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Water adsorption isotherms and thermodynamic properties of cassava bagasse

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Highlights

Adsorption isotherms and composition of cassava bagasse were determined>

GAB equation was the best-fitted model to sorption data of type II isotherm>

Isosteric heat of sorption was calculated in a range of equilibrium moisture content>

Differential enthalpy and entropy confirmed the isokinetic compensation theory>

Water adsorption by cassava bagasse is considered an enthalpy driven process>

Abstract

Losses of food industry are generally wet products that must be dried to posterior use and
storage. In order to optimize drying processes, the study of isotherms and thermodynamic
properties become essential to understand the water sorption mechanisms of cassava bagasse.
For this, cassava bagasse was chemically analyzed and had its adsorption isotherms determined
in the range of 293.15 to 353.15 K through the static gravimetric method. The models of GAB,

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Halsey, Henderson, Oswin and Peleg were fitted, and best adjustments were found for GAB model with $R^2 > 0.998$ and no pattern distribution of residual plots. Isosteric heat of adsorption and thermodynamic parameters could be determined as a function of moisture content. Compensation theory was confirmed, with linear relationship between enthalpy and entropy and higher values of isokinetic temperature ($T_B = 395.62$ K) than harmonic temperature. Water adsorption was considered driven by enthalpy, clarifying the mechanisms of water vapor sorption in cassava bagasse.

Keywords: isotherm of sorption, entropy, enthalpy, isokinetic temperature, compensation theory.

1. Introduction

Worldwide, several studies have been developed to encourage more efficient applications of byproducts and/or residues from agroindustry. They intend to satisfy environmental and economic concerns by exploring valuable properties in food wastes. The big availability of these raw materials is a result from the large food processing in countries with economy based on agriculture, such as Brazil. It implies in the generation of many kinds of residues, including orange seeds/skin, sugarcane bagasse, coffee pulp/husks, corn stover, peanut shells, grape pomace and cassava bagasse.

Cassava bagasse, specifically, is a residue obtained from the starch extraction process from cassava. It is a fibrous material that still presents approximately 50% of residual starch in the dry matter. In addition to that, the relative low contents in proteins and ashes reinforce advantages to the application of bioconversion processes in comparison to other residues [1]. The poor conditions of starch extraction plants cause a low efficiency of 25% based on wet material and

consequently an annual amount of almost 2 million tons of wet cassava bagasse, solely in Brazil [2].

The main problem found during residues management is linked to their handling. The majority of resources should pass through a moisture removal procedure to reduce mass and volume. The dehydration process is one capable way to minimize the storage and transportation costs, besides extending the product shelf life and maintaining the initial characteristics until its destination [3]. The knowledge of water sorption behavior becomes a necessary study to correctly design equipment and drying processes [4]. The use of more accurate methods on the product drying can avoid undesirable effects that may occur on the composition [5, 6]. Therefore, sorption isotherms appear to provide information about equilibrium moisture content (X_{eq}) and water activity (a_w) by simulating different relative humidity in equilibrium with the product. Sorption properties are useful in drying kinetics studies involving the application of Fick's law for thin layers of wet residues (Equation 1), for example:

$$\frac{\overline{X} - X_{eq}}{X_0 - X_{eq}} = 2\sum_{n=0}^{\infty}\frac{1}{\gamma_n^2}\exp\left(-\gamma_n^2 Dt \Big/ l^2\right) \tag{1}$$

Where $\overline{X}$ is the average moisture content in the product, X_0 is the initial moisture content, D is the diffusion coefficient, l is the characteristic dimension, t is time and $\gamma_n^2 = (2n+1)\dfrac{\pi}{2}$.

The determination and modeling of sorption isotherms in different temperatures gives information about the product conditions during storage, since the material stability can be predicted by the availability of water molecules in front of variations in temperature and relative humidity [7]. Moreover, the degree of interactions between water molecules and the residue matrix is as important as the amount of water molecules. It can be measured by the isosteric heat

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of sorption and many other thermodynamic functions capable of being calculated by isotherms data [8, 9].

Thermodynamic parameters are variables responsible by providing insights about the material microstructure, as well as theoretical interpretations for matrix–water interactions [10]. Among them, it could be found the differential enthalpy, differential entropy and free Gibbs energy. Differential enthalpy is valuable for designing equipment involved in water removal processes, once it represents the binding strength of water to the food compounds. On the other hand, differential entropy represents the amount of available sorption sites in a specific energy level [11]. Free Gibbs energy intend to correlate these two functions, corresponding qualitatively to the difference between the total energy available (enthalpy) and the unavailable energy (entropy) [10]. The presence of a linear correlation states that the isokinetic, or enthalpy–entropy, compensation theory exists due to changes in the sorbent-sorbate interaction. The corresponding slope is the isokinetic temperature, representing the temperature at which all reactions in series proceed at the same rate.

Thus, this work intended to characterize the composition of cassava bagasse and present the water sorption properties of cassava bagasse. Among the water sorption properties, adsorption isotherms of powdered cassava bagasse were acquired and modeled in different moisture and temperature conditions. In addition, the application of experimental data of isotherms was used to evaluate thermodynamic properties and the enthalpy-entropy compensation theory, clarifying the water adsorption mechanisms.

2. Material and methods

2.1. Raw material

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The cassava bagasse was obtained directly from a starch extraction industry in northwest of São Paulo state, Brazil. The industrial waste was collected at the entrance of the storage silo and transported in coolers until the Laboratory of Physical Measurements of UNESP (Campus of São José do Rio Preto), where it was stored in plastic bags at 258.15 K in a freezer. The bagasse was naturally thawed to proceed to the analyses.

In order to carry out the isotherms analyses, cassava waste was dried in a convective tray dryer as reported by Rosa et al. [4] at 323.15 K by approximately 24 hours. The dried waste was then milled using a rotor mill (model MA340, Marconi, Piracicaba, São Paulo, Brazil) equipped with a 30 mesh sieve to obtain a powdered cassava bagasse with particle size less than 595 μm.

Saturated salt solutions were prepared to obtain an a_w range from 0.046 to 0.873 using lithium bromide (LiBr), lithium chloride (LiCl), lithium iodide (LiI), potassium acetate (CH$_3$OOK), magnesium chloride (MgCl$_2$), magnesium nitrate (Mg(NO$_3$)$_2$), sodium bromide (NaBr), sodium nitrate (NaNO$_3$), sodium chloride (NaCl), potassium bromide (KBr) and potassium chloride (KCl), obtained from Sigma-Aldrich (St. Louis, MO, USA). Table 1 contains the specifications for each salt.

2.2. Cassava bagasse composition

Eleven samples of wet fibrous mass of cassava of different production days were acquired from the starch extraction industry. They were characterized with respect to moisture and dry matter in an overnight oven at 378.15 K, ashes in a muffle at 823.15 K by 4 hours, fats by Soxhlet extraction, proteins by micro-Kjeldahl method and carbohydrates content by difference. All methods were applied as recommended by AOAC [12].

2.2. Experimental analysis

Static gravimetric method was used to determine the isotherms of water sorption along the temperature range [13]. Different equilibrium relative humidites ($RH = a_w \times 100$) were reached by using glass desiccators with saturated salt solutions of LiBr, LiCl, LiI, CH_3OOK, $MgCl_2$, $Mg(NO_3)_2$, NaBr, $NaNO_3$, NaCl, KBr and KCl dissolved into de-ionized water. The temperature of desiccators were set in a controlled temperature chambers type BOD (MA415, Marconi, Piracicaba, Brazil) to maintain temperatures of 293.15, 303.15, 313.15 K and an oven (MA030, Marconi, Piracicaba, Brazil) for higher temperatures of 323.15, 328.15, 338.15, 343.15, 348.15 and 353.15 K. All experiments were carried out at atmospheric pressure P_{atm}=95.47 kPa, measured by a barometer. Table 2 contains all values of a_w obtained from the study reported by Labuza [14] for each salt solution versus experimental data of X_{eq} at each specific temperature. Approximately 3.0 g of powdered cassava bagasse in triplicate were weighed in small containers and placed into the desiccator. Samples were previously weighted and had the initial moisture content determined. The weights of the samples were measured every 4 days using an analytical balance (AUW220D, Shimadzu, Japan) until reach constant weight (about 4 weeks). Throughout the weight difference from the initial moisture, the equilibrium moisture content (X_{eq}) of each condition was determined.

2.3. Isotherms modeling

The mean equilibrium moisture content was plotted against water activities to represent the water adsorption by the nine isotherms obtained. Although isotherms provide information about equilibrium moisture, their modeling also gives water activity values for specific equilibrium moisture content. Using the software OriginPro 8.0 (OriginLab Corporation, Northampton, MA,

USA), non-linear regressions were performed to adjust the mathematical models commonly found in literature, such as:

Peleg's model [15]:

$$X_{eq} = k_1 a_w^{n_1} + k_2 a_w^{n_2}$$ (12)

Halsey's model [16]:

$$X_{eq} = \left(-h_1 \ln(a_w)\right)^{-\frac{1}{h_2}}$$ (13)

Henderson's model [17]:

$$X_{eq} = \left(-\frac{1}{H_1} \ln(1 - a_w)\right)^{\frac{1}{H_2}}$$ (14)

Oswin's model [18]:

$$X_{eq} = M\left(\frac{a_w}{1 - a_w}\right)^{N}$$ (15)

Guggenheim, Anderson and de Boer – GAB model [19], which has been widely applied in foodstuffs:

$$X_{eq} = \frac{X_m C k a_w}{\left(1 - Ka_w\right)\left(1 + \left(C - 1\right)Ka_w\right)}$$ (16)

Where k_1, k_2, n_1, n_2, h_1, h_2, H_1, H_2, M, N, k, C and X_m are constants of de models.

The fit accuracy for each model was evaluated based on the adjusted coefficient of determination (R_{adj}^2), the root mean square error (*RMSE*) and residual distribution. Adjustments with low R_{adj}^2 and high *RMSE* and/or clear pattern in residual plots should be discarded [20].

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2.4. Thermodynamic approach

The temperature dependence of the isotherm can be represented by the net isosteric heat of adsorption, which assumes to be invariant with temperature. Plotting $\ln(a_w)$ as a function of $(1/T)$ in a fixed equilibrium moisture, the net isosteric heat of sorption or enthalpy of sorption (q_{st}) can be determined by the slope from Clausius-Clapeyron equation (Equation 17). The application of this method requires the measurement of adsorption isotherms at least three temperatures [21]. In addition, the q_{st} is also defined as the difference between integral heat of sorption (Q_{st}) and the heat of vaporization of water (λ) [10]:

$$\frac{\partial\left(\ln a_w\right)}{\partial\left(1/T\right)}\bigg|_{X_{eq}} = -\frac{Q_{st}-\lambda}{R} = -\frac{q_{st}}{R} \tag{17}$$

After obtained values of q_{st}, it is common to express the net isosteric heat of sorption as a function of equilibrium moisture content by Riedel's equation:

$$q_{st} = C_r \exp\left(-B_r X_{eq}\right) \tag{18}$$

Since thermodynamic properties can express the behavior of water adsorption, Equation (18) represents the variation in molar differential entropy of adsorption (ΔS) by Gibbs-Helmholtz equation:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{19}$$

Considering that Gibbs free energy is calculated as:

$$\Delta G = RT \ln a_w \tag{20}$$

Combining Equation (19) and Equation (18), the change in Gibbs free energy is expressed by variations on both enthalpy and entropy, resulting in Equation (21):

$$\ln a_w = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{21}$$

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In this way, enthalpy of adsorption and entropy can be calculated from Equation (21) by same procedure as described for net isosteric heat of sorption, extracting values of slope ($\Delta H/R$) and the linear coefficient ($\Delta S/R$).

Correlating the obtained values of ΔH versus ΔS for adsorption data, a linear tendency is expected to confirm the compensation theory for adsorption [22]:

$$\Delta H = T_B(\Delta S) + \Delta G_B \tag{22}$$

In this relation, T_B is the isokinetic temperature and represents the temperature at which all reactions in the series proceed at the same rate.

Another test for validating the compensation theory is comparing the isokinetic temperature with the harmonic mean temperature T_{hm} [23, 24], that is defined as:

$$T_{hm} = \frac{n}{\sum_{i=1}^{n}(1/T)} \tag{23}$$

For a $(1-\alpha)100\%$ confidence interval, T_B may be calculated from:

$$T_B = T_B \pm t_{m-2,\alpha/2}\sqrt{\text{Var}(T_B)} \tag{24}$$

Where

$$T_B = \frac{\sum(\Delta H - \overline{\Delta H})(\Delta S - \overline{\Delta S})}{\sum(\Delta S - \overline{\Delta S})^2} \tag{24}$$

$$\text{Var}(T_B) = \frac{\sum(\Delta H - \overline{\Delta G_B} - T_B\Delta S)^2}{(m-2)\sum(\Delta S - \overline{\Delta S})^2} \tag{25}$$

And m is the number of (ΔH, ΔS) data pairs, $\overline{\Delta H}$ the average enthalpy, and $\overline{\Delta S}$ the average entropy.

3. Results and discussion

3.1. Cassava bagasse composition

Cassava bagasse composition was chemically determined based on analyses of eleven samples collected in eleven different days of starch production. It allowed the evaluation of the changes on waste composition to provide significant data.

By composition data presented in Table 3, the moisture content of cassava bagasse showed high values ranging from 81.08 to 85.92% (w. b.), which confirms the necessity of drying process to remove water and extend the storage for longer periods until its destination. Relatively low contents of proteins, ashes and fats were evidenced, and their variations could be related to the use of different cassava varieties and to the poor conditions found in cassava processing [1]. The dry matter content was similar to those encountered by Teixeira et al. [25] (17.5%) and Cereda [26] (14.88%) for cassava bagasse. It was evidenced that dry matter is mainly composed by carbohydrates, reaching a value of 82.85% (d. b.). Many authors have highlighted great contents (>50%) of starch in this dry matter [1, 26, 27]. Starch is a compound with valuable properties and can be used in various processes. Its composition of glucose monomers bounded by α-(1,4) linkage emphasizes the capacity of release fermentable matter as substrate for microorganisms and for bioethanol production.

3.2. Adsorption isotherms

Values of equilibrium moisture content (X_{eq}) and water activity (a_w) were obtained in the range of 0.024 to 0.269 g/g dried matter and 0.046 and 0.873, respectively. Equilibrium moisture content decreased as the temperature increased at fixed water activities, while an increase was observed in X_{eq} with increasing water activity values at a stablished temperature. Data pairs (X_{eq},

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a_w) were plotted and fitted to Equations (12)-(16) for all temperatures. By the graph in Figure 1, curves shape seemed to follow a sigmoid behavior, typical of type II isotherms [28]. This kind of isotherm can be classified into three regions: the first one correspond to the monolayer moisture strongly bounded into the product matrix; the second is almost linear, corresponding to the multilayered water; and the third region is related to the free water available for chemical reactions [29].

After evaluation of fitting parameters to the experimental data disposed in Table 4, Henderson model demonstrated the lower R^2_{adj} followed by Oswin and Halsey equation. Peleg's model indicated good accuracy of experimental data, but the quantity of parameters implied in lower R^2_{adj} and higher *RMSE* than GAB equation. In this way, the GAB model (Equation 15) showed to be the best form to represent adsorption isotherms, as shown in Figure 1 for some intermediate temperatures. Besides the adjustments to GAB equation had greater R^2_{adj} and lower *RMSE*, no pattern distribution in the residual plots was verified (Figure 2). According to Al-Muhtaseb et al. [9] and Telis et al. [30], GAB model is considered the most versatile model available in literature for sorption isotherms. The same authors concluded that GAB model represents adequately the sorption isotherms of starchy products, such as potato and wheat starch, and lignocellulosic materials such as persimmon skin.

Analyzing GAB parameters (C, k and X_m), it could be seen a similarity to those reported for bagasse dehydrate yacon [31], dried pulp of mango [32] and even composites of cassava bagasse [33]. As verified by Blahovec [34], values of C and k are in accordance with type II isotherms from Brunauer classification. In this classification, k has to be higher than 0 and less than 1, while C values should be higher than 2. Although lower values of C were expected as temperature increases [34], a not clear tendency could be verified for the whole range of

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temperature probably due to the regression methods used during the adjustments [35]. With respect to k, it is common to find higher values for dried material when compared to fresh products [36]. It confirms the tendency reported in this study, which observed increasing values of k as temperature gets higher and, consequently, equilibrium moisture content and monolayer moisture content decrease. Monolayer moisture content (X_m) assumes the role of the first shell of water that covers the sorbent surface. Above this value of moisture, there are the multilayers of water, representing less interaction with the food matrix than monolayer moisture [35]. In addition, X_m seemed to present highly dependence on temperature, where lower values were found when the temperature increases. It could be attributed to a reduction in active sorption sites due to changes in both physical and chemical aspects [37]. Specially in the case of adsorption phenomenon, Van den Berg [38] proposed that the few available sites for sorption have a greater binding energy on comparison to desorption isotherms. As known that cassava bagasse is very rich in starch, the decrease in monolayer moisture is related to the degree of hydrogen bonding when temperature increases, reducing the availability of active sites for water binding [39].

3.2. Thermodynamic properties

Water activities were determined for fixed equilibrium moisture content by GAB fitted equations in the different temperatures. It allowed to calculate the isosteric heat of adsorption (q_{st}) by Equation (17), which were plotted against equilibrium moisture content and fitted to Equation (18) (Figure 3). Riedel's equation could express q_{st} values as a function of moisture content with more than 98.2% of accuracy, with $C_r =72264.02$ J/mol and $B_r =24.35$. The higher values are encountered at lower moisture content, when water is strongly bonded into the material structure of cellulose fibers and starch granules. But, a rapid decrease occurs in the isosteric heat of

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sorption when moisture content begins to increase due to the adsorption of water molecules in the multilayer. The same exponential decrease was also observed for different products with great contents of sugar and starch such as grapes and potatoes, respectively [40].

Focusing on the thermodynamic approach, the behavior of water adsorption can be evaluated according to the differential enthalpy and entropy by Equation (17) in a range of X_{eq} from 0.05 to 0.30. As expected, the change in enthalpy was represented by negative values ranging from -21.55 to -0.85 kJ/mol while entropy presented positive values ranging from 53.88 to 1.74 J/mol. Both, in modulus, tend to lower values as the moisture content increases (Figure 4) and followed the same trend as hydrolyzed starch [41] and persimmon skin and pulp [30]. The enthalpy, similarly as isosteric heat of sorption, illustrates the required energy to do a useful work. At higher moisture contents, less energy is needed to remove a same amount of water in more dried sample due to the fewer available binding sites to promote sorption [42]. On the other hand, entropy represents lost work or energy not available to perform a determined process. Samples with low moisture content present higher values of entropy, indicating that more energy (or enthalpy values) is necessary to remove the water molecules in that conditions [10].

One first important requirement to confirm the enthalpy-entropy compensation theory, is the presence of a linear relationship between enthalpy and entropy. The linear tendency observed in Figure 5, with R^2_{adj} >0.999, means that the change in enthalpy is accompanied by simultaneous changes in both entropy and Gibbs free energy. In turn, Gibbs free energy tends towards to assume values around zero as the moisture content increases, indicating that dehydration process is more spontaneous when powdered cassava bagasse is adsorbed by multilayers of water molecules.

Using the same graph in Figure 5 and value of Var(T_B), the temperature at which all reaction in series occur at the same rate (T_B) was stablished at 395.62 ± 6.64 K [30]. The presence of higher values of T_B (above 300 K) were characteristics observed for products with high sugar or starch content such as potatoes, prune and apricot [43, 44]. If this temperature is different from harmonic temperature (T_{hm}), the second requirement to confirm a linear chemical compensation pattern is evidenced [23, 24]. Applying Equation (23), T_{hm} resulted in a value of 325.84 K, which is significant lower than isokinetic temperature (T_B) with 95% of confidence. Besides proving the isokinetic compensation theory, the study reported by Leffler [45] allowed to assume the water adsorption as an enthalpy driven process since $T_B > T_{hm}$.

4. Conclusions

The water sorption behavior of cassava bagasse was evaluated in order to optimize drying kinetics and minimize the energy expenses involved in dehydration processes. Thus, adsorption isotherms of powdered cassava bagasse were studied in temperatures from 293.15 to 353.15 K, presenting increasing values of equilibrium moisture content when relative humidity increased and temperature decreased. These data could be well-fitted to the GAB model with great accuracy (R^2_{adj} >0.998 and $RMSE$<0.001), making available data of monolayer moisture content from 0.056 to 0.033. Thermodynamic properties were determined as a function of equilibrium moisture content. In an interval of X_{eq} of 0.05–0.30, enthalpy and entropy values ranged from -21.55 to -0.85 kJ/mol and from 53.88 to 1.74 J/mol K, respectively. The linear relationship between them showed that lower energy is necessary to remove a certain amount of water at higher moisture contents, which is associated to the decrease in the number of available sites to sorption followed by a reduction of interactions between cassava bagasse matrix and water

molecules in the multilayer. This phenomenon makes the water removal process "more spontaneous" when cassava bagasse presents higher moisture contents. It was found a higher value of 395.62 ± 6.64 K for isokinetic temperature than for harmonic temperature (325.84 K), confirming the consideration of enthalpy driven process to water adsorption of cassava bagasse.

Acknowledgements

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Figure Captions

Figure 1. Adsorption isotherms fitted to GAB equation of powdered cassava bagasse in intermediate temperatures.

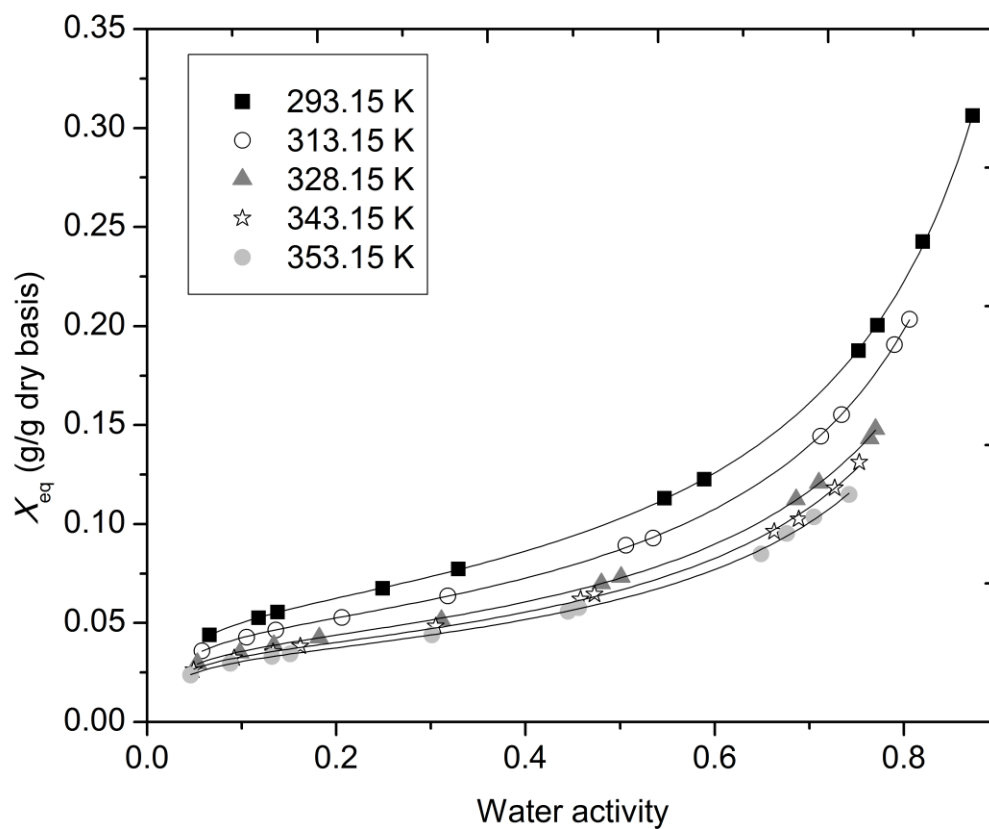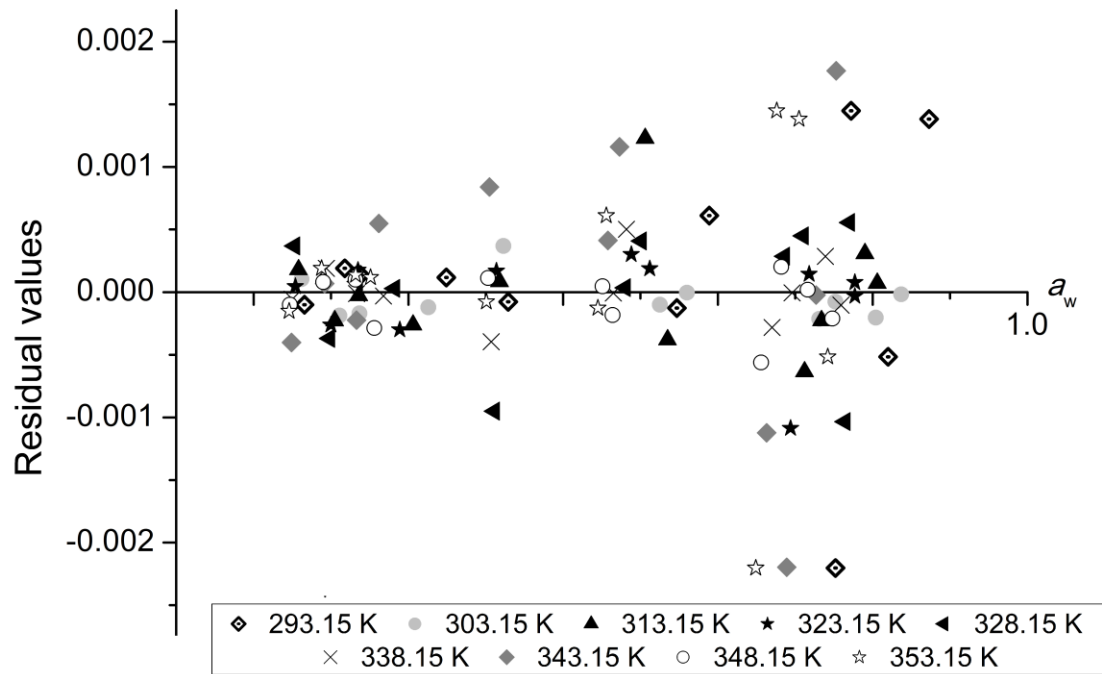

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Figure 2. Residual plot distributions for GAB equation in all temperatures.

Figure 3. Net isosteric heat of adsorption for powdered cassava bagasse as a function of equilibrium moisture content.
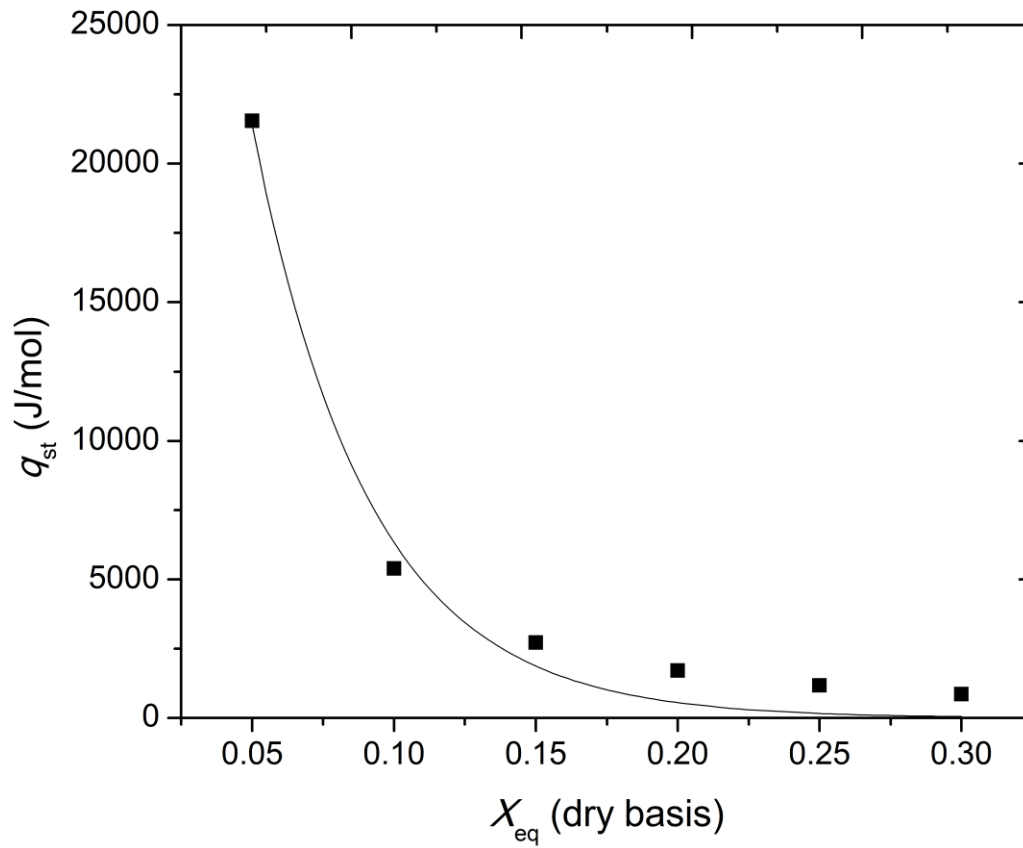
Figure 4. Change in enthalpy and entropy as a function of equilibrium moisture contents.
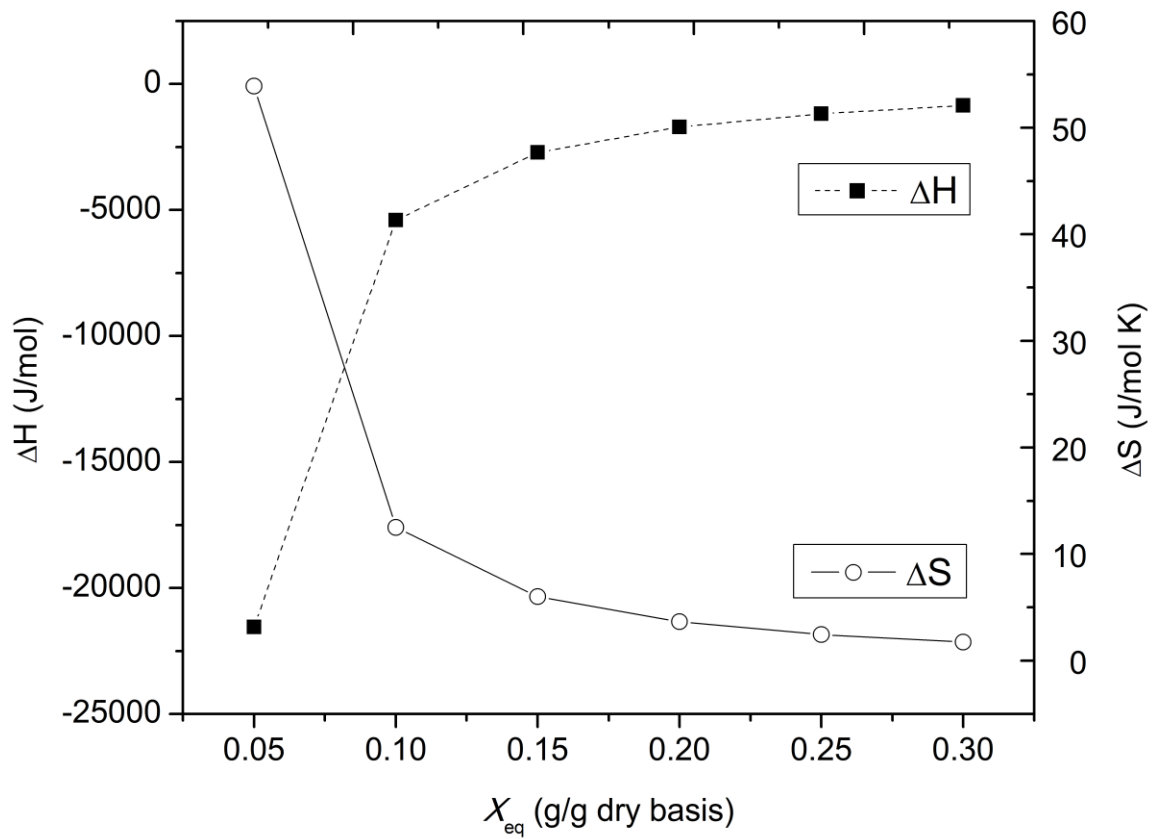
Figure 5. Linear regression of differential enthalpy versus differential entropy values.
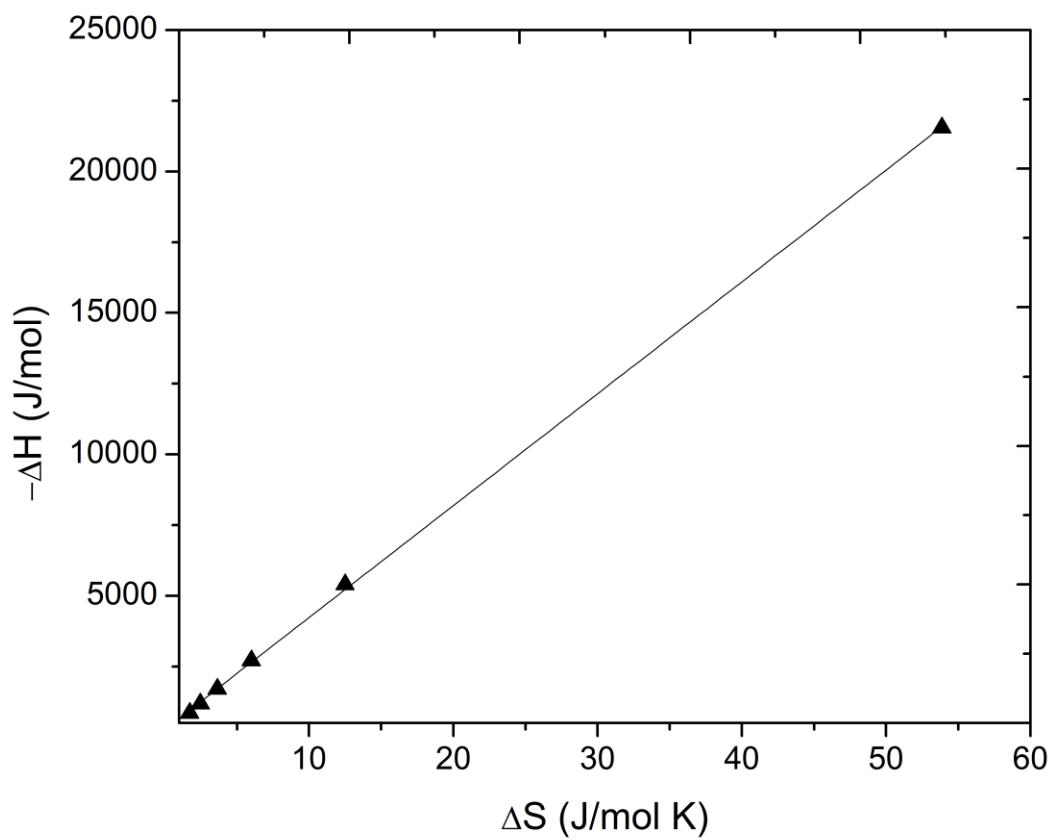
Table 1. Sample table with salt specifications.

Salt	Supplier	Purity (%)
LiBr	Sigma-Aldrich	≥ 99.0
LiCl	Sigma-Aldrich	≥ 99.0
LiI	Aldrich (Sigma-Aldrich)	99.0
CH_3OOK	Sigma-Aldrich	≥ 99.0
$MgCl_2$	Sigma (Sigma-Aldrich)	≥ 98.0
$Mg(NO_3)_2$	Vetec (Sigma-Aldrich)	98.0
NaBr	Sigma-Aldrich	≥ 99.0
$NaNO_3$	Sigma-Aldrich	≥ 99.0
NaCl	Sigma-Aldrich	≥ 99.0
KBr	Sigma-Aldrich	≥ 99.0
KCl	Sigma-Aldrich	≥ 99.0

Table 2. Experimental data of equilibrium moisture content versus specific water activity in the

studied temperatures at atmospheric pressure (P_{atm}=95.47 kPa).

					Temperature (Kelvin)					
	293.15		303.15		313.15		323.15		328.15	
a_w*	X_{eq}	a_w*	X_{eq}	a_w*	X_{eq}	a_w*	X_{eq}	a_w*	X_{eq}
0.066	0.044 ± 0.001	0.062	0.045 ± 0.002	0.058	0.036 ± 0.000	0.054	0.031 ± 0.001	0.053	0.030 ± 0.001
0.118	0.052 ± 0.001	0.111	0.051 ± 0.001	0.105	0.043 ± 0.000	0.100	0.037 ± 0.000	0.098	0.035 ± 0.000
0.138	0.055 ± 0.000	0.137	0.054 ± 0.001	0.136	0.046 ± 0.000	0.135	0.041 ± 0.000	0.134	0.039 ± 0.000
0.249	0.068 ± 0.001	0.226	0.063 ± 0.001	0.206	0.053 ± 0.000	0.189	0.045 ± 0.001	0.182	0.043 ± 0.000
0.329	0.077 ± 0.001	0.323	0.073 ± 0.002	0.318	0.064 ± 0.001	0.314	0.055 ± 0.001	0.311	0.051 ± 0.001
0.547	0.113 ± 0.002	0.525	0.101 ± 0.003	0.506	0.089 ± 0.001	0.488	0.074 ± 0.001	0.480	0.070 ± 0.002
0.589	0.122 ± 0.003	0.560	0.109 ± 0.004	0.535	0.093 ± 0.000	0.512	0.078 ± 0.000	0.501	0.073 ± 0.000
0.752	0.187 ± 0.003	0.731	0.165 ± 0.005	0.712	0.144 ± 0.001	0.694	0.119 ± 0.002	0.686	0.112 ± 0.000
0.772	0.200 ± 0.004	0.752	0.177 ± 0.005	0.734	0.155 ± 0.002	0.718	0.129 ± 0.002	0.710	0.121 ± 0.001
0.820	0.243 ± 0.003	0.804	0.212 ± 0.004	0.790	0.190 ± 0.005	0.777	0.159 ± 0.002	0.770	0.148 ± 0.001
0.873	0.306 ± 0.002	0.837	0.243 ± 0.001	0.806	0.203 ± 0.001	0.777	0.159 ± 0.002	0.764	0.143 ± 0.001

	338.15		343.15		348.15		353.15	
a_w*	X_{eq}	a_w*	X_{eq}	a_w*	X_{eq}	a_w*	X_{eq}
0.050	0.027 ± 0.000	0.049	0.026 ± 0.001	0.047	0.024 ± 0.000	0.046	0.024 ± 0.000
0.094	0.033 ± 0.001	0.092	0.032 ± 0.001	0.090	0.030 ± 0.000	0.088	0.030 ± 0.001
0.133	0.036 ± 0.000	0.133	0.035 ± 0.001	0.132	0.034 ± 0.001	0.132	0.033 ± 0.001
0.168	0.039 ± 0.001	0.162	0.038 ± 0.001	0.156	0.035 ± 0.000	0.151	0.034 ± 0.001
0.307	0.049 ± 0.000	0.305	0.048 ± 0.001	0.303	0.046 ± 0.000	0.301	0.044 ± 0.001
0.465	0.064 ± 0.000	0.458	0.062 ± 0.001	0.451	0.058 ± 0.000	0.445	0.056 ± 0.002
0.482	0.067 ± 0.000	0.473	0.064 ± 0.001	0.464	0.060 ± 0.000	0.456	0.058 ± 0.002
0.670	0.101 ± 0.002	0.663	0.096 ± 0.003	0.656	0.091 ± 0.001	0.649	0.085 ± 0.002
0.696	0.109 ± 0.002	0.689	0.102 ± 0.005	0.682	0.098 ± 0.003	0.676	0.095 ± 0.002
0.759	0.134 ± 0.001	0.753	0.131 ± 0.002	0.748	0.121 ± 0.000	0.742	0.115 ± 0.002
0.739	0.125 ± 0.000	0.727	0.118 ± 0.003	0.716	0.109 ± 0.000	0.705	0.103 ± 0.002

* Data obtained from Labuza [14]. a_w – water activity; X_{eq} – equilibrium moisture content.

Table 3. Chemical composition of wet cassava bagasse composition obtained in 11 different days.

Sample	Moisture (% - w. b.)	Dry matter (% - w. b.)	Proteins (% - d. b.)	Ashes (% - d. b.)	Fats (% - d. b.)	Carbohydrates (% - d. b.)
1	85.08	14.92	11.60	15.80	7.94	64.67
2	85.92	14.09	11.19	14.73	7.69	66.39
3	81.58	18.42	8.39	10.44	5.71	75.46
4	81.08	18.92	7.02	6.28	3.85	82.85
5	85.08	14.92	11.60	15.80	7.94	64.67
6	82.58	17.42	10.29	11.37	6.39	71.96
7	82.58	17.42	6.38	7.58	4.24	81.80
8	83.92	16.08	7.85	9.59	5.87	76.69
9	82.90	17.10	10.69	13.05	6.32	69.94
10	85.04	14.96	10.50	10.18	6.79	72.53
11	81.79	18.22	8.34	12.35	5.54	73.77
Mean	83.41	16.59	9.44	11.56	6.21	72.79
Standard deviation	1.67	1.67	1.89	3.16	1.37	6.22

w. b. – wet basis based on mass
d. b. – dry basis based on mass

Table 4. Parameters of the proposed models fitted to adsorption data.

Temperature (K)	GAB				
	X_m	C	k	R^2_{adj}	$RMSE$
293.15	0.0561	41.1140	0.9370	0.9999	0.0007
303.15	0.0524	64.3790	0.9382	0.9999	0.0002
313.15	0.0464	45.5290	0.9592	0.9999	0.0005
323.15	0.0403	46.7159	0.9627	0.9999	0.0004
328.15	0.0386	47.4302	0.9611	0.9998	0.0005
338.15	0.0365	46.0861	0.9619	0.9999	0.0002
343.15	0.0349	53.3952	0.9722	0.9989	0.0010
348.15	0.0340	45.4132	0.9645	0.9999	0.0001
353.15	0.0327	49.5185	0.9685	0.9989	0.0009

	Peleg					
	k_1	n_1	k_2	n_2	R^2_{adj}	$RMSE$
293.15	0.4190	6.0511	0.1278	0.4205	0.9989	0.0023
303.15	0.3491	5.1683	0.1082	0.3398	0.9989	0.0019
313.15	0.0994	0.3759	0.3396	5.2030	0.9991	0.0015
323.15	0.2821	4.9145	0.0840	0.3599	0.9993	0.0010
328.15	0.2410	4.3305	0.0749	0.3254	0.9993	0.0009
338.15	0.0728	0.3398	0.2311	4.4810	0.9995	0.0007
343.15	0.0771	0.3732	0.3042	5.6677	0.9988	0.0010
348.15	0.0682	0.3430	0.2178	4.5169	0.9997	0.0005
353.15	0.2147	4.5018	0.0652	0.3319	0.9986	0.0010

	Halsey			
	h_1	h_2	R^2_{adj}	$RMSE$
293.15	44.6828	1.5254	0.9994	0.0020
303.15	51.8888	1.5595	0.9983	0.0026
313.15	48.2298	1.4585	0.9983	0.0023
323.15	59.6340	1.4640	0.9980	0.0020
328.15	65.7929	1.4767	0.9982	0.0017
338.15	72.7467	1.4827	0.9981	0.0015
343.15	74.9732	1.4811	0.9957	0.0022
348.15	80.8784	1.4828	0.9980	0.0014
353.15	85.6269	1.4885	0.9964	0.0018

	Henderson			
	H_1	H_2	R^2_{adj}	$RMSE$
293.15	10.4505	1.2655	0.9485	0.0181
303.15	16.5886	1.4636	0.9438	0.0151
313.15	18.1248	1.4335	0.9503	0.0124
323.15	27.3243	1.5210	0.9511	0.0098
328.15	33.2394	1.5708	0.9521	0.0088
338.15	43.7914	1.6405	0.9528	0.0077
343.15	49.7869	1.6739	0.9463	0.0078

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			R^2_{adj}	RMSE
348.15	57.3988	1.6953	0.9530	0.0068
353.15	66.7030	1.7318	0.9491	0.0067
	Oswin			
	M	*N*	R^2_{adj}	*RMSE*
293.15	0.1115	0.5049	0.9864	0.0093
303.15	0.1075	0.4695	0.9802	0.0089
313.15	0.0967	0.4909	0.9814	0.0076
323.15	0.0844	0.4763	0.9804	0.0062
328.15	0.0806	0.4667	0.9804	0.0056
338.15	0.0759	0.4555	0.9802	0.0050
343.15	0.0741	0.4511	0.9753	0.0053
348.15	0.0705	0.4476	0.9797	0.0045
353.15	0.0685	0.4419	0.9766	0.0045

X_m (monolayer moisture content), *C* and *k* (constants related to the energy of interaction between the first and multilayers water molecules) – Parameters of GAB model; k_1, k_2, n_1, n_2 – Parameters of Peleg model; h_1, h_2 – Parameters of Halsey model; H_1, H_2 – Parameters of Henderson model; *M*, *N* – Parameters of Oswin model; R^2_{adj} – Adjusted correlation coefficient; *RSME* – root mean square error.