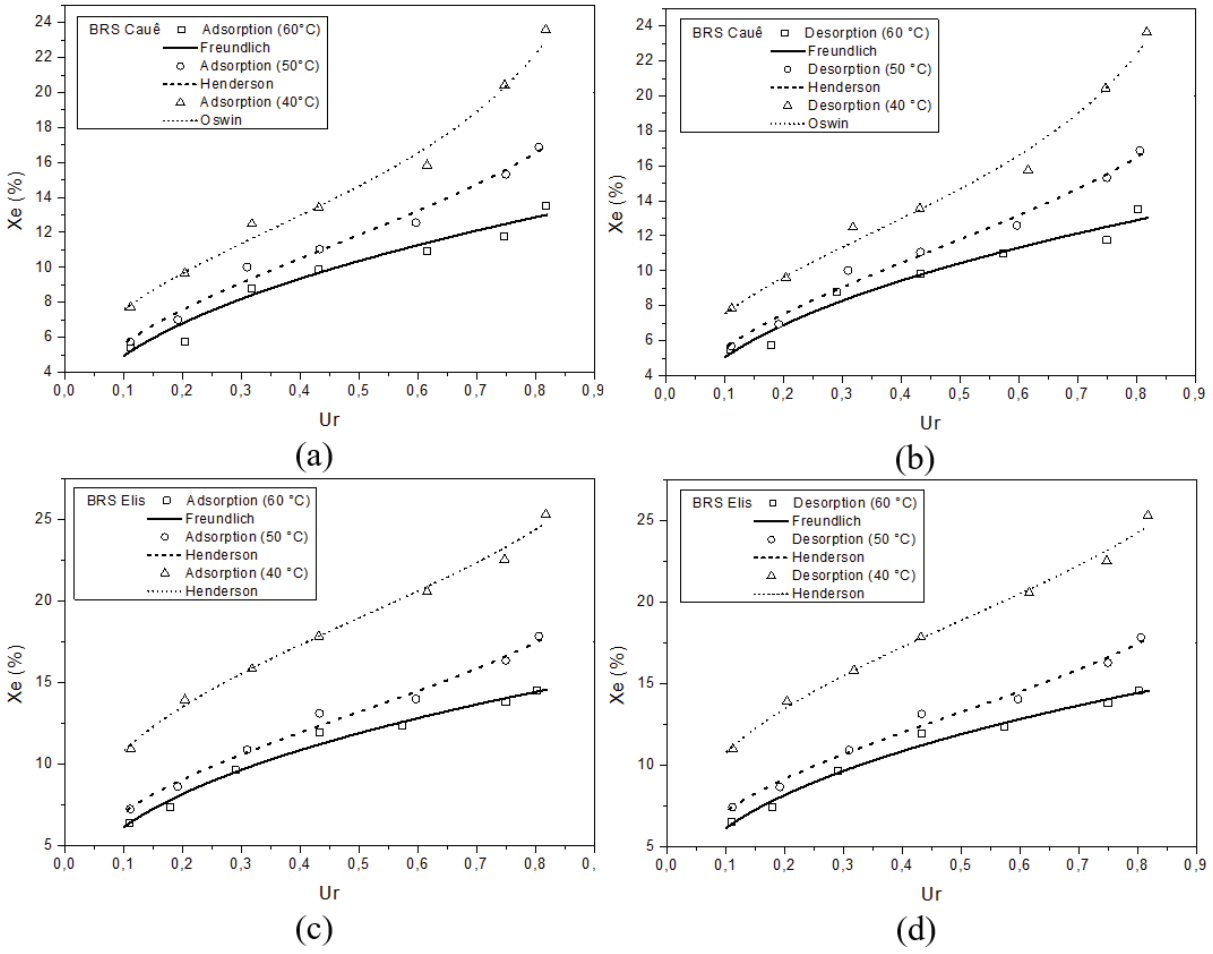

Figure 2. Experimental and predicted data for water sorption and desorption at 40, 50 and 60°C: (a) and (b) for barley BRS Cauê cultivar and (c) and (d) for barley BRS Elis cultivar.

Determination of the net isosteric heat of sorption

The net isosteric heat of sorption and desorption was estimated with the best model at which temperature for both BRS Cauê and BRS Elis cultivar, since these models were considered to provide the best fit. The results obtained showed a similar behavior between the two cultivars (Figure 3). For BRS Cauê cultivar, the isosteric heat decreases from 173.3 to 74.6 kJ mol^{-1} for adsorption as the moisture content increases up to 15%. For BRS Elis cultivar, the isosteric heat decreases 195.5 to 93.7 kJ mol^{-1} for adsorption as the moisture content increases up to 14%. For both barley cultivars, the adsorption and desorption calculated values of isosteric heat were equal, as expected due to statistical analyses and modeling approach discussed above. The decrease in the isosteric heat with the increase of moisture content indicates that the energy needed to remove water decreases with the increase of moisture content. A similar behavior was found by Gely and Pagano (2012) for malting barley cultivar Scarlett.

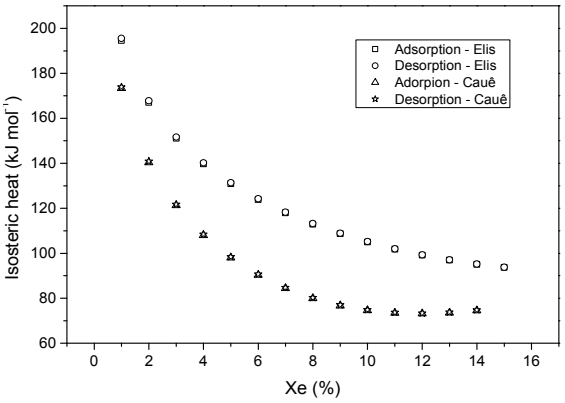

Figure 3. Sorption isosteric heats of BRS Cauê and BRS Elis cultivars as a function of moisture content.

Conclusion

The moisture sorption isotherms of BRS Elis and BRS Cauê barley cultivars present a significant decrease in the equilibrium moisture content with increase in the temperature. The seven models passed all five tests for BRS Cauê. For BRS Elis cultivar, only the GAB model failed one test at 60°C. The analysis with the AICc revealed that the Oswin and Henderson models showed best results at 40 and 50°C. At 60°C, the Freundlich model was the best. The solid surface increased with increase in temperature, while the isosteric heat decreased with increase in moisture content.

References

Akaike, H. (1974). A new look at the statistical model identification. *IEEE Transactionson Automatic Control, 19*(6), 716-723. doi: 10.1109/TAC.1974.1100705

Al-Muhtaseb, A. H., McMinn, W. A. M., & Magee, T. R. A. (2002). Moisture sorption isotherm characteristics of food products: a review. *Food and Bioproducts Processing, 80*(2), 118-128. doi: 10.1205/09603080252938753

Åman, P., & Newman, C. W. (1986). Chemical composition of some different types of barley grown in Montana, U.S.A. *Journal of Cereal Science, 4*(2), 133-141. doi: 10.1016/S0733-5210(86)80016-9

Arslan, N., & Toğrul, H. (2006). The fitting of various models to water sorption isotherms of tea stored in a chamber under controlled temperature and humidity. *Journal of Stored Products Research, 42*(2), 112-135. doi: 10.1016/j.jspr.2005.01.001

Basunia, M. A., & Abe, T. (2005). Adsorption isotherms of barley at low and high temperatures. *Journal of Food Engineering, 66*(1), 129-136. doi: 10.1016/j.jfoodeng.2004.03.006

Briggs, D. E., Houge, J. S., Stevens, R., & Young, T. W. (1981). *Malting and brewing science: malt and sweet wort* (vol. 1). London: GB: Springer.

Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society, 60*(1), 309-319. doi: 10.1021/ja01269a023

Burnham, K. P., & Anderson, R. P. (2004). Multimodel inference: understanding AIC and BIC in model selection. *Sociological Methods & Research, 33*(2), 261-304. doi: 10.1177/0049124104268644

Cassini, A. S., & Marczak, L. D. F. (2006). Water adsorption isotherms of texturized soy protein. *Journal of Food Enginnering,* 77(1), 194-199. doi: 10.1016/j.jfoodeng.2005.05.059

Food and Agriculture Organization of the United Nations. (2015). *Database, Food and Agricultural Organization*. Rome, IT: Faostat.

Gely, M. C., & Pagano, A. M. (2012). Moisture desorption isotherms and isosteric heat of sorption characteristics of malting barley (*Hordeum Distichum L.*). *Latin American Applied Research, 42*(3), 237-243. doi: 10.1590/2317-1545v37n3149549

Ghosh, P. K., Jayas, D. S., & Gruwel, M. L. H. (2009). Measurement of water diffusivities in barley components using diffusion weighted imaging and validation with a drying model. *Drying Technology, 27*(3), 382-392. doi: 10.1080/07373930802682973

Gomes, E. M., Araújo, R. R. L., Lenzi, M. K., Silva, F. R. G. B., & Lenzi, E. K. (2013). Parametric analysis of a heavy metal sorption isotherm based on fractional calculus. *Mathematical Problems in Engineering*, *2013*, 1-10. doi: 10.1155/2013/642101

Halsey, G. (1948). Physical adsorption on non-uniform surfaces. *The Journal of Chemical Physics, 16*(1), 931-937. doi: 10.1063/1.1746689

Hassini, L., Bettaieb, E., Desmorieux, H., Torres, S. S., & Touil, A. (2015). Desorption isotherms and thermodynamic properties of prickly pear seeds. *Industrial Crops and Products, 67*, 457-465. doi: 10.1016/j.indcrop.2015.01.078

Henderson, S. M. (1952). A basic concept of equilibrium moisture. *Transactions of the American Society of Agricultural Engineers, 33*, 29-32.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society, 40*(9), 1361-1403. doi: 10.1021/ja02242a004

Massey, F. J. (1951). The Kolmogorov-Smirnov test for goodness of fit. *Journal of the American Statistical Association, 46*(253), 68-78.

Mazza, G., & LeMaguer, M. (1978). Water sorption properties of yellow globe onion (*Allium cepa L.*). *Canadian Institute of Food Science and Technology Journal, 11*(4), 189-193. doi: 10.1016/S0315-5463(78)73269-4

Montanuci, F. D., Jorge, L. M. M., & Jorge, R. M. M. (2013). Kinetic, thermodynamic properties and optimization of barley hydration. *Food Science and Technology, 33*(4), 690-698. doi: 10.1590/S0101-20612013000400014

Oscarsson, M., Andersson, R., Salomonsson, A.-C., & Åman, P. (1996). Chemical composition of barley samples focusing on dietary fibre components. *Journal of Cereal Science, 24*(2), 161-170. doi: 10.1006/jcrs.1996.0049

Oswin, C. R. (1946). The kinetics of package life. III. The isotherm. *Journal of the Society of Chemical Industry, 65*(12), 419-421. doi: 10.1002/jctb.5000651216

Palipane, K. B., & Driscoll, R. H. (1993). Moisture sorption characteristics of in-shell macadamia nuts. *Journal of Food Engineering, 18*(1), 63-76. doi: 10.1016/0260-8774(93)90075-U

Perry, R. H., & Chilton, C. H. (1973). *Chemical engineer's handbook*. New York, NY: McGraw-Hill Co.

Polachini, T. C., Betiol, L. F. L., Lopes-Filho, J. F., & Telis-Romero, J. (2016). Water adsorption isotherms and thermodynamic properties of cassava bagasse. *Thermochimica Acta, 632*, 79-85. doi: 10.1016/j.tca.2016.03.032

Santos, I. J. (1999). *Efeito da temperatura de secagem nas atividades da alfa e betaamilase durante o processo de malteação de cevada (Hordeum vulgare L.) para produção de cerveja*. Viçosa, MG: Universidade Federal de Viçosa.

Sharma, P., Singh, H., & Rosell, C. M. (2011). Effects of roasting on barley b-glucan, thermal, textural and pasting properties. *Journal of Cereal Science, 53*(1), 25-30. doi: 10.1016/j.jcs.2010.08.005

Smith, S. E. (1947). The sorption of water vapor by high polymers. *Journal of the American Chemical Society, 69*(3), 646-651. doi: 10.1021/ja01195a053

Spiess, A.-N., & Neumeyer, N. (2010). An evaluation of R2 as an inadequate measure for nonlinear models in pharmacological and biochemical research: a Monte Carlo approach. *BMC Pharmacology, 10*, 6. doi: 10.1186/1471-2210-10-6

Thys, R. C. S., Noreña, C. P. Z., Marczak, D. L. F., Aires, A. G., & Cladera-Olivera, F. (2010). Adsorption isotherms of pinhão (*Araucaria angustifolia* seeds) starch and thermodynamic analysis. *Journal of Food Engineering, 100*(3), 468-473. doi: 10.1016/j.jfoodeng.2010.04.033

Togrul, H., & Arslan, N. (2007). Moisture sorption isotherms and thermodynamic properties of walnut kernels. *Journal of Stored Products Research, 43*(3), 252-264. doi: 10.1016/j.jspr.2006.06.006

Torres, M. D., & Seijo, J. (2016). Water sorption behaviour of by-products from the rice industry. *Industrial Crops and Products, 86*, 273-278. doi: 10.1016/j.indcrop.2016.04.014

Van den Berg, C., & Bruin, S. (1981). Water activity and its estimation in food systems: theoretical aspects. In G. F. Stewart & L. B. Rockland (Eds.), *Water activity: Influences on food quality* (p. 2-61). New York, NY: Academic Press.

Wani, S. A., & Kumar, P. (2016). Moisture sorption isotherms and evaluation of quality changes in extruded snacks during storage. *LWT - Food Science and Technology, 74*, 448-455. doi: 10.1016/j.lwt.2016.08.005

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