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# Evaluation of sorption isotherms in snacks with pregelatinized cassava

## Evaluación de las isothermas de sorción en snacks con mandioca pregelatinizada

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### Abstract

Sorption characteristics are studied for their influence on the storage stability of dehydrated products and their effect on water vapour diffusion. In the present work, the adsorption curves of snacks with and without substitution of wheat flour by dehydrated cassava puree (PDM) were analysed using saturated salt solutions at 10, 30 and 50 °C. Type III curves were obtained for the samples with PDM and type II for the control sample. Mathematical modelling was then performed using 8 different equations, obtaining the best fits for the Peleg ( $R^2_{\text{adjust}}=0.999-0.988$ ), Ferro Fontan ( $R^2_{\text{adjust}}=0.998-0.970$ ) and GAB ( $R^2_{\text{adjust}}=0.999-0.955$ ) models. The values of the model constants in some cases turned out to be formulation and temperature dependent, and in general do not show a definite trend. This can be seen graphically as crossovers between the curves. This crossover of curves has been attributed to the increased exposure of hydrophilic groups due to increased molecular mobility at high humidity and occurrence of the glass transition in the system and/or endothermic dissolution of sugars.

Keywords: Isotherms; Adsorption; Pregelatinized starch; Cassava; Snack.

### Resumen

Las características de sorción se estudian por su influencia en la estabilidad de almacenamiento de los productos deshidratados y por su efecto sobre la difusión del vapor de agua. En el presente trabajo se analizaron las curvas de adsorción de snacks con y sin sustitución de harina de trigo por puré deshidratado de mandioca (PDM) mediante soluciones salinas saturadas a 10, 30 y 50 °C. Se obtuvieron curvas tipo III para las muestras con PDM y tipo II para la muestra control. Luego se procedió al modelado matemático utilizando 8 ecuaciones diferentes obteniéndose los mejores ajustes para los modelos de Peleg ( $R^2_{\text{ajust}}=0,999-0,988$ ), Ferro Fontan ( $R^2_{\text{ajust}}=0,998-0,970$ ) y GAB ( $R^2_{\text{ajust}}=0,999-0,955$ ). Los valores de las constantes de los modelos en algunos casos resultaron dependientes de la formulación y de la temperatura, y en general no presentan una tendencia definida. Esto se puede ver gráficamente como cruces entre las curvas. Este entrecruzamiento de curvas se ha atribuido a la mayor exposición de grupos hidrofílicos debido a un aumento de la movilidad molecular a altas humedades y ocurrencia de la transición vítrea en el sistema y/o a la disolución endotérmica de azúcares.

Palabras clave: Isothermas; Adsorción; Almidón pregelatinizado; Mandioca; Snack.

### Introduction

In areas and countries that do not produce wheat flour, there has been a growing interest in replacing it with local products due to the need to reduce imports and increase food sovereignty [1]. Cassava is a crop of great importance for the region of Misiones, Corrientes and Formosa (Argentina). However, due to its seasonality and easy deterioration, processing is necessary for the sustained production of cassava-based foods. Examples of this processing are cassava flour or *fariña* and starch, a

product widely used by various industries such as textiles and pharmaceuticals, but also by the food industry mainly as an additive [2]. A new product called dehydrated cassava puree (DMP) has been added to this list in order to preserve the raw material and improve availability in times of scarcity [3]. The production methodology differs from traditional products (starch and starch) as well as their physicochemical and functional properties [4].

The PDM production process involves a cooking process in water until complete gelatinisation and a subsequent drying process, whereby the starch contained

in PDM is pre-gelatinised [5]. Therefore, the effect of replacing wheat flour with PDM in different products should be studied in terms of the effect on shelf life, drying characteristics, packaging requirements, storage, etc. Regarding these characteristics, sorption isotherms, i.e. the ratio between water activity ( $a_w$ ) and equilibrium moisture content, provide information on the moisture holding capacity of a material at a given relative humidity allowing the analysis of the plasticising effect of moisture. In addition, they allow prediction of moisture sorption properties by means of empirical, semi-empirical and theoretical mathematical models [6,7]. The main theoretically based mathematical model for sorption-desorption curves is currently the GAB model, based on the BET model. Both models are able to predict the moisture content of the monolayer. This monolayer is the water that is tightly bound to the active sites of the adsorbent solid phase of the feed, and is considered to be the value at which the feed is stable during storage [8]. There are also multiple empirical or semi-empirical models used to predict the amount of moisture present in the food at untested relative humidities.

Therefore, the aim of the present study was to determine and analyse the adsorption curves of snacks with and without wheat flour substitution by PDM at different temperatures and to find the mathematical models that best describe them.

## Materials and methods

**Materials:** Wheat flour and ALDEMA brand dehydrated cassava puree (PDM), produced by Cooperativa Agrícola e Industrial San Alberto Limitada (C.A.I.S.A.), were used to prepare the snack samples. Both were purchased on the local market (Argentina). The PDM package claims 1.17 g of protein, 88.33 g of carbohydrates and 1.67 g of fibre per 100 g of product. The ingredients declared on the PDM packaging are: cassava, sodium bisulphite (preservative) and glycerol monostearate (emulsifier).

The proportions of the ingredients used are given in Table 1. All doughs were made with the same amount of salt, sugar and sunflower oil (0.2, 0.3 and 4.5% of the dough weight, respectively).

First, the PDM, wheat flour, sugar and salt were mixed. Then, the oil and finally the water were incorporated and mixed. Subsequently, the ingredients were mixed by hand for approximately 2 to 3 minutes until a homogeneous dough was formed.

**Table 1:** Proportions used to produce 100 g of dough.

Formulation	A	B	C	D
PDM (g)	0	30,5	43	54
Flour (g)	63	30,5	14,5	0
Water (g)	32	34	37,5	41

The doughs were left to rest for 30 minutes in hermetically sealed containers. They were then rolled by rollers to a thickness of approximately 2 mm. Finally, the snacks were formed using a 20 mm hexagonal cutting mould.

The baking temperature was set at 220°C by means of a digital controller with a thermocouple. After the oven conditions had stabilised, 15 samples at a time were placed in a disposable aluminium tray. The different formulations were baked at different times so that physicochemical characteristics such as moisture, colour, porosity and expansion or contraction during baking were similar as described in our previous work [9]. Sample A was baked for 7 minutes, samples B and C for 5 minutes and sample D for 4.5 minutes.

**Determination of adsorption curves:** To obtain the equilibrium moisture content (EMC) data, the static gravimetric method was used, in which the samples are placed in static and thermally stabilised systems and after the first 20 days, the weight of the samples is monitored daily until a constant weight is achieved. To determine the adsorption values, the snack samples were broken into small pieces and weighed on glass plates until a sample of  $2 \pm 0,02$  g was achieved. They were then placed in airtight containers prepared with saturated solutions of LiCl, CH<sub>3</sub>CO<sub>2</sub>K, K<sub>2</sub>CO<sub>3</sub>, NaBr, KI, NaCl, KCl, K<sub>2</sub>SO<sub>4</sub>. The containers were placed in a refrigerator or oven to maintain them at 10, 30 and 50  $\pm$  1 °C. Samples were allowed to equilibrate to constant weight values ( $\pm$  0.001 g) which occurred over a period of 25 to 30 days. Determinations were carried out in triplicate. The dry mass was determined gravimetrically by oven drying at 105 °C for 24h.



**Figure 1:** Methodology used for the determination of equilibrium moisture content.

**Mathematical modelling:** The mathematical models used to fit the CHE (g H<sub>2</sub>O/g dry solids) and  $a_w$  data are presented in table 2.

Non-linear regression was performed using GraphPad Prism 4 statistical software. The statistical parameters R<sup>2</sup><sub>adjusted</sub>, RMSE and AIC<sub>c</sub> corresponding to equations 1, 2 and 3, respectively, were used as criteria for fitting the model to the experimental data.

$$R_{a_{just}}^2 = 1 - \frac{SS_r / (n - K)}{SS_t / (n - 1)} \quad (1)$$

Where,  $SS_r$  is the sum of squares of the discrepancy between the Y value of the curve and the data;  $SS_t$  is the sum of squares of the differences between the overall mean Y and each Y value; n is the number of data points and K is the number of fitted parameters.

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

Where,  $MR_{exp,i}$  is the experimentally observed value and  $MR_{pre,i}$  is the value predicted by the model. N is the number of observations.

$$AICc = 2k - 2 \ln(L) + \frac{2k^2 + 2k}{n - k - 1} \quad (3)$$

Where k is the number of parameters in the statistical model, L is the maximum value of the likelihood function for the estimated model and n is the sample size.

**Table 2:** Mathematical models used to describe water sorption isotherms.

Model	Equation	Parameters
GAB 0,050 <aw< 0,980*	$X = \frac{X_m \cdot C \cdot k \cdot a_w}{(1 - k a_w) \cdot (1 + (C - 1) \cdot k a_w)}$	$X_m$ : Monolayer moisture. Product moisture corresponding to the situation where the primary adsorption sites are saturated by water molecules (g water/g dry solids). C: ratio between the partition function of the first molecule adsorbed on a site and the partition function of the molecules sorbed beyond the first molecule in the multilayer. k: correction factor because it corrects for the properties of the multilayer molecules relative to the bulk liquid.
FERRO FONTAN aw < 0,900*	$X = \left[ \frac{A}{\ln\left(\frac{B}{a_w}\right)} \right]^{\frac{1}{C}}$	A: Constant. B: Parameter representing the structure of the adsorbed water. C: Parameter related to the net isosteric heat.
HALSEY 0,100 <aw< 0,800*	$X = \left[ \frac{A}{\ln\left(\frac{1}{a_w}\right)} \right]^B$	A: constant of the model and characteristic for each foodstuff. B: parameter characterising the type of interaction between solid and vapour.
HENDERSON aw < 0,950*	$X = \left( \frac{-\ln(1 - a_w)}{A} \right)^{\frac{1}{B}}$	A and B: model constants and characteristics for each food item.
OSWIN aw < 0,980*	$X = A \cdot \left[ \frac{a_w}{1 - a_w} \right]^B$	A and B: model constants and characteristics for each food item.
PELEG aw < 0,980*	$X = k_1 \cdot a_w^{n_1} + k_2 \cdot a_w^{n_2} \quad (8)$	$k_1, k_2, n_1, n_2$ constants Peleg equation (dimensionless).
SMITH 0,350 <aw< 0,900*	$X = B - A \cdot \ln(1 - a_w)$	A and B: model constants and characteristics for each food.
Chung & Pfost aw < 0,950*	$Y = (1/B) \cdot (\ln(\ln(X)/-A))$	A and B: model constants and characteristics for each food item.

\*Water activity range for the model.

## Results and discussion

Figure 2 and 3 show the water adsorption curves for each formulation at 10, 30 and 50°C and for all formulations at the different working temperatures. Data from three replicates of each sample are presented.

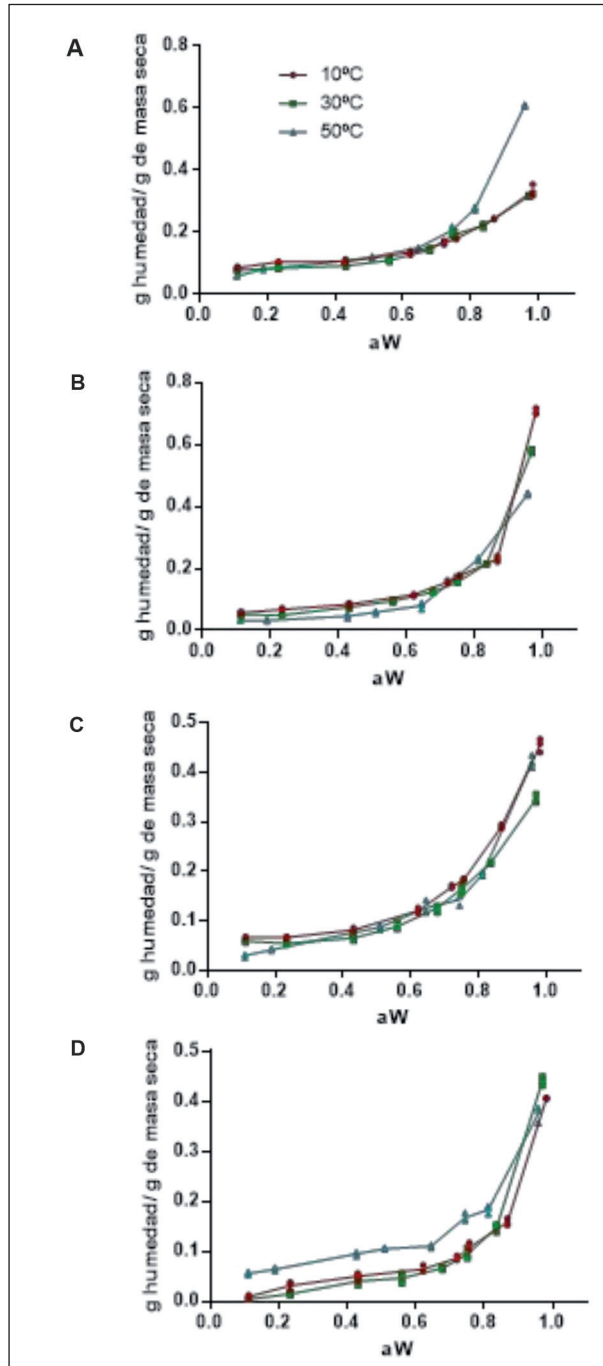


Figure 2: Adsorption curves by formulation.

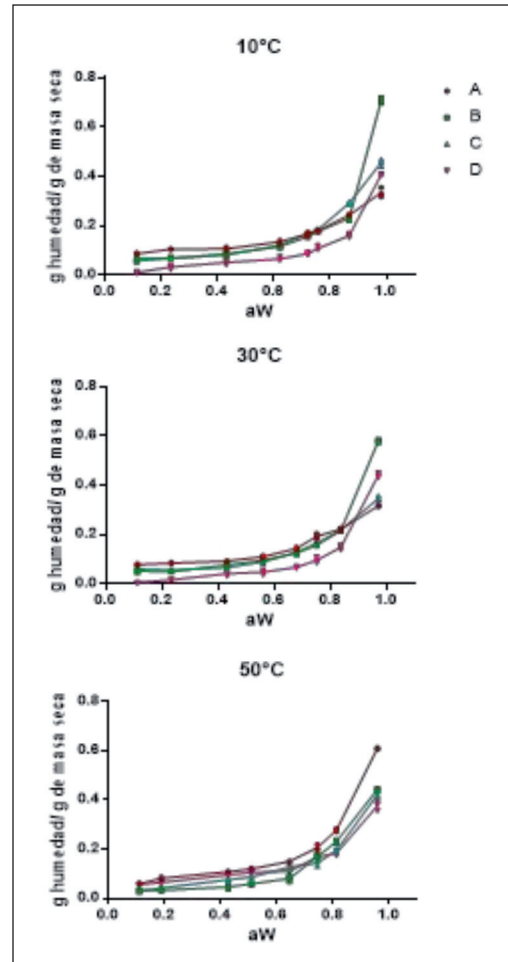


Figure 3: Temperature adsorption curves.

In figure 2, it can be observed an increase in the CHE with increasing water activity at constant temperature forming a type III curve for samples with PDM and type II for sample A according to Brunauer's classification [10]. Type III curves were obtained by other authors in banana, apple, pineapple, apricot, sultanas, cured meat and those rich in soluble components such as sugars, due to their solubility in water, e.g. starch gels with added sucrose produce a drastic increase in water sorption at water activities above 0.850 [10]. However, cassava-like foods such as potato, starch gels, maize, rice, nixtamalised maize flour, and from cassava such as fariña, cassava starch and PDM showed behaviours compatible with type II curves as did sample A [6,8,10-12]. This could indicate that the process of obtaining PDM added to the snack manufacturing process could lead to the degradation of the starch molecule into shorter chain polymers with greater solubility such as dextrans or disaccharides such as maltose.

Water adsorption on starchy foods is mainly due to hydrogen bonding of the water molecules to the hydroxyl groups available on the substrate surface. In native starches, the crystalline fractions are resistant to solvent penetration, so that water is adsorbed mainly to the amorphous fractions

of the granule. However, in foods in which the starch has undergone prior gelatinisation and drying processes, i.e. pre-gelatinisation, as in the case of PDM and snacks with PDM, the starch has a higher hydration capacity [5]. This is due to the higher macromolecular disorganisation and degradation of the starch during the thermal processes applied (drying of PDM and baking of snacks).

Figure 2 also shows the effect of temperature on the moisture sorption characteristics of formulation “D”. The equilibrium moisture content increases with increasing temperature (with constant water activity), which indicates that the feed becomes more hygroscopic, however, no apparent difference is observed between temperatures 10 and 30 °C. The other formulations showed no apparent difference between temperatures, this will be analysed in detail later in this work by ANOVA test.

A crossover of the curves at water activities higher than 0.8 can also be observed in those samples containing PDM. This crossover can be described as a pronounced increase in CHE at aw values higher than 0.8. This has been previously observed by other authors in carbohydrate-rich foods such as bananas, sugar beets, sultanas, barley malt and the soy protein-sugar system, among others [6]. The best explanation for the behaviour of sample D is the

endothermic dissolution of sugars at high water activity. But the behaviour of samples B and C with wheat flour and PDM blends seems to be better explained by an increased exposure of active sites or hydrophilic groups to high aw as the temperature increases. The increased exposure of active sites is due to an increase in molecular mobility resulting from the onset of the glass transition range where the amorphous regions of starch begin to plasticise, increasing the availability of hydroxyl groups leading to an increase in sorption [13]. Although it is not excluded that both situations could be occurring simultaneously.

Table 3 below shows the parameter values of the 4 equations with the best fits. Table 4 shows the values of the fit parameters and constants of the other models. When analysing the statistical data of the models, it can be seen that the Peleg model is the one that best describes the adsorption data of the snacks with and without PDM substitution. The error values (RMSE) are within a range of 0.001 to 0.007g H<sub>2</sub>O/g SS and the R<sup>2</sup>ajus values vary within a range of 0.989 to 0.999. Previously, good fits for this model have been reported for potato starch, pea and ham starch, oat flour and rice flour [13,14]. However, being an empirical model, its constants do not allow estimation of food characteristics.

**Table 3:** Parameters and fit constants obtained for GAB, Oswin, Peleg and Ferro Fontan.

		A			B			C			D		
T (°C)		50	30	10	50	30	10	50	30	10	50	30	10
GAB	X <sub>m</sub>	0,063	0,067	0,073	0,043	0,044	0,045	0,045	0,052	0,061	0,052	0,024	0,028
	C	29,66*	21,05*	2,25*	45,73*	34,09*	9,019*	42,01*	35,55*	3,75*	37,74*	8,636*	36,61*
	K	0,935	0,816	0,797	0,943	0,953	0,953	0,932	0,878	0,884	0,897	0,974	0,949
	R <sup>2</sup> <sub>ajus</sub>	0,997	0,977	0,982	0,955	0,999	0,994	0,988	0,977	0,986	0,987	0,989	0,993
	RMSE	0,009	0,012	0,010	0,02	0,001	0,005	0,004	0,004	0,005	0,003	0,004	0,002
	AICc	-218	-205	-211	-163,4	-252,2	-193	-201,4	-195,9	-193,5	-163,4	-252,2	-193
Oswin	A	0,125	0,122	0,132	0,082	0,088	0,097	0,089	0,100	0,123	0,103	0,046	0,058
	B	0,505	0,283	0,240	0,546	0,542	0,496	0,497	0,365	0,336	0,410	0,651	0,487
	R <sup>2</sup> <sub>ajus</sub>	0,993	0,942	0,951	0,960	0,997	0,996	0,995	0,953	0,953	0,985	0,995	0,993
	RMSE	0,014	0,008	0,007	0,020	0,002	0,01	0,002	0,009	0,02	0,003	0,002	0,002
	AICc	-186,5	-184,5	-187,4	-167,8	-217,3	-203,1	-222,1	-180,8	-166,5	-206,9	-216,3	-217,3
Peleg	K1	0,630	0,273	0,241	0,502	0,607	0,708	0,402	0,335	0,412	0,341	0,479	0,369
	n1	7,306	3,238	4,413	4,527	9,905	16,08	8,933	3,718	4,63	7,547	10,91	12,59
	k2	0,150	0,071	0,112	0,030	0,132	0,180	0,152	0,046	0,076	0,130	0,100	0,114
	n2	0,401	-0,053	0,104	-0,038	0,555	0,673	0,777	-0,115	0,067	0,398	1,239	0,987
	R <sup>2</sup> <sub>ajus</sub>	0,999	0,990	0,990	0,995	0,997	0,995	0,994	0,996	0,998	0,989	0,997	0,996
	RMSE	0,001	0,001	0,007	0,002	0,001	0,004	0,001	0,001	0,001	0,002	0,001	0,001
	AICc	-244,1	-223,1	-223,1	-211,9	-218,7	-193,5	-217,7	-238,8	-237,8	-209,7	-227,1	-222,8
Ferro Fontan	A	0,033	0,024	0,083	0,242	0,0200	0,01	0,032	0,053	0,055	0,009	0,048	0,020
	B	1,026	1,135	1,087	1,385	1,014	1	1,055	1,159	1,13	1,015	1,068	1,043
	C	1,461	1,629	2,188	0,517	1,461	1,859	1,273	1,147	1,194	1,908	0,850	1,207
	R <sup>2</sup> <sub>ajus</sub>	0,996	0,970	0,975	0,985	0,999	0,998	0,994	0,980	0,986	0,989	0,997	0,995
	RMSE	0,003	0,004	0,012	0,006	0,001	0,001	0,002	0,0004	0,05	0,002	0,001	0,001
	AICc	-211,4	-198,2	-202,8	-190	-238,6	-222,3	-218,4	-199,3	-194,4	-212	-225,1	-224,2



**Table 4.** Parameters and fit constants obtained for *Smith, Henderson, Halsey and Chung & Pfost*.

Model	T (°C)	A			B			C			D		
		50	30	10	50	30	10	50	30	10	50	30	10
Smith	A	0,149	0,111	0,047	-0,063	0,005	0,104	0,017	-0,010	0,1365	0,0425	0,072	0,07529
	B	0,012	0,025	0,095	0,170	0,113	0,023	0,102	0,125	2,10E-13	0,0842	~ 1,5e-016	1,2 e-013
	r2	0,952	0,96	0,983	0,936	0,978	0,980	0,946	0,984	0,9764	0,8982	0,870	0,936
	RMSE	0,014	0,001	0,005	0,005	0,001	0,001	0,001	0,001	0,011	0,002	0,003	0,001
	AICc	-121,6	-131,6	-146,4	-113,3	-140,6	-141,1	-131,3	-142,4	-128,6	-126,7	-120,4	-131,9
Henderson	A	5,035	25,38	36,33	6,121	5,371	5,291	7,167	12,90	10,48	10,5	5,851	8,207
	B	0,889	1,701	1,956	0,816	0,759	0,755	0,921	1,229	1,226	1,167	0,622	0,785
	r2	0,968	0,938	0,321	0,977	0,978	0,971	0,981	0,962	0,968	0,941	0,994	0,990
	RMSE	0,030	0,019	0,010	0,010	0,013	0,034	0,006	0,008	0,012	0,013	0,002	0,003
	AICc	-162,4	-182,9	-180,5	-180,9	-172,6	-156,1	-191,6	-185,4	-175,7	-173,9	-215,2	-206,6
Halsey	A	0,018	0,001	0,0003	0,012	0,012	0,009	0,009	0,002	0,002	0,005	0,01	0,003
	B	0,567	0,322	0,264	0,610	0,593	0,535	0,560	0,409	0,370	0,469	0,710	0,528
	r2	0,994	0,926	0,936	0,948	0,998	0,998	0,988	0,939	0,935	0,988	0,990	0,987
	RMSE	0,013	0,026	0,020	0,021	0,001	0,020	0,004	0,013	0,024	0,002	0,004	0,004
	AICc	-202	-178,4	-181,9	-161,4	-228,2	-225,2	-202,2	-174,1	-159	-212,6	-201,5	-199,8
Chung y Pfost	B	7,496	16,42	18,25	9,29	8,195	7,564	10,37	13,68	11,44	12,68	10,09	12,39
	A	2,095	5,275	7,967	1,672	1,662	1,635	2,012	2,855	2,818	2,954	1,232	1,497
	r2	0,89	0,947	0,958	0,899	0,868	0,862	0,924	0,941	0,952	0,915	0,867	0,915
	RMSE	0,055	0,007	0,016	0,041	0,081	0,126	0,025	0,012	0,018	0,018	0,054	0,027
	AICc	-132,7	-186,7	-192,3	-145,7	-129,3	-118,8	-158,4	-175,3	-166	-165,3	-139,1	-155,4

Another difficulty encountered in using this model was that the 95% confidence limits of the  $n_2$  parameter in some cases go from positive to negative values, making it difficult to find true significant differences between one data set and the other when applying an analysis of variance.

The second model that achieved superior fit variables to the other models was Ferro Fontan, with an RMSE between 0.0004 and 0.05 g H<sub>2</sub>O/g SS and R<sup>2</sup>ajus values varying within a range of 0.999 and 0.97. This model has been found to be suitable for describing the sorption isotherm of more than 92 different food products and also for PDM adsorption curves [12,15]. This model is a semi-empirical model since “A” is a constant without theoretical significance. Parameters B and C have theoretical significance; B allows an approximation of the structure of the adsorbed water and C is a constant linking the isosteric heat of sorption to the moisture content [16]. Analysis of variance ( $p < 0.05$ ) of the values of the constants in this model showed that the constants A and B do not differ significantly between the formulations, so the adsorbed water structure tends to be similar.

For the constant C, it was found that at 10 and 30°C the value of the constant tends to increase with the PDM content in the formulation. However, at 50°C, no definite tendency to increase or decrease with the percentage of PDM in the sample was found. On the other hand, it was also observed for all the formulations that constants A and

B did not vary significantly with the temperatures studied. The constant C only showed variations in the case of samples B and D where it was found that for temperatures 10 and 30 °C they did not show statistical difference between them, but it was different from the values of the constant obtained at 50°C where it presented the lowest value for both samples.

The third model that presented fit parameters that would indicate a good representation of the data found was the GAB model, with RMSE between 0.017 and 0.0004 g H<sub>2</sub>O/g SS and R<sup>2</sup>ajus values varying within a range of 0.999 and 0.955. The GAB model has been one of the most versatile models, being able to correctly represent sorption data for 75% of the foods studied [10]. In addition, it is of interest as a model that allows obtaining parameters with physical significance.

In this model, the variable  $X_m$  represents the humidity of the monolayer (g water/g s.s), the values found were in the range between 0.02 and 0.07 g H<sub>2</sub>O/g SS. The analysis of variance ( $p < 0.01$ ) of the results obtained for this constant showed significant differences between the formulations tested, but no tendency to increase or decrease with the amount of PDM (Table 5). Significant differences between temperatures were also found for samples A, C and D, but not for sample B. For samples A and C, the  $X_m$  constant tends to decrease with temperature while for formulation D it tends to increase; and for formulation B no differences between temperatures were found. The GAB

constant C in all cases presented standard deviations too large to be evaluated by analysis of variance (coefficients of variation greater than 100%).

On the other hand, the values of the k constant remained between 0.79 and 0.95. When k approaches one, it indicates that there is almost no distinction between multilayer molecules and molecules with liquid behaviour. In that case, the water molecules beyond the monolayer are not structured in a multilayer, but have the same characteristics as molecules in the bulk liquid [17]. Analysis of variance ( $p < 0.01$ ) showed significant differences between formulations at the same temperature in the constant k, but the difference does not show a trend with the PDM content in the samples at 10 and 30°C. At 50°C only sample D was shown to be significantly higher than the others. When analysing the k constant from the temperature factor, no significant differences between temperatures were observed for sample B, but for samples A, C and D. In formulations A and C the k value at temperatures 10 and 30°C did not show significant differences; however, at 50°C the value was significantly higher. The k value for formulation D showed no trend with temperature. This is evident in figure 2, when observing the location of the 50°C curve with respect to the others in each of the samples.

The Ferro Fontan model showed significant differences between samples ( $p < 0.01$ ) for all three constants, except for the “A” constant at 30°C and the “C” constant at 10°C. However, no tendency to increase or decrease with the

amount of PDM was found either. For formulation A, significant differences were found between temperatures with a tendency to decrease with decreasing temperature.

For formulation B, significant differences were found with a tendency to increase with temperature for parameters A and B, while for parameter C the trend was reversed. For formulation C no significant difference was found between temperatures for any of the constants of the GAB model. For formulation D, differences with temperature were observed but the trend was not defined.

Values after  $\pm$  are standard deviations. There are no statistically significant differences between levels sharing the same superscript in the same column. Superscripts in letters are comparisons between formulations at the same temperature and in numbers are comparisons between temperatures for the same formulation.

The Smith, Henderson, and Chung & Pfoest models had the largest errors in predicting the data with respect to the experimental values. In the case of the Oswin and Halsey models, they fitted with relatively low errors only for some formulations and temperatures, making them inadequate for comparisons between the formulations studied.

## Conclusions

The water adsorption isotherms obtained for the snack formulations containing PDM presented type III curves,

**Table 5:** Analysis of variance for GAB and Ferro Fontan constants.

Xm		GAB		Ferro Fontan		
		k	A	B	C	
10°C	A	0,073± 0,002 <sup>d2</sup>	0,797± 0,008 <sup>a1</sup>	0,008± 0,004 <sup>a1</sup>	1,075± 0,020 <sup>bc12</sup>	2,180± 0,200 <sup>a2</sup>
	B	0,045± 0,001 <sup>b1</sup>	0,950± 0,020 <sup>c1</sup>	0,010± 0,001 <sup>a1</sup>	1,000± 0,002 <sup>a1</sup>	1,860± 0,080 <sup>a3</sup>
	C	0,061± 0,002 <sup>c3</sup>	0,884± 0,005 <sup>b1</sup>	0,055± 0,016 <sup>b1</sup>	1,130± 0,030 <sup>c1</sup>	1,190± 0,130 <sup>a1</sup>
	D	0,028± 0,001 <sup>a1</sup>	0,949± 0,003 <sup>c2</sup>	0,020± 0,005 <sup>a1</sup>	1,040± 0,010 <sup>ab12</sup>	1,207± 0,892 <sup>a1</sup>
30°C	A	0,067± 0,002 <sup>d1</sup>	0,820± 0,010 <sup>a1</sup>	0,024± 0,010 <sup>b2</sup>	1,135± 0,050 <sup>b2</sup>	1,630± 0,200 <sup>c1</sup>
	B	0,044± 0,0005 <sup>b1</sup>	0,950± 0,001 <sup>c1</sup>	0,020± 0,002 <sup>a1</sup>	1,010± 0,004 <sup>a1</sup>	1,460± 0,050 <sup>bc2</sup>
	C	0,052± 0,002 <sup>c2</sup>	0,878± 0,007 <sup>b1</sup>	0,053± 0,020 <sup>a1</sup>	1,160± 0,050 <sup>b1</sup>	1,150± 0,150 <sup>ab1</sup>
	D	0,024± 0,001 <sup>a1</sup>	0,974± 0,003 <sup>d3</sup>	0,048± 0,011 <sup>b2</sup>	1,070± 0,020 <sup>ab2</sup>	0,850± 0,080 <sup>a1</sup>
50°C	A	0,063± 0,001 <sup>c1</sup>	0,935± 0,002 <sup>b2</sup>	0,033± 0,005 <sup>a1</sup>	1,026± 0,010 <sup>a1</sup>	1,460± 0,100 <sup>b1</sup>
	B	0,043± 0,003 <sup>a1</sup>	0,940± 0,010 <sup>b1</sup>	0,24± 0,097 <sup>b2</sup>	1,400± 0,200 <sup>b2</sup>	0,520± 0,100 <sup>a1</sup>
	C	0,045± 0,001 <sup>a1</sup>	0,932± 0,005 <sup>b2</sup>	0,032± 0,007 <sup>a1</sup>	1,055± 0,015 <sup>a1</sup>	1,270± 0,090 <sup>b1</sup>
	D	0,052± 0,002 <sup>b2</sup>	0,897± 0,006 <sup>a1</sup>	0,009± 0,003 <sup>a1</sup>	1,015± 0,011 <sup>a1</sup>	1,910± 0,150 <sup>c1</sup>

probably due to the higher sugar content in these systems, as a consequence of starch degradation during the PDM and snack manufacturing process.

The crosslinking observed between the curves of the PDM samples (B, C and D) was previously observed and attributed to the higher exposure of active sites or hydrophilic groups due, in part, to an increase in molecular mobility at high humidities as a consequence of plasticisation by water and the occurrence of the glass transition in the system. However, for the sample without wheat flour, endothermic dissolution of sugars seems a better explanation.

All models evaluated fitted the data adequately with  $R^2_{ajus}$  greater than 0.862. The models with the best fitting parameters were Peleg ( $R^2_{ajus} = 0.999-0.988$ ), Ferro Fontan ( $R^2_{ajus} = 0.998-0.970$ ) and GAB ( $R^2_{ajus} = 0.999-0.955$ ). However, Peleg and GAB present some difficulties to be used to compare the formulations studied.

The GAB and Ferro Fontan parameters did not show definite trends of moisture content with PDM content in the formulation with temperature.

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