



Research article

Sorption isotherms and thermodynamic properties of the dry silage of red tilapia viscera (*Oreochromis* spp.) obtained in a direct solar dryer

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ABSTRACT

The sorption isotherms, thermodynamic properties and calculation for confirming the isokinetic theory of dry chemical silage of red tilapia viscera (*Oreochromis* spp.) obtained in a direct passive solar dryer were determined. Sorption isotherms were carried out at 15, 25, 35 and 45 °C using a static gravimetric method. The curves obtained were adjusted to eight equations. The isothermic heat of sorption (net and total) and the thermodynamic parameters were determined based on the Clausius-Clapeyron equation and the enthalpy–entropy compensation theory was applied to adsorption isotherms. The sorption isotherms obtained were of type III of Brunauer classification. The Peleg model best described the experimental data. In all cases, the isothermic heat decreased while the moisture content increased. The value of isokinetic temperature (T_B) was found to be less than harmonic mean temperature (T_{hm}), the sorption of water in dry chemical silage is therefore controlled by entropic mechanisms and proceeds spontaneously.

1. Introduction

Currently, aquaculture and fish consumption are constantly expanding worldwide, to the extent that this is one of the sectors with the highest growth rates in the world. This trend is mainly due to the increase in demand for fish as a result of population growth and a greater interest in aquaculture products, associated with health benefits derived from its consumption (FAO, 2018). Between 2000 and 2017, global fish production was at 5.8%, reaching a maximum of 171 million tons in 2016, of which aquaculture represented 47% with a specific growth rate of 6.3%, and a production of 111.95 million metric tons in 2017, of which 87% was destined for human consumption (FAO, 2018). Likewise, in Colombia, aquaculture presented a growth of 9% in 2017 compared to 2016, of which the red tilapia (*Oreochromis* spp.) was the main exponent, representing 61% of production (Colombian Ministry of Agriculture, 2018). Increased production is associated with an increase in waste generation, which represents between 60 and 70% of the production. The inadequate dumping of this can generate a significant impact on the environment (Martínez-Alvarez et al., 2015).

The alternative uses that have been found for this fish waste include silage (van 't Land and Raes, 2019), which consists of adding enzymes, lactic acid bacteria and organic or inorganic acids to previously homogenized residues to produce a decrease in pH that both inactivates the

pathogenic microbial flora and activates the endogenous proteolytic enzymes responsible for the liquefaction of proteins, producing peptides, free amino acids and partially hydrolyzed proteins (Olsen et al., 2017), which are of great interest for their application in animal nutrition (Goosen et al., 2016). This process reduces the environmental impact that dumping this waste would generate and produces added value (Perea et al., 2018). Furthermore, it is possible to implement this process at an artisanal level and in rural areas because it does not require complex technologies, does not have a high energy consumption, does not generate polluting effluents, generally has minimal emissions, is based on biological agents and can be implemented at any scale of production.

Silage is usually made and stored in liquid form (Goddard and Perret, 2005), which represents a challenge while transporting and storing it due to its high water content (Camaño et al., 2020). In addition, it must be kept in hermetic containers because allowing oxygen to enter would lead to the growth of aerobic pathogens and the putrefaction of the silage (Suarez et al., 2018). Drying the silage therefore represents an alternative of interest, since this would increase its added value, facilitate handling, reduce packaging, transport and storage costs, limit microbial growth, allow the silage to be incorporated into dry products and increase its protein concentration, which facilitates its incorporation into diets that require a high protein content (van 't Land and Raes, 2019). However, traditional drying techniques are often expensive, require significant amounts of energy and

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technological resources, and negatively impact the environment. For this reason, solar drying is considered as an alternative option, as it is low cost and environmentally friendly. However, this drying technique has disadvantages such as longer process lengths, non-homogeneous drying and possible microbial contamination (Goddard and Perret, 2005; van 't Land and Raes, 2019). This means that products obtained through this method must be thoroughly examined to ensure that they meet the characteristics required for use in industrial application processes.

For dry products it is important to have some quality control, the type of which depends on the product's physical, chemical and microbiological stability. This is partly due to the relationship between equilibrium moisture content (X_w) and water activity (a_w) at a given temperature, as a_w participates in the degradation of biosystems depending on both the water content and the diffusion properties of the water to the surface (Ayala-Aponte, 2011; Martínez-Las Heras et al., 2014). However, models based on fundamental phenomena that explain the behavior of the equilibrium moisture content in complex solids such as food have not yet been sufficiently developed (Zapata et al., 2014). Therefore, empirical correlations between the product's equilibrium moisture content and its water activity (a_w), called moisture sorption isotherms, are usually used, which give satisfactory results in a certain range of a_w . This strategy correlates the product's equilibrium moisture content against the water's thermodynamic activity at a given pressure and temperature (Guzmán-Hincapié and Zapata, 2018).

Sorption isotherms are unique to the food matrix and essential for modeling mass and heat transport phenomena during processes such as drying, preserving, and conditioning food materials (Bensebia and Allia, 2016). In addition, they are useful for establishing conditions during storage and predicting the food's stability and shelf life (Ayala-Aponte, 2011; Leonardo et al., 2020). Likewise, they allow the maximum dehydration point for obtaining a stable product to be determined, as well as the amount of energy required to remove a certain amount of water and obtain a desired moisture level (Rao et al., 2005). Sorption isotherms are the basis for determining thermodynamic parameters with information on the material's microstructure, which outline its behavior with respect to water. This is the case of the net isosteric heat of sorption (q_{stn}), which identifies the energy requirements needed to convert the unit of mass of a liquid matrix to steam at a given temperature. The total isosteric heat of sorption (Q_{st}) also corresponds to the net isosteric heat of sorption (q_{stn}) in terms of the enthalpy of vaporization of pure water, since as the percentage of moisture decreases, the adsorbed water's heat increases above the vaporization of pure water (Arslan-Tontul, 2020). Additionally, differential enthalpy and entropy can indicate the binding strength of water to the food matrix and the amount of sorption sites available at a specific energy level, respectively (Polachini et al., 2016). Finally, the linear correlation between these last two parameters indicates the Gibbs free energy and isokinetic temperature (T_B), which is compared with the average harmonic temperature (T_{hm}) to establish the confirmation of the isokinetic compensation theory that is used as a tool to recognize the different mechanisms of water sorption in different conditions (Spada et al., 2013).

In this context, this work aimed to evaluate the sorption isotherms of dry chemical silage (DCS) of red tilapia (*Oreochromis* spp.) viscera, obtained by solar drying, analyzing the thermodynamic properties and validation of the enthalpy-entropy compensation theory (isokinetic theory) and its influence on water sorption in DCS.

Hypotheses. Measurements of sorption isotherms of dry chemical silage is a great tool that allows obtaining information on the processes of sorption of water in the matrix, being ideal to predict drying and storage conditions.

2. Material and methods

2.1. Raw material

The red tilapia (*Oreochromis* spp.) viscera were supplied by a commercial producer in the municipality of San Jerónimo, Colombia

(6°27'45.0"N 75°46'43.2"W), following the methodology described by Camaño et al. (2020). The viscera were transferred to the laboratory in refrigerated conditions. They were then heated to 67 °C for 30 min and stored at freezing temperature (-20 °C) for 12 h. During this period, the fat was removed by decantation (Arias et al., 2017) and the protein-rich aqueous fraction was transferred to silage. The fresh viscera (FV) and degreased viscera (DV) were characterized bromatologically

2.2. Analytical methods

All bromatological analyses were performed according to the methods established by the AOAC (AOAC, 2000). Protein was determined by the Kjeldahl method (Velp scientifica, Italy) (AOAC 954.01). The moisture content was determined in an air oven (Thermo Scientific™, USA) (AOAC 930.15). The ash content was determined by incineration in a muffle (Terrigeno, Colombia) (AOAC 942.05) and the fat was estimated using a Soxhlet extractor (Radleys, USA) (AOAC 920.39).

2.3. Red tilapia viscera dry chemical silage (DCS)

To obtain the DCS, the degreased viscera were initially crushed using a food processor (Black and Decker, USA). They were then packed in plastic polyethylene containers, to which 1.16% formic acid, 0.03% sulfuric acid, 0.12% potassium sorbate and 0.002% butyl hydroxytoluene were added, and stored hermetically at room temperature (25 °C) for a period of 10 days until it reached a pH of 4 (Suarez et al., 2018), which was analyzed bromatologically. Next was the drying process; a 1.48 m long, 0.63 m wide and 0.12 m deep direct solar collector was used, in which Petri dishes were placed as drying beds and the silage was added up to a film thickness of 2.4 mm, based on a study by Camaño et al. (2020). Once dry, bromatological characterization was obtained, obtaining 9.94 (%) of moisture and 40.70, 21.43, and 5.77 (% dry matter (dm)) of protein, fat, and ash respectively.

2.4. Determination of sorption isotherms

The static gravimetric technique was used as a sorption method that involves saturated saline solutions to reach a stable relative humidity (RH) when equilibrium is reached. This ensures a mass transfer between the product and the atmosphere around it, which occurs through the diffusion of water vapor, where the product's a_w is equal to the RH of the atmosphere under equilibrium conditions at a given temperature (Martínez-Las Heras et al., 2014). In this case, different standard salts with known standard RHs were used. The salts used were LiCl, $MgCl_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, NaCl, $Ba(Cl)_2 \cdot 2H_2O$ and K_2SO_4 (>20%), with 11, 33, 58, 75, 84 and 97% respectively. A LabMaster- a_w model CH-8853 Lachen (Novasina, Switzerland) a_w measurement kit was used, in which approximately 1 g of fully dry DCS sample (dried at 105 °C for 24 h) was placed in a glass probe that had been previously tared with the aforementioned salts. Once equilibrium was reached, weight measurements were taken using a TXB2201L analytical balance (Shimadzu, Japan), with an accuracy of 0.01 g, and the corresponding a_w . A previously tared desiccator was used to weigh the sample and avoid environmental moisture gain during weighing. All adsorption isotherms were evaluated in triplicate and average values were reported. The results were expressed as the mass of water per mass of the total dry sample, referring to the equilibrium moisture content (X_w). Equilibrium curves of X_w vs a_w were constructed for each working temperature (15, 25, 35 and 45 °C). These temperatures were chosen because 15, 25 and 35 °C are usually stored temperatures, whereas 45 °C is usually a temperature used for drying process. This allows to study the adsorption process completely (Vega-Gálvez et al., 2008; Sormoli and Langrish, 2015; Arslan-Tontul, 2020).

2.5. Modelling of sorption isotherms

Currently, a large number of models have been proposed to describe sorption processes in food, in this case describing the relationship between X_w and a_w . In the DCS samples for each working temperature, 8 mathematical models commonly used in food areas were used: the equations of BET, Caurie, Freundlich, GAB, Henderson, Oswin, Peleg and Smith (Martinez-Las Heras et al., 2014; Polachini et al., 2016), as shown in Table 1. To obtain the model parameters, the least squares method was used using the “Mathlab” software (License 914762, 2018 version). The goodness-of-fit of each of the models was evaluated based on the coefficient of determination (R^2) and the mean squared error (RMSE).

2.6. Determination of isosteric sorption heat

Isosteric heat in terms of desorption refers to the energy required to break the intermolecular forces between the steam molecules and the surface of the absorbent, while in adsorption processes it corresponds to the energy required for the opposite to occur (Galvez et al., 2006). The total isosteric heat of sorption (Q_{st}) (KJ/mol) is the net isosteric heat of sorption (q_{stn}) plus the enthalpy of vaporization of pure water, in this case 43.6 KJ/mol for the average working temperature (30 °C), which was calculated with Eq. (1).

$$Q_{st} = q_{sm} + \Delta H_{H_2O} \tag{1}$$

Meanwhile, the q_{stn} (KJ/mol) could be calculated by applying the Clausius-Clapeyron equation (Equation 2) (Tsami, 1991) to the isotherms obtained at different working temperatures, assuming that the q_{stn} does not vary with the temperature (Wan et al., 2016). Data were taken from a_w for each of the isotherms at different temperatures for a given equilibrium moisture content. $\ln(a_w)$ vs $1/T$ was plotted for each of the moisture values, which varied between 0.01 and 0.18 KgH₂O/Kg dm. Several straight lines were obtained, in which q_{stn} was determined by the slope, where T was used on the absolute temperature scale (K) and R is the universal gas constant (8.31 J/mol.K).

$$\left[\frac{\partial(\ln a_w)}{\partial(1/T)} \right]_{X_w} = - \frac{Q_{st} - \Delta H_{H_2O}}{R} = - \frac{q_{stn}}{R} \tag{2}$$

These q_{stn} values can be expressed as a function of X_w , following the empirical model shown in Eq. (3), proposed by Tsami et al. (1990), recently used by Tadapaneni et al. (2017), in which “a” represents the isosteric heat of sorption (KJ/mol) of the first molecule of water in the food and “b” is the characteristic moisture content for each product when q_{stn} has reduced by 63%. R^2 was used as the goodness-of-fit for this model.

$$q_{sm} = a \exp(-bX_w) \tag{3}$$

2.7. Determination of differential sorption enthalpy and sorption entropy

The differential enthalpy ΔH is used as an indicator of the state of the water in a biological material depending on the type of force between the water vapor and the sorption sites (Spada et al., 2013). These are negative values because adsorption is an exothermic process and is equivalent to the net heat of sorption (q_{stn}) (Guzmán-Hincapié and Zapata, 2018). Meanwhile, the differential entropy ΔS (J/molK) relates the number of sorption sites with a certain level of power inherent in biological materials (Spada et al., 2013) and is given by Eq. (4). Gibbs free energy (ΔG) is associated with the spontaneity of the processes and is defined by Eq. (5), where T is the reaction temperature on an absolute scale and R is the gases’ universal constant.

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{4}$$

$$\Delta G = RT \ln(a_w) \tag{5}$$

In this way, by joining Eqs. (4) and (5) the differential sorption enthalpy and entropy can be calculated using Eq. (6), the slope of which corresponds to $\Delta H/R$ and the intercept to $\Delta S/R$ (Polachini et al., 2016).

$$\ln(a_w) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{6}$$

2.8. Enthalpy-entropy compensation theory (isokinetic theory)

This theory focuses on the physical and chemical phenomena involved in water sorption; for this reason it is considered to be a tool for recognizing the mechanisms of water sorption in different conditions (Spada et al., 2013). This includes a linear relationship between ΔH and ΔS for the sorption of water in food and it is given by Eq. (7), in which the linear fit between ΔS and ΔH provides T_B as a slope and ΔG_B as an intercept (Ferro-Fontan et al., 1982). T_B is the isokinetic temperature (K), which is the temperature at which all series reactions proceed at the same speed and ΔG_B is the Gibb free energy (J/mol) at T_B .

$$\Delta H = T_B \Delta S + \Delta G_B \tag{7}$$

Having the established values of T_B and ΔG_B , the isokinetic theory could be verified by using a mathematical comparison between T_B and the average harmonic temperature (T_{hm}), which was calculated using Eq. (8), where N corresponds to the total number of isotherms and T to the

Table 1. The models used to adjust the sorption isotherms for dry chemical silage.

Model name	Formula	Parameters
BET	$X_w = \frac{X_m C a_w}{(1 - a_w)[1 + (C - 1)a_w]}$	X_m : is the product moisture corresponding to a monolayer water adsorbed. C: characteristic of the material constant related to the heat released in the sorption process
Caurie	$X_w = \exp \left[a_w \ln(v) - \left(\frac{1}{4.5 X_s} \right) \right]$	X_s : moisture content security that provides maximum stability for the dehydrated food during storage. V: constant characteristic of the material
Freundlich	$X_w = \frac{1}{K a_w^n}$	K y n: Sorption constants characteristic for each product.
GAB	$X_w = \frac{X_m C K a_w}{(1 - K a_w)[1 + (C - 1)K a_w]}$	X_m : is the product moisture corresponding to the situation where the primary sorption sites are saturated with water molecules. C: is the Guggenheim constant, characteristic of the product and related with the heat of sorption of the monolayer. K: is a correction factor related to the heat of sorption of the multilayer.
Henderson	$X_w = 0.01 \left[\frac{-\log_{10}(1 - a_w)}{10^f} \right]^{\frac{1}{n}}$	f y n: are the model constants and characteristic for each food.
Oswin	$X_w = A \left[\frac{a_w}{1 - a_w} \right]^B$	A y B: are the model constants and characteristic for each food.
Peleg	$X_w = A a_w^B + C a_w^D$	A, B, C y D: are the model constants and characteristic for each food.
Smith	$X_w = B + A \text{Log}_{10}(1 - a_w)$	A y B: are the model constants and characteristic for each food.

temperature in Kelvin. Where the theory is validated only if $T_B \neq T_{hm}$ (Krug et al., 1976).

$$T_{hm} = \frac{N}{\sum_1^N (1/T)} \tag{8}$$

3. Results and discussion

3.1. DCS moisture sorption isotherms

Figure 1 shows the DCS sorption isotherms obtained at 15, 25, 35 and 45 °C, constructed with experimental X_w and a_w values, which were in the range between 0.004-0.16 Kg H₂O/Kg dm and 0.11–0.73, for X_w and a_w , respectively. These values indicate the low water sorption capacity of this matrix. This property depends directly on its chemical composition (Arslan-Tontul, 2020), especially on the amount of low molecular weight compounds such as those found in sugars, which are quite low in DCS. These make this matrix less hygroscopic than other food matrices such as microcapsules of hydrolyzed starch with X_w of 0.40 Kg H₂O/Kg dm (Spada et al., 2013) and dry wheat noodles with 0.35 Kg H₂O/Kg dm (Li et al., 2016). Meanwhile, the DCS samples' moisture content X_w was found to increase as a_w increases at all temperatures, since the increase in pressure of the steam surrounding the sample causes increasing vapor pressure inside them (Arslan-Tontul, 2020). The curves in Figure 1 indicate that the isotherms are type III according to the Brunauer classification (Brunauer et al., 1940) and according to the parameters C and K ($0 < K \leq 1, 0 \leq C \leq 2$) of the GAB model. This classification mainly refers to products with high protein or salt content (Erbaş et al., 2016). This is

similar to what was found in studies of sorption in ham (Leonardo et al., 2020), bulgur (Erbaş et al., 2016) and a dry algae-based product (Zuo et al., 2015), which all had a high protein content.

Meanwhile, in Figure 1 the value of X_w can be seen to increase as the temperature increases, which may be due to the fact that the active sites or hydrophilic groups of the matrix gain mobility as the temperature increases. They therefore have greater exposure to water molecules. This may also be associated with some components of the food reaching the glass transition temperature, changing its crystal structure, therefore affecting the number of exposed sorption sites (Zapata et al., 2014). This coincides with what Zuo et al. (2015) and Puri and Khamrui (2016) found in protein-rich matrices. They found that the trend for increased water sorption with increased temperatures is due to a complex association between food components and water vapor that can vary according to temperature and the value of a_w . These results do not match those reported for matrices of a different chemical composition, such as those rich in starch (Zuo et al., 2015), in which the negative influence of temperature on X_w has been clearly demonstrated (Arslan-Tontul, 2020).

3.2. Modelling of DCS sorption isotherms

The experimental results presented in the DCS isotherms were used to fit the models presented in Table 2, whose parameters and respective goodness-of-fits (R^2 and RMSE) are presented in Table 2. Based on the R^2 and RMSE values, it was found that the four models with the best fit, in descending order, were Peleg, Freundlich, Caurie and Henderson, with $R^2 > 0.99$ and RMSE < 0.0068. The curves predicted with these models were presented in Figure 1, in contrast to the experimental data, allowing the

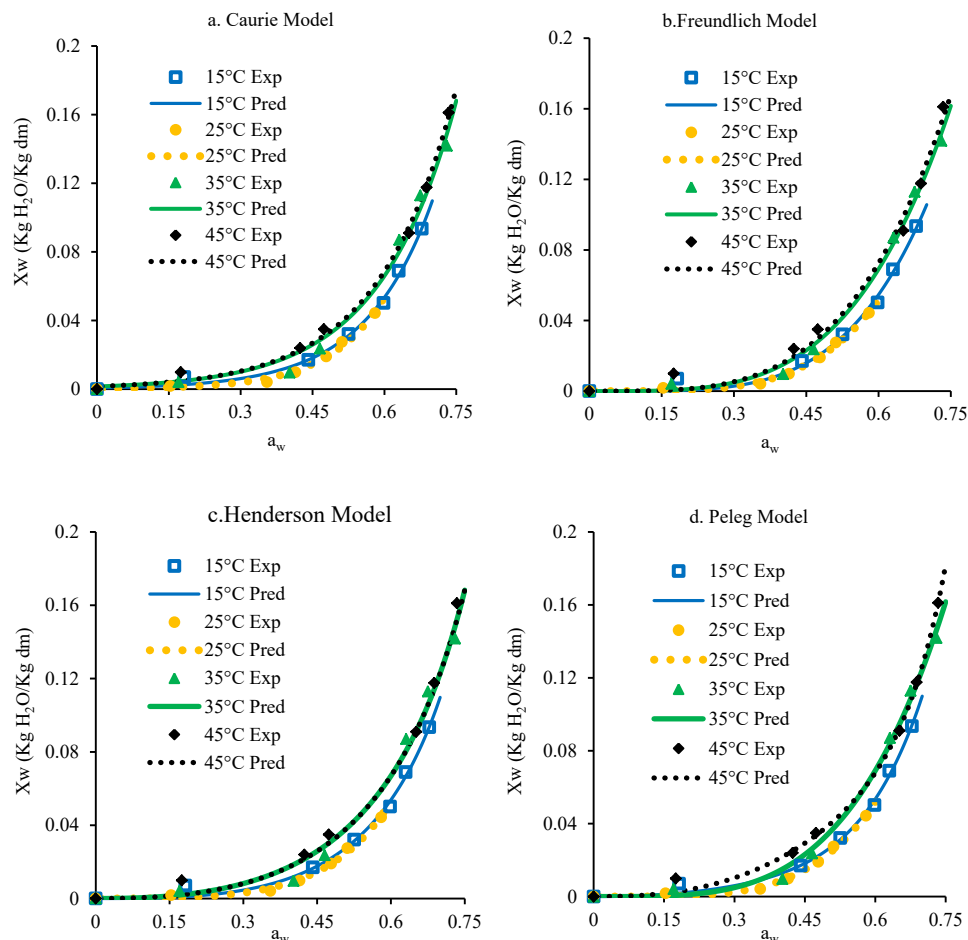


Figure 1. The average moisture sorption isotherms of dry chemical silage fitted with four models in different temperatures. a) Caurie, b) Freundlich, c) Henderson y d) Peleg. The lines represent predicted values and the markers experimental values.

Table 2. Parameter values obtained for the eight models used to describe sorption isotherms of dry chemical silage.

Model name	Adjustment constants and parameters	15 °C	25 °C	35 °C	45 °C
BET	X _m	0.1575	0.1527	0.1506	0.1535
	C	0.1080	0.0069	0.1033	0.1052
	R ²	0.9922	0.9631	0.9622	0.9960
	RMSE	0.0034	0.0039	0.0106	0.0048
Caurie	V	1326.5381	5935.3166	510.0707	520.6784
	X _s	0.0307	0.0273	0.0344	0.0346
	R ²	0.9975	0.9907	0.9863	0.9980
	RMSE	0.0016	0.0015	0.0067	0.0026
Freundlich	K _f	0.4860	0.4643	0.4837	0.4957
	n	0.2338	0.2324	0.2625	0.2657
	R ²	0.9959	0.9969	0.9955	0.9921
	RMSE	0.0021	0.0009	0.0038	0.0052
GAB	X _m	0.1365	0.1316	0.1044	0.0924
	C	0.0889	0.0590	0.1667	0.2107
	K	1.0700	1.2490	1.0274	1.0446
	R ²	0.9962	0.9828	0.9700	0.9989
Henderson	R ²	0.9962	0.9828	0.9700	0.9989
	RMSE	0.0020	0.0099	0.0096	0.0034
	n	0.3834	0.3329	0.4489	0.4489
	f	-0.6805	-0.6414	-0.7707	-0.7707
Oswin	R ²	0.9940	0.9940	0.9873	0.9980
	RMSE	0.0016	0.0012	0.0064	0.0045
	A	0.0266	0.0266	0.0369	0.0382
	B	1.7023	1.7023	1.4068	1.4150
Peleg	R ²	0.9972	0.9823	0.9784	0.9996
	RMSE	0.0017	0.0036	0.0083	0.0011
	A	0.0807	0.2207	0.1122	0.2227
	B	2.2070	11.6083	42.5218	2.5570
Smith	C	0.7125	0.4741	0.4838	1.4511
	D	6.3806	4.3481	3.8093	10.2830
	R ²	0.9976	0.9967	0.9955	0.9997
	RMSE	0.0016	0.0009	0.0038	0.0009
Smith	A	-0.1780	-0.1096	-0.2679	-0.2758
	B	-0.0128	-0.0080	-0.0262	-0.0231
	R ²	0.8834	0.7524	0.8803	0.8932
	RMSE	0.0128	0.0075	0.0188	0.0185

obtained adjustment to be visualized. However, the other four models also presented good fits, with the least well-fitting being the Smith model. Peleg's model has previously been reported as a high-performing model in adjusting food isotherms (Arslan-Tontul, 2020), as in the case of ham (Leonardo et al., 2020) and starch microcapsules (Spada et al., 2013).

Despite not being the highest performing, semi-empirical models such as GAB and Caurie obtained perfectly acceptable adjustments and are of great importance for the analysis due to the physical parameters they contain. With GAB, the monolayer moisture content (X_m) is determined, which is a very interesting physical parameter because it provides information about the water that is in direct contact with the surface of the solid and that is critical for defining storage conditions (Ayala-Aponte, 2011; Leonardo et al., 2020). In this case, the X_m obtained by the GAB model decreases while the temperature increases, which is very likely due to the fact that the union of water in this matrix is associated with the union with the polar amino group of mediating hydrogen bridge proteins, which weaken as the temperature increases, causing the water in the monolayer to decrease (Erbaş et al., 2016). Similar results have been observed in protein matrices (Leonardo et al., 2020), while the values of X_m, C and K have values similar to those found in other food matrices (Leonardo et al., 2020; Zuo et al., 2015). On the other hand, the Caurie model is useful because it allows the safety moisture content (X_s) to be determined for each temperature, which indicates the product's moisture

content at which maximum stability of the food can be achieved during storage (Gálvez et al., 2006).

3.3. Isostatic heat of sorption

Figure 2 shows the linear representation of Ln (a_w) vs 1/T derived from the Clausius-Clapeyron equation (Equation 2), from which the q_{stn}

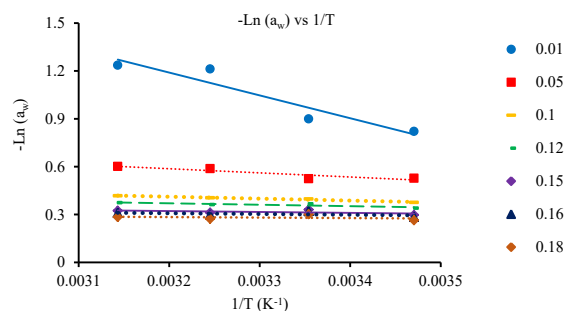


Figure 2. -Ln (a_w) vs 1/T graphs for calculating the heat of sorption of dry chemical silage for values different of X_w (KgH₂O/Kg dm).

was estimated for moisture content values in equilibrium (X_w) that vary between 0.01-0.18 KgH₂O/Kg dm.

Figure 3 shows the correlation between the net isosteric heat of sorption (q_{stn}), the total isosteric heat of sorption (Q_{st}) and the enthalpy of vaporization (ΔH), with the moisture content X_w , which allows the magnitude of the binding energy and the availability of polar sites for water vapor to be analyzed as sorption progresses. The q_{stn} also reflects the strength of the bonds between water and solid molecules compared to free water molecules (Jin et al., 2019). It is observed that the q_{stn} decreases from 11.89 KJ/mol for 0.01 KgH₂O/Kg dm, to 0.26 KJ/mol for 0.18 KgH₂O/Kg dm, with a rapid decrease until it reaches X_w of 0.05 Kg H₂O/Kg dm, similar to what was found by Arslan-Tontul (2020) in chia seeds. Subsequently, the decline was lower and lower, approaching zero. Similar behavior was observed for Q_{st} , with a rapid decrease to a X_w of 0.05 Kg H₂O/Kg dm, with a slight subsequent decrease, but in much higher values, of between 55.50 KJ/mol and 43.61 KJ/mol, for 0.01 and 0.18 KgH₂O/Kg dm. The values of Q_{st} tend towards those of pure water vaporization enthalpy ($\Delta H_{\text{water vapor}}$), as X_w increases. This behavior is due to the fact that in the first stages of sorption, at low X_w values, there is more interaction between the matrix of the solid and the water because adsorption is initially generated in the monolayer, where there is a greater quantity of active sorption sites, associated with higher values of binding energy, which is manifested in high q_{stn} values and therefore higher Q_{st} values. As these active sites are occupied, sorption begins to occur in less active sites in the multilayer, where less energy is involved in the binding, reflected by lower values of both isosteric heats of sorption. Similar results were reported by Chen et al. (2019) and Li et al. (2016), who showed curves with similar trends in milled rice and dry noodles, respectively.

In addition, the q_{stn} analysis enables us to observe that it was lower than the ΔH of pure water vaporization (43.6 KJ/mol), at all evaluated X_w values, which indicates that the binding energy between the molecules of water and active sorption sites is lower than the energy involved in the phase change from liquid to vapor, again demonstrating weak interaction. Similar q_{stn} values have been found in other studies on food matrices such as orange juice powder (Sormoli and Langrish, 2015), dry noodles (Li et al., 2016), milk powder, almond flour (Tadapaneni et al., 2017) and cheddar cheese powder (Jin et al., 2019) with 9.05, 11, 14, 15.02 and 15 KJ/mol respectively. Meanwhile, other studies in matrices rich in carbohydrates such as corn starch and yuca flour found higher q_{stn} values, including values that were even above the ΔH of water vaporization with values of 62 and 77 KJ/mol respectively (Ayala-Aponte, 2011; Jin et al., 2019). This highlights the relationship of these physicochemical parameters and the macromolecules present in the food matrix (Tadapaneni et al., 2017). In that sense Jin et al. (2019), they found that the samples with a high carbohydrate content had the highest

q_{stn} values, followed by the samples with the highest amount of protein and finally the foods rich in fat, because the hydrophilic groups present in the matrix favor the increase in q_{stn} Jin et al. (2019).

The net isosteric heat of sorption was expressed as a function of the moisture content X_w by means of Eq. (3) with the empirical Tsami exponential model, for which the values of the parameters 17.39 KJ/mol and 38.42 Kg H₂O/Kg dm were obtained for "a" and "b" respectively, with R^2 of 0.99, as indicated in Eq. (3) parametrically. This can be a very useful tool for predicting the DCS's q_{stn} in the range of X_w in this study. These results match those found in other food matrices such as powdered milk, wheat flour, almond powder (Tadapaneni et al., 2017) and cheddar cheese powder, with the latter being the most similar due to its protein composition (Jin et al., 2019).

3.4. Thermodynamic properties

The thermodynamic focus of these processes is related to differential enthalpy and entropy (ΔH and ΔS), since these two variables allow the thermodynamic behavior of water in sorption to be evaluated. The ΔH values were negative, as expected, because sorption is an exothermic process. The values ranged from -11.89 KJ/mol to -0.26 KJ/mol equivalent to q_{stn} . Meanwhile ΔS showed positive values from 47.94 J/mol.K to 3.2J/mol.K in the range of X_w 0.01 to 0.18 KgH₂O/Kg dm as shown in Figure 4A, in which it is observed that both decreased with the increase of X_w , a similar result to that found by (Polachini et al., 2016), who obtained ΔS values of up to 53.88J/mol.K. This differential entropy refers to a transitory variation of the total entropy of water when new water molecules are absorbed in the food matrix at a certain level of moisture (Hill et al., 1951). In this case, it was observed that ΔS showed its maximum value at lower X_w values, where the sorption of water in the monolayer occurs. This is where the most active sites are found, allowing maximum positive change in the order of the molecules after sorption, in other words, the water molecules lose mobility because there is greater polarity at the surface, which means that these molecules will be less available for deterioration reactions (Azuara and Beristain, 2006).

3.5. Enthalpy-entropy compensation theory

In order to evaluate the physical and chemical phenomenon of water sorption in DCS, it was necessary to use the enthalpy-entropy compensation theory, which establishes that there is a linear relationship between these two thermodynamic variables. Figure 4B shows the linear behavior when graphing ΔH vs ΔS , which is adjusted according to Eq. (7). R^2 of 0.999 was obtained, indicating that the change in enthalpy (ΔH) is proportional to the change in entropy (ΔS) and to Gibbs free energy, evidencing a compensation, similar to what was found by Polachini et al.

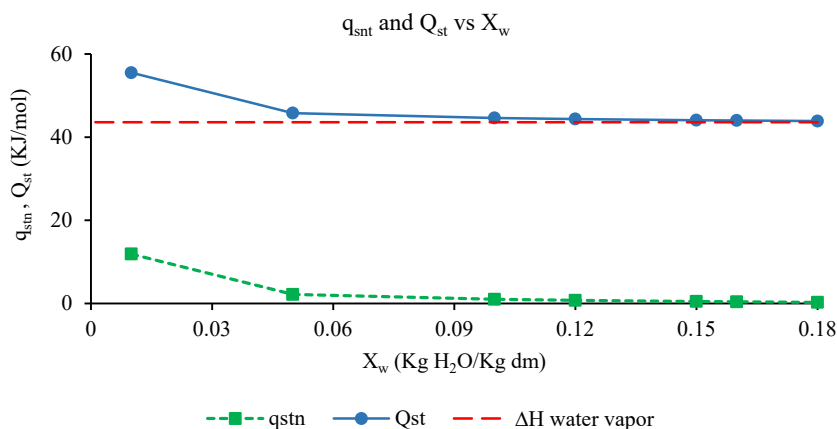


Figure 3. Isosteric heat of sorption q_{stn} and Q_{st} as function of equilibrium moisture content X_w .

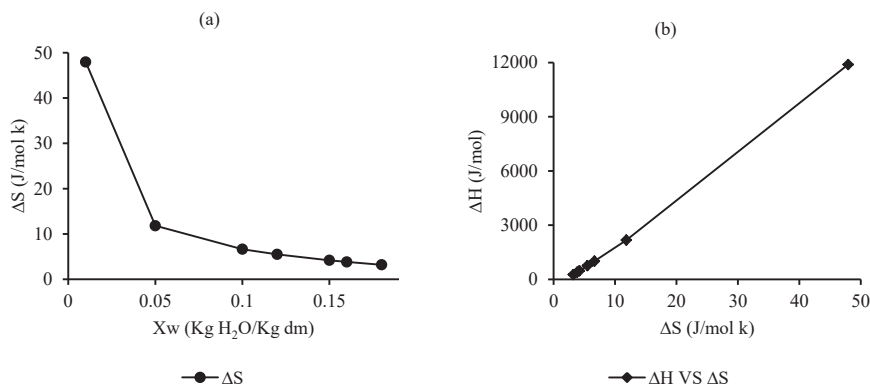


Figure 4. a) Change in entropy as a function of equilibrium moisture contents. b) Enthalpy-entropy relationship for water sorption in dry chemical silage.

(2016) and Spada et al. (2013) in food matrices. Meanwhile, the linear regression parameters were used to calculate T_B and ΔG_B for which values of 261.21 K and -679.86 J/mol respectively were obtained.

To confirm this theory, the second requirement was taken into account, comparing the isokinetic temperature T_B with the average harmonic temperature T_{hm} . The latter was determined with Eq. (8), giving a value of 302.73 K, which is completely different from T_B . This allows the linearity pattern of the chemical compensation theory to be validated, as established by Krug et al. (1976) ($T_{hm} \neq T_B$). In addition to these results, it can be said that the water sorption mechanism in DCS samples is driven and controlled by entropy mechanisms because $T_B < T_{hm}$ ($T_B = 261.21$ K < $T_{hm} = 302.73$ K) following the theory of Leffler (1955). Furthermore, the sorption of water in the DCS is a spontaneous process, since Gibbs free energy at T_B (ΔG_B) was less than zero ($\Delta G_B < 0$) corresponding to -679.86 J/mol. These results are different from those found in food matrices with high sugar or starch content, in which $T_B > 300$ K have generally been reported (Polachini et al., 2016). Meanwhile, in other protein-rich matrices such as dry yogurt, trends similar to those obtained in this study have been shown with close T_B and T_{hm} values ($T_B = 241$ K < $T_{hm} = 307$ K), in which the authors confirm that the sorption of water in these products with low moisture is clearly due to sorption processes with spontaneous entropic mechanisms ($\Delta G_B = -13.46$ J/mol < 0) (Azuara and Beristain, 2006).

4. Conclusions

The sorption isotherms for the dry chemical silage presented a type III shape according to the BET classification and temperature was observed to influence the sorption behavior of the water in the matrix. The Peleg, Caurie, Freundlich, Henderson, GAB and BET models provide the best fit for the experimental data and are useful tools for describing the dry chemical silage samples' storage conditions. The net isosteric heat of sorption can be used as a tool to predict the energy requirement in dry chemical silage dehydration processes and the behavior of water molecules in sorption. The sorption of water in dry chemical silage samples is controlled by entropic mechanisms that are spontaneous.

Declarations

Author contribution statement

Jairo A. Camaño E.: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Ana M. Rivera T.: Performed the experiments.

José E. Zapata M.: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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