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## Water sorption kinetics of damaged beans: GAB model

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### Key words:

hysteresis  
adsorption  
desorption  
*Phaseolus vulgaris* L.

### ABSTRACT

The objective of this study was to model the water sorption kinetics of damaged beans. Grains with initial moisture content of 53.85%, dry basis (d.b.), were used. One portion of the grains was used to obtain desorption isotherms, while the other was subjected to drying until the moisture content of 5.26% (d.b.), so that it was subjected to the adsorption. For the induction of damage, a Stein Breakage Tester was used. To obtain the equilibrium moisture content, grains were placed in a climatic chamber at 20, 30, 40 and 50 ± 1 °C combined with relative humidity of 30, 40, 50, 70 and 90 ± 3%. The GAB model fitted well to the equilibrium moisture experimental data of damaged grains and control. With increasing temperature, the monolayer moisture contents decreased in adsorption and desorption processes, ranging from 9.84 to 5.10% d.b. The lower moisture content in the monolayer in damaged grains indicates that lower moisture content is necessary to ensure their conservation.

### Palavras-chave:

histerese  
adsorção  
dessorção  
*Phaseolus vulgaris* L.

## Cinética de sorção de água de grãos de feijão danificado: Modelo de GAB

### RESUMO

Objetivou-se, neste trabalho, modelar a cinética de sorção de água de grãos de feijão danificado. Foram utilizados grãos com teor de água inicial de 53,85% base seca (bs). Parte dos grãos foi utilizada para se obter as isotermas de dessorção enquanto outra foi submetida à secagem até o teor de água de 5,26% (bs), para que a mesma fosse submetida à adsorção. Para a indução da danificação foi utilizado um Stein Breakage Tester. Visando obter o teor de água de equilíbrio, os grãos foram colocados em câmara climática cujas temperaturas foram de 20, 30, 40 e 50 ± 1 °C combinadas com umidades relativas de 30, 40, 50, 70 e 90 ± 3%. O modelo de GAB ajustou-se bem aos dados experimentais de equilíbrio higroscópico de grãos danificados e testemunha. Com o aumento de temperatura os valores do teor de água da monocamada diminuíram para processos de adsorção e dessorção variando entre 9,84 a 5,10% b.s. O menor teor de água da monocamada nos grãos danificados indica que é necessário menor teor de água para garantir sua conservação.



## INTRODUCTION

The mechanical injuries caused by the mechanization of agricultural activities constitute an almost inevitable problem and result mainly from harvest, processing, storage and transport. There are various factors causing these damages in seeds and grains, such as the forces applied to separate them from their containing structure, threshing cylinder rotation, moisture content, genotypic characteristics of the product, falls in the silos, efforts of compression due to the column above them, etc.

Immediate damages are those visible to naked eye, such as integument rupture and separated and broken cotyledons. On the other hand, latent damages occur in the storage with the reduction in the physiological quality of the product, represented by microscopic cracks, abrasions and internal damages in the embryo (Costa et al., 1979). Particularly, common bean is sensitive to these damages because its embryo axis is located under a not much thick integument, which provides almost no protection (Almeida et al., 2004).

Factors such as temperature, relative humidity, physical structure and chemical composition directly influence water sorption in porous and hygroscopic materials, like agricultural products (Gunasekaran & Muthukumarappan, 1993); however, little is known about how the mechanical damage can interfere with the water sorption processes. Thus, this study aimed to represent the water sorption kinetics of damaged bean grains using the GAB model to obtain parameters with physical meaning, which represent the process and can be used in the development and/or improvement of post-harvest equipment.

## MATERIAL AND METHODS

The experiment used grains of common bean (*Phaseolus vulgaris* L.) with initial moisture content of 53.85% (d.b.), of the red group, which were harvested and threshed manually to avoid as much as possible any type of mechanical damage.

One portion of these grains was used to obtain the desorption isotherms and the other was subjected to drying at temperature of 40 °C until the moisture content of 5.26% (d.b.), so that it was later subjected to the adsorption process.

The moisture content of the product was determined by the gravimetric method, in an oven at  $105 \pm 1$  °C, for 24 h, in three replicates (BRASIL, 2009).

Mechanical damage was induced using, as source of impact, a Stein Breakage Tester, model M-CK2. This device has an aluminum cylinder and a helix that spins at constant rotation of 1800 rpm, which throws the product against the walls of the cylinder, promoting impacts and abrasion. Thus, the grains had broken parts and abrasion on the surface.

The samples of the product were subjected to mechanical damage, for 4 min. The damage level in the product was indirectly evaluated based on the electrical conductivity of the solution of the bean grain exudates using a portable conductivity meter (Digimed, model DM3). This test used three subsamples of 50 grains from each treatment (with and without damage). The samples were placed in plastic cups with 75 mL of deionized water and maintained in a chamber with

temperature controlled at 25 °C for 24 h (Santos et al., 2011). The bean samples subjected to induced mechanical damage showed mean electrical conductivity of grain exudates of  $152.38 \pm 0.05 \mu\text{S cm}^{-1} \text{g}^{-1}$ , while the control sample showed mean value of  $29.88 \pm 0.03 \mu\text{S cm}^{-1} \text{g}^{-1}$ .

To obtain the hygroscopic equilibrium moisture content through the dynamic method (Brooker et al., 1992), the grains were placed inside a climatic chamber with control of temperature and relative humidity. The temperatures were 20, 30, 40 and  $50 \pm 1$  °C, combined with relative humidity values of 30, 40, 50, 70 and  $90 \pm 3\%$ . Three replicates were used for each condition of temperature and relative humidity.

The Guggenheim-Anderson-de Boer (GAB) model (Eq. 1) was fitted to the observed data of hygroscopic equilibrium.

$$U_e = \frac{x_m \cdot k \cdot C \cdot a_w}{(1 - k \cdot a_w) [1 + (C - 1)k \cdot a_w]} \quad (1)$$

where:

$U_e$  - equilibrium moisture content, % d.b.;

$x_m$  - monolayer moisture content, % d.b.;

$a_w$  - water activity, decimal; and,

C and k - GAB model parameters respectively related to the properties of the monolayer and multilayers, dimensionless.

After obtaining the coefficients of the GAB model, the enthalpy values associated with the variation of each coefficient with the temperature were calculated through the graphical representation of  $\ln(x_m)$ ,  $\ln(C)$  and  $\ln(k)$  versus the inverse of absolute temperature ( $T^{-1}$ ) (Simal et al., 2000).

$$k = k_0 \exp\left(\frac{\Delta H_k}{RT}\right) = k_0 \exp\left(\frac{H_L - H_n}{RT}\right) \quad (2)$$

$$C = C_0 \exp\left(\frac{\Delta H_c}{RT}\right) = C_0 \exp\left(\frac{H_m - H_n}{RT}\right) \quad (3)$$

$$x_m = x_0 \exp\left(\frac{\Delta H_x}{RT}\right) \quad (4)$$

where:

$k_0$  and  $C_0$  - pre-exponential factors, dimensionless;

$x_0$  - pre-exponential factor, % d.b.;

$H_m$  - sorption enthalpy of the monolayer,  $\text{kJ mol}^{-1}$ ;

$H_n$  - sorption enthalpy of the multilayer,  $\text{kJ mol}^{-1}$ ;

$H_L$  - sorption enthalpy of liquid water,  $\text{kJ mol}^{-1}$ ;

$\Delta H_x$  - parameter to express the dependence of the monolayer moisture content on the temperature,  $\text{kJ mol}^{-1}$ ;

R - universal gas constant,  $\text{kJ mol}^{-1} \text{K}^{-1}$ ; and,

T - temperature, K.

The model was fitted through nonlinear regression by the Gauss-Newton method, using the software Statistica 7.0<sup>®</sup> (Statsoft, 2004). The degree of fit of the model was evaluated based on the magnitude of the coefficient of determination ( $R^2$ ), estimated mean error (Eq. 5), relative mean error (P) (Eq. 6) and the residual distribution.

$$SE = \sqrt{\frac{\sum_{i=1}^n (Y_i - \hat{Y}_i)^2}{RDF}} \tag{5}$$

$$P = \frac{100}{n} \sum_{i=1}^n \frac{|Y_i - \hat{Y}_i|}{Y_i} \tag{6}$$

where:

$Y_i$  - observed value;

$\hat{Y}_i$  - estimated value;

$n$  - number of observed data; and,

RDF - residual degrees of freedom (number of observed data minus the number of parameters of the model).

### RESULTS AND DISCUSSION

Table 1 shows the coefficients and statistical parameters of the GAB model fit, relative to damaged and control bean grains, at different temperatures.

According to Table 1, the GAB model satisfactorily fitted to the hygroscopic equilibrium data of damaged and control bean grains, since the statistical parameters are consistent with those recommended by many researchers (Resende et al., 2014; Chaves et al., 2015; Sousa et al., 2015), i.e., high coefficient of determination, relative mean error of up to 10% and reduced estimated mean error. However, according to Oliveira et al. (2011), these three statistical parameters only

Table 1. Coefficients and statistical parameters of the GAB model fit, relative to damaged and control bean grains, at different temperatures

Parameters	Temperature (°C)			
	20	30	40	50
Adsorption of damaged beans				
$x_m$	7.6902**	7.4261**	7.2066**	7.0425**
$k$	0.8382**	0.8411**	0.8437**	0.8458**
$C$	9.8118**	8.8089**	7.3273**	5.8583**
P (%)	5.2454	3.1433	4.4579	3.6465
SE	0.8023	0.6355	0.8803	0.4463
$R^2$	0.9795	0.9974	0.9958	0.9987
Adsorption of control beans				
$x_m$	7.1884**	6.6859**	6.3852**	6.2025**
$k$	0.8702**	0.8792**	0.8862**	0.8940**
$C$	10.3527**	9.5831**	8.8463**	8.3340**
P (%)	6.8534	2.8797	1.8006**	3.4920**
SE	1.0063	0.4409	0.2226	0.4215**
$R^2$	0.9715	0.9990	0.9997	0.9989
Desorption of damaged beans				
$x_m$	9.1319**	7.7679**	6.6347**	5.1039**
$k$	0.7788**	0.8333**	0.8781**	0.9135**
$C$	11.4646**	20.0855**	29.9641**	40.4473**
P (%)	3.2679	4.9384	7.1446	4.6606
SE	0.6052	1.0855	1.0495	0.5645
$R^2$	0.9849	0.9928	0.9948	0.9979
Desorption of control beans				
$x_m$	9.8475**	8.1662**	6.6859**	5.6549**
$k$	0.7711**	0.8187**	0.8607**	0.8954**
$C$	9.5124**	16.7156**	29.2833**	45.7586**
P (%)	4.0072	4.2403	6.2592	1.8746
SE	0.6984	1.2008	1.9059	0.2827
$R^2$	0.9829	0.9917	0.9832	0.9995

\*\*Significant at 0.01 probability level by t-test

are not sufficient to ensure correct evaluation of adequacy of a model. Analysis of residuals is necessary, because the model may exhibit biased distribution, being ineffective to represent the experimental data, despite showing good statistical parameters. Hence, Figure 1 was elaborated to indicate that the residual distribution for damaged and control bean grains in the adsorption and desorption was random.

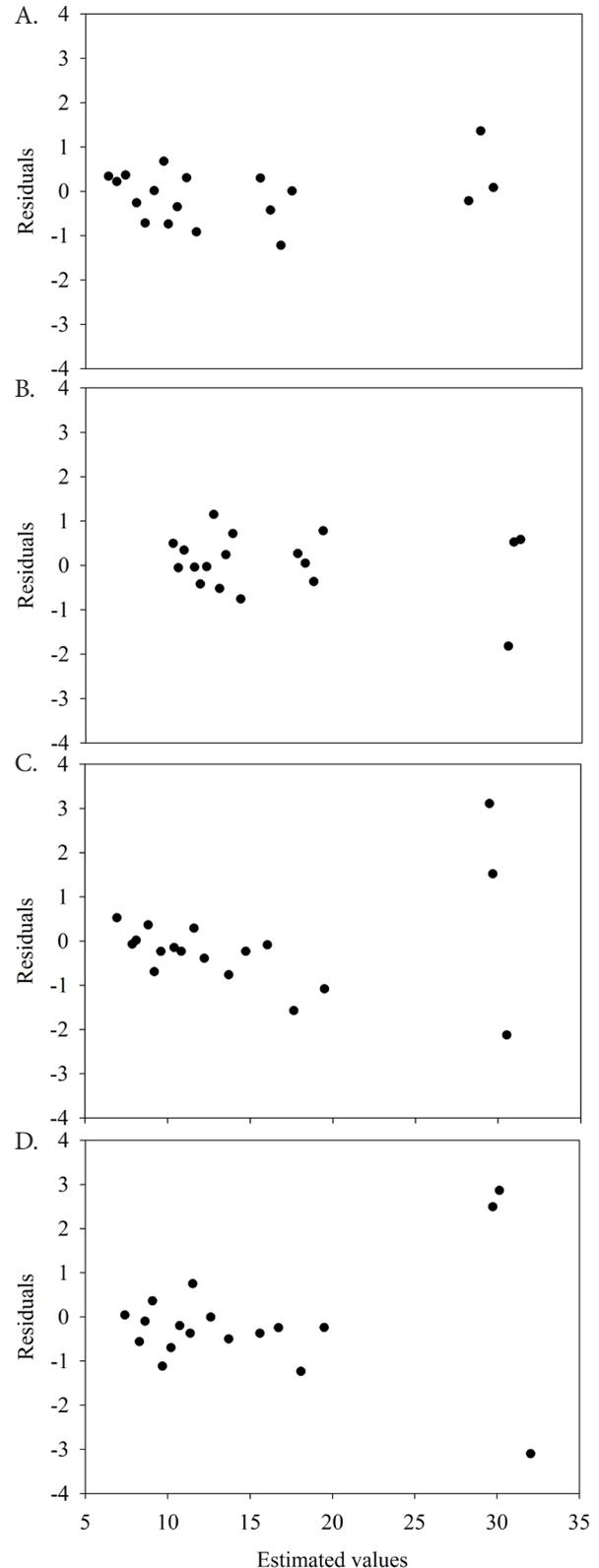


Figure 1. Residual distribution of the GAB model: (A) damaged - adsorption, (B) control - adsorption, (C) damaged - desorption and (D) control - desorption

Since the monolayer moisture content indicates the amount of water strongly bound to specific regions in the food, this is a value that must be achieved to ensure stability of the foods (Lavoyer et al., 2013). In products with moisture content lower than the monolayer moisture content, lower deterioration is expected, because the water is strongly bound to the food and does not participate in reactions (Dalgiç et al., 2012). As the temperature increases, the values of monolayer moisture content for both processes ranged between 9.84 and 5.10% (d.b.). In the literature, this phenomenon has been attributed to the reduction in the number of active sites and to the high vapor pressure inside the grain at high temperatures, which makes water available to act in reactions of deterioration (Kaleemullah & Kailappan, 2007; Perdomo et al., 2009).

The lower monolayer moisture content observed for damaged beans, compared with the control, in the desorption, indicates that it is necessary to reach a lower moisture content to ensure conservation. This can be explained by the fact that the cells are more exposed and, consequently, the water is bound with less energy to the matrix of the product (Botelho, 2009). On the other hand, in the adsorption, the opposite result was observed. Probably, with the damage, the starchy compounds of the porous matrix, which are highly hydrophilic, remain more exposed.

The parameter  $C$  is associated with the differences of chemical potentials between the monolayer and the upper layers. This parameter represents the binding energy of the water molecules in the monolayer with the sorption sites on the surface of the product. The higher the  $C$  value, the stronger the bond (Quirijns et al., 2005). In the adsorption process, there was a reduction of this binding energy with the increment of temperature, undoubtedly due to the higher excitation state of the water molecules at high temperatures. Likewise, there were lower values for the damaged sample, due to the rupture of some cell structures that can affect the sorption sites on the surface. In the desorption process, the opposite phenomenon occurred. The highest values of the parameter  $C$  were observed at high temperatures, a phenomenon that may be related to the superficial hardening that occurs when the speed of superficial evaporation exceeds the speed of moisture diffusion inside the product (Potter & Hotchkiss, 1995), which alters the physical structure of the grains, closing their pores.

The parameter  $k$  is a correction factor for the water molecules of the multilayer. When its value is closer to 1, the characteristics of the water molecules become closer to those of pure water, i.e., the vaporization heat is close to the water heat of vaporization (Quirijns et al., 2005). For both processes, the parameter  $k$  has a direct relationship with the temperature, being more accentuated in the desorption, because the latent heat of vaporization decreases with the temperatures.

The estimated coefficients and enthalpies associated with the GAB model for damaged and control bean grains are presented in Table 2.

The negative values of  $\Delta H_k$  indicate that the water molecules are bound with less energy in the multilayer. The sorption heat of the multilayer is higher than the water heat of condensation,

Table 2. Estimated coefficients and enthalpies associated with the GAB model for damaged and control bean grains

Parameters	Adsorption		Desorption	
	Damaged	Control	Damaged	Control
$x_{m0}$	2.9633	1.4566	0.0206	0.0239
$H_x$ (kJ mol <sup>-1</sup> )	2.3198	3.8678	14.9281	14.6825
$K_0$	0.9244	1.1608	4.3870	5.4477
$H_k$ (kJ mol <sup>-1</sup> )	-0.2382	-0.7017	-4.1937	-4.7899
$C_0$	0.0388	0.9734	$7.9423 \times 10^6$	$2.4383 \times 10^8$
$H_c$ (kJ mol <sup>-1</sup> )	13.5676	5.7604	-33.0574	-41.5633

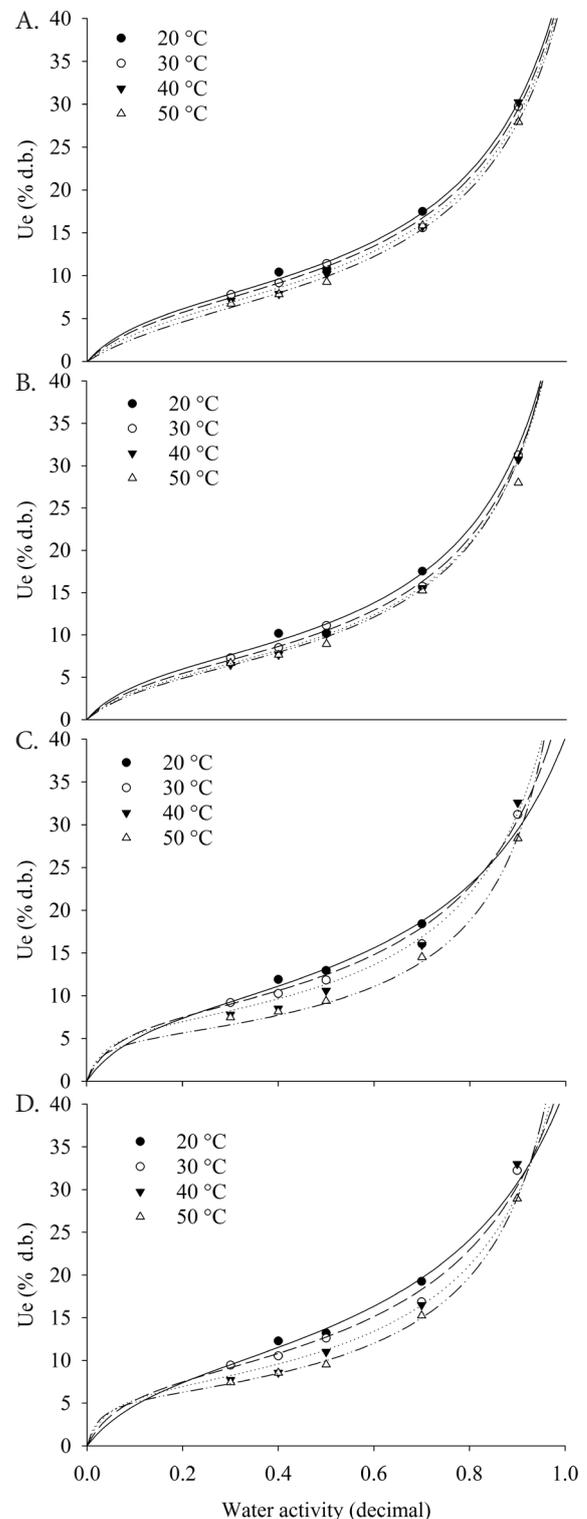


Figure 2. Sorption isotherms of bean grains: (A) Adsorption - Damaged, (B) Adsorption - Control, (C) Desorption - Damaged and (D) Desorption - Control

due to the endothermal dissolution of molecular solutes (Bensebia & Allia, 2016). The differences between adsorption and desorption for the differential value  $\Delta H_c$  indicate the irreversibility of the process. The positive values for the adsorption process and negative values for the desorption process are due to the exothermal and endothermal natures, respectively.

The water sorption isotherms of bean grains are presented in Figure 2.

There is an increase in the equilibrium moisture content with the increment in water activity for a value of constant temperature. The curves showed a sigmoid shape, type II, according to the classification of Brunauer et al. (1940).

The equilibrium moisture contents decreased with the increment of temperature for a constant value of water activity. This occurs due to the reduction of the available sites in the product for water molecules to bind, caused by its higher mobility with the increment of temperature; thus, the amount of sorbed water changes.

Figure 3 shows the hysteresis at 20 °C for damaged and control bean grains.

The equilibrium isotherms demonstrate that the adsorption curve is below the desorption curve in almost all the interval of water activity. According to Ayrosa (2005), this occurs because of the phenomenon of hysteresis, which requires a lower vapor pressure to reach the correct moisture content by the desorption process, compared with the adsorption process.

Caurie (2007) reports that hysteresis can be used as food quality index, since its increase indicates reduction in the stability of the food. On the other hand, its reduction or absence points to better stability of the stored products.

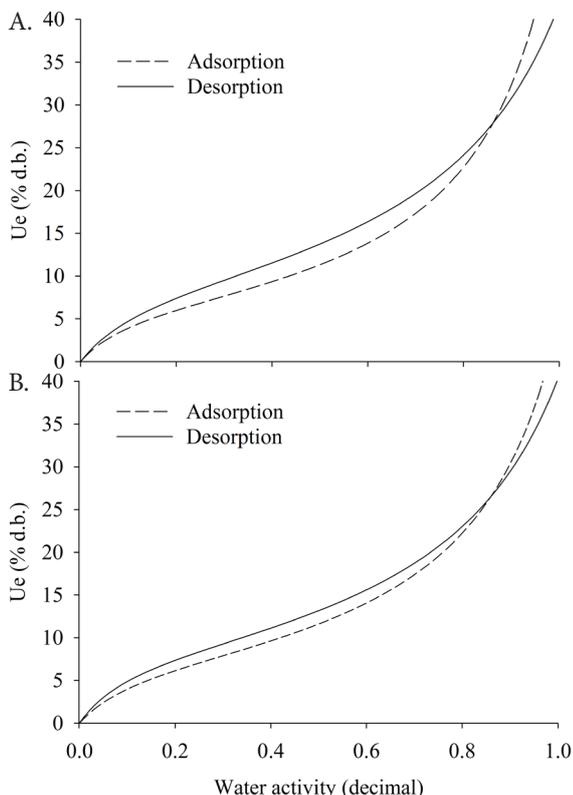


Figure 3. Hysteresis at 20 °C: (A) control and (B) damaged beans

## CONCLUSIONS

1. The GAB model fitted well to the experimental data of hygroscopic equilibrium of damaged and control bean grains.

2. The lower monolayer moisture content in damaged bean grains in the desorption indicates that it is indispensable to reach a lower moisture content to ensure stability and conservation.

3. In the adsorption process, the parameter C decreased with the increment of temperature. In the desorption, the opposite occurred. The parameter k showed direct relationship with the temperature, being more accentuated in the desorption.

4. The equilibrium moisture contents decreased with the increase of temperature for a constant value of water activity. The phenomenon of hysteresis was observed, reaching values between 2.19 and 2.42 in the control and 1.35 and 1.56 in damaged grains at 20 °C.

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