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Sorption and mass exchange characteristics of extrudates enriched with cocoa bean shells

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Abstract. The aim of the experimental work was to determine the sorption isotherms of wheat extrudates enriched with cocoa bean shells at different temperatures (10 °C, 25 °C, 40 °C) and water activities (0.11 to 0.85) using the static gravimetric method. Five three parameter models (Chung-Pfost, Halsey, Oswin, Henderson, GAB) were applied to survey the experimental data. It was established that the isotherms demonstrate Types II, according to the Brunauer's classification and the Oswin and Chung-Pfost models were suitable for describing the relationship between the equilibrium moisture content and the water activity. The monolayer moisture content was established using the Brunauer-Emmett-Teller equation and ranged within 5.08 % d.b. and 7.80 % d.b., respectively. The increase of temperature decreases the sorption characheristics of the examined extrudates. The specific surface area of sorption for wheat extrudates enriched with cocoa bean shells varies between 181.59 (m^2/g) and 278.82 (m^2/g). It was found that the increase of temperature of the matrix in the range of 10 °C to 40 °C decreases the values of monolayer moisture content and the specific surface area of sorption.

1 Introduction

Food industry is one of the processing branches which produces a huge quantity of waste products annually. The accumulation of these by-products has a negative effect on the environment mainly due to the problems related to their recasting. In the recent years the main task of the food industry is focused on the reuse and utilization of the wastes [1, 2].

Extrusion cooking is widely used in the food industry. During the process food materials with rich carbohydrates content such as flour, semolina and starch from wheat, corn, potatoes, soybeans, etc. are processed in which they are transformed into a various types of snacks and structured products [3]. During the last few years one of the possibilities that has been actively explored is related to the addition of enriched flours, dried fruits, vegetables, waste raw materials obtained during the extrusion of different semolinas in order to increase the nutritional and biological value of the extruded products [4, 5].

The cocoa bean shells (Figure 1) well known as 'waste' are by-products of cocoa beans derived from the chocolate production. They are excellent source of valuable biologically active components - polysaccharides, proteins, vitamins, caffeine, tannin, theobromine, organic acids, etc. [6]. The cocoa bean shells can be successfully used as additives in various foods due to their high antioxidant capacity [7].

Fig. 1. Cocoa bean shells [8].

The water is a major component of food products and in particular of the extruded ones. The changes in food quality, technological and nutritional properties is related to the water lack or excess. The relationship between the water activity and the moisture content of the product at a certain temperature is given by the experimentally obtained equilibrium sorption isotherms. The knowledge of the sorption isotherms of food products as well as their modeling has a great practical and theoretical applications [9]. The equilibrium sorption isotherms represent a valuable source of information about the type and forms of binding of water to the product, for

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determining the bond energy between water and the solid skeleton, for finding the thermodynamic and mass exchange characteristics of the moist material, etc. [10, 11].

The objective of this experimental work was to obtain the equilibrium moisture isotherms of extrudates enriched with cocoa bean shells at different temperatures (10 °C, 25 °C and 40 °C), to chose a fit model for their describing and to calculate the monolayer moisture content and specific surface area of sorption.

2 Materials and methods

2.1 Materials

The study was carried out with cocoa bean shells from enterprise “Gaillot Chocolate” Plovdiv (Figure 1). Their mean chemical composition was 10 % moisture content, 14 % proteins, 45 % carbohydrates, 3 % fats and 1.2 % theobromine. The wheat semolina (13 % moisture content) was provided by the Dimitar Pilev Mill Complex in the village of Konush. In order to achieve the specified moisture content water was added to the mixture of cocoa bean shells and the wheat semolina according to Table 1.

Table 1. Experimental design with natural and coded values of the factors

№	Natural values			Coded values		
	Cocoa bean shells content, %	Moisture content, %	Temperature of the matrix, ºC	X_1	X_2	X_3
1	5	14	180	-1	-1	+1
2	5	14	160	-1	-1	-1
3	10	14	160	+1	-1	-1
4	5	20	160	-1	+1	-1
5	5	20	180	-1	+1	+1
6	10	14	180	+1	-1	+1
7	10	20	180	+1	+1	+1
8	10	20	160	+1	+1	-1

2.2 Extrusion

The Brabender 20 DN single-screw laboratory extruder was used for the extrusion cooking [12]. A full factorial experiment 2^3 was conducted with independent variables - cocoa bean shells content (5 % and 10 %), feed moisture content (14 % and 20 %) and temperature of the matrix (160 °C and 180 °C) as the staging of the experiment was detailed described in previous publication [8]. The nozzle diameter 3 mm, screw compression ratio 3:1, extruder screw speed 200 min^{-1}, feed screw speed 30 min^{-1} and temperatures in the first and second extruder zones 140 °C and 150 °C were constant during extrusion.

2.3 Sorption isotherms

The sorption isotherms of the examined extrudates were determined by the static gravimetric method recommended for food products [13]. This method is founded on the usage of saturated salt solutions to maintain a fixed water activity. Fifteen days before the adsorption experiment the extrudates were dehydrated in a dryer with P_20_5 at a room temperature. For desorption process, they were hydrated in a glass jar over distilled water at a room temperature. The samples with weight (1 g ± 0.01 g) were then put in hygrostats with six saturated salt solutions (LiCl, CH_3COOK, $MgCl_2$, NaBr, NaCl, KI), used to obtain a constant relative air humidity [14, 15]. At high water activity ($a_w > 0.5$) thymol crystals were added in the hydrostats to prevent undesirable microbiological contamination of the extrudates [16]. The hygrostats were kept in a thermostat at a constant temperatures of 10 ºC, 25 ºC and 40 ºC ± 0.1 ºC. Samples were weighed (with an accuracy of ± 0.0001 g) every five days.

The equilibrium was established when three consecutive weight measurements showed a difference less than 0.001 g. The equilibrium moisture content of each sample was determined by the drying method according to [17] in triplicates.

Five three parameter models (Chung-Pfost, Halsey, Oswin, Henderson, GAB) recommended in [18] were applied to describe the sorption isotherms of extrudates:

$$\text{Chung-Pfost} \qquad a_w = \exp\left[\frac{-A}{t+B}\exp(-CM)\right] \tag{1}$$

$$\text{Halsey} \qquad a_w = \exp\left[\frac{-\exp(A+Bt)}{M^C}\right] \tag{2}$$

$$\text{Oswin} \qquad M = (A+Bt)\left(\frac{a_w}{1-a_w}\right)^C \tag{3}$$

$$\text{Henderson} \qquad 1 - a_w = \exp[-A(t+B)M^C] \tag{4}$$

$$\text{GAB} \qquad M = \frac{AB'C'a_w}{(1-B'a_w)(1-B'a_w+B'C'a_w)} \tag{5}$$

In the GAB model, the coefficients B' and C' were presented in the form:

$$B' = B\exp\left(\frac{h_1}{RT}\right) \tag{6}$$

$$C' = C\exp\left(\frac{h_2}{RT}\right) \tag{7}$$

where: M – moisture content, % d.b.; a_w – water activity, dimensionless; t – temperature, °C; T – temperature, K; A, B, C, h_1, h_2 – constants; R – universal gas constant (R = 8314 J/(mol.K)).

2.4. Analysis of data

2.4.1 Analysis of sorption characteristics

A nonlinear, least-squares regression program was used to fit the models to the experimental data (all replications). The suitability of the equations was evaluated and compared using the mean relative error (*MRE*, %), standard error of estimation (*SEE*) and randomness of residuals (*e*) [18]:

$$MRE = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{M_i - M_{cal}}{M_i}\right| \tag{8}$$

$$SEE = \sqrt{\frac{\sum_{i=1}^{n}(M_i - M_{cal})^2}{df}} \tag{9}$$

$$e = M_i - M_{cal} \tag{10}$$

where: M_i – experimentally equilibrium moisture content, % d.b.; M_{cal} – calculated moisture content by model; n – number of data points; df – degree of freedom (number of data points minus number of constants in the model).

The monolayer moisture content (M_m) was calculated by using the Brunauer-Emmett-Teller (BET) equation and the experimental data for water activities up to 0.5 [19, 20]:

$$M = \frac{M_m C a_w}{(1 - a_w)(1 - a_w + C a_w)} \tag{11}$$

where: M_m – monolayer moisture content, % d.b.; a_w – water activity, dimensionless; C – constant, dimensionless.

2.4.2 Analysis of mass exchange characteristics

The specific surface area of sorption S_m, (m^2/g) was determined by the values of the equilibrium moisture content corresponding to the monomolecular layer [21]:

$$S_m = M_m . \frac{1}{M_{H2O}} . N_a . A_{H2O} \tag{12}$$

where: M_m - monolayer moisture content, g water/g d.b.; M_{H2O} – water molecular mass (M_{H2O} = 18 g/mol); N_a – Avogadro's number (N_a = 6.022×10^{23} 1/mol); A_{H2O} – water settling surface (A_{H2O} = 10.6×10^{-20} m^2).

3 Results and discussion

Wheat extrudates enriched with cocoa bean shells (Sample № 2 and Sample № 8, Figure 2) were used to investigate the sorption characteristics. In previous experiment was found that these samples were with the highest (Sample № 2) and the lowest (Sample № 8) expansion ratio [12].

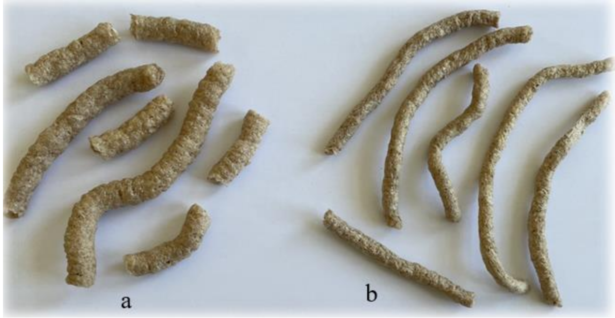

Fig. 2. Wheat extrudates enriched with cocoa bean shells:
a) Sample № 2; b) Sample № 8.

The equilibrium sorption isotherms of wheat extrudates enriched with cocoa bean shells at temperatures of 10 ºC, 25 ºC and 40 ºC are presented in Figures 3 and 4. The data show that the isotherms demonstrate Types II, according to the Brunauer's classification [22]. It was also found that the sorption capacity of the extrudates decrease when the temperature increases. Similar results for extrudates and food materials have been reported in the literature [20, 23, 24, 25, 26].

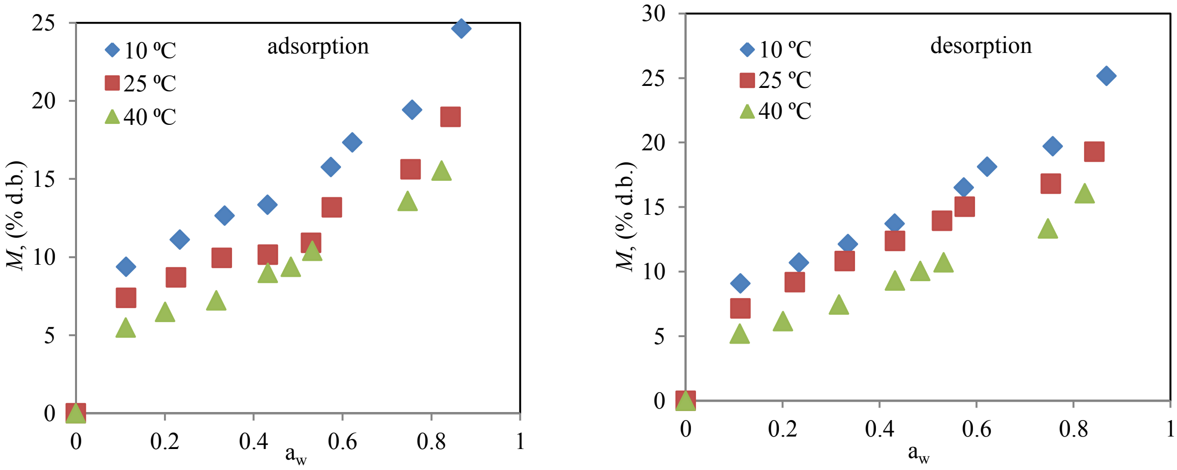

Fig. 3. Equilibrium sorption isotherms of wheat extrudates enriched with cocoa bean shells (Sample № 2).

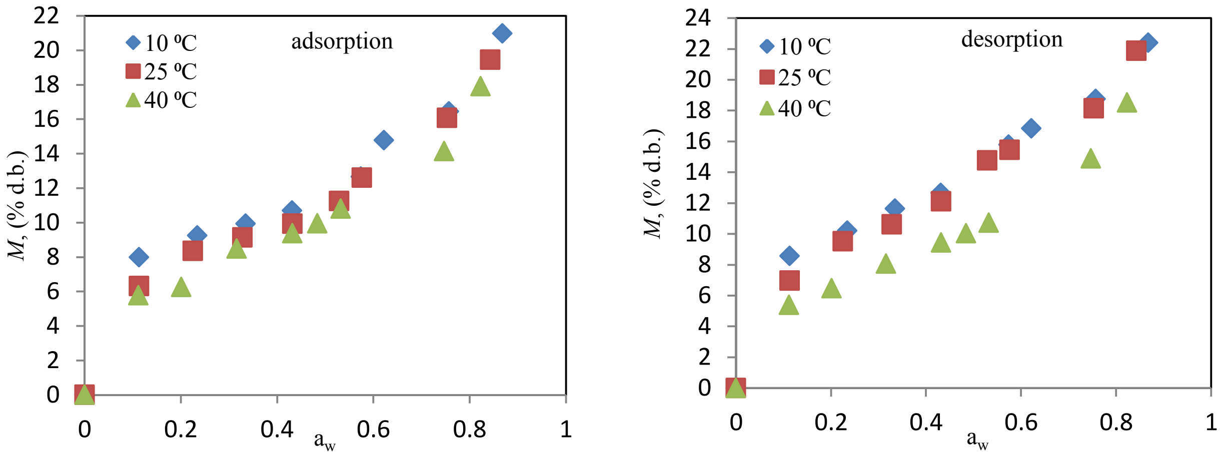

Fig. 4. Equilibrium sorption isotherms of wheat extrudates enriched with cocoa bean shells (Sample № 8).

The comparison of sorption isotherms at temperature of 10 °C for both examined samples is presented in Figure 5. It was established that for the extrudates (Sample № 8) we had the presence of a statistically significant hysteresis effect (significance level α = 0.05), while for the extrudates from the other experiment (Sample № 2) there was no such statistically significant hysteresis. As the temperature increases the hysteresis effect for Sample № 8 decreases but stil remains statistically significant. According to the Sample № 2 there was no statistically significant hysteresis even at higher temperatures.

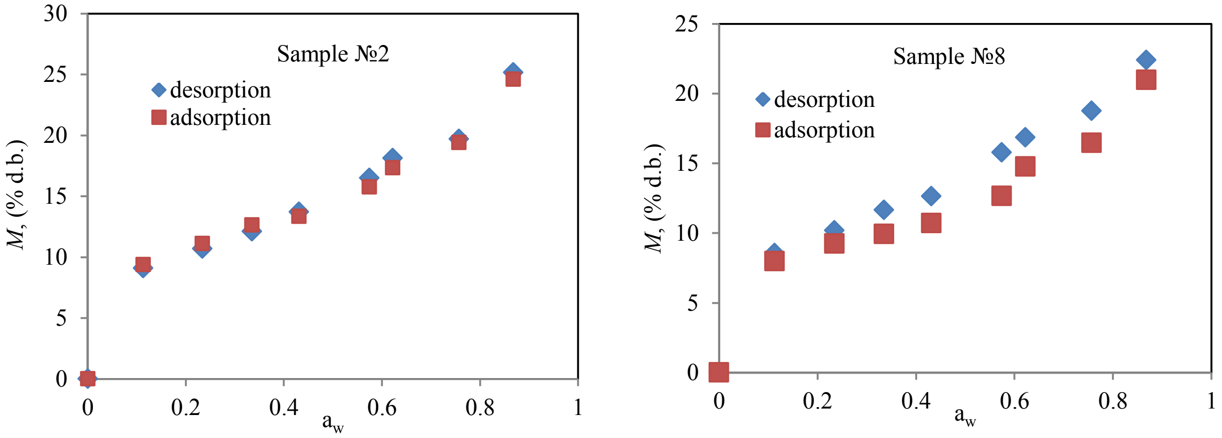

Fig. 5. Comparison of sorption isotherms at temperature of 10 °C.

The obtained coefficients of the models, *MRE* and *SEE* and *Residuals* are presented in Table 2 for desorption and in Table 3 for adsorption. It can be seen that during absorption process the lowest values of *MRE* and *SEE* for both samples were obtained with the Oswin model. In this model the distribution of the residuals was random and it was the most suitable for the description of the sorption isotherms. The second best model, also with a random distribution of residuals, was the Chung-Pfost model. Data analyze from Table 3 shows that for the adsorption process these two models (Oswin and Chung-Pfost) again had the lowest values of *MRE*, *SEE* and *Residuals* and that's why they can be recommended as the most appropriate models.

The comparison of *MRE* and *SEE* demonstrate that for the extrudates (Sample № 8) their values were lower at Chung-Pfost model while for those for Sample № 2 at Oswin model respectively.

The calculation of monolayer moisture content was carried out by linearization of BET model, shown in equation (11) and transformed into equation (13):

$$\frac{a_w}{(1-a_w)M} = P + Q a_w \tag{13}$$

The linearization of the experimental data ($a_w < 0.5$) for the extrudates (Sample № 8) during adsorption process is shown in Figure 6.

Table 2. Coefficients of the models (*A*, *B*, *C*, h_1, h_2), Mean relative error (*MRE*, %), Standard error of estimation (*SEE*) and *Residuals* for desorption process.

Model	*A*	*B*	*C*	h_1	h_2	*MRE*	*SEE*	*Residuals*
	Sample № 2							
Chung-Pfost	**268.2769**	**12.40936**	**0.18672**	**-**	**-**	**5.92**	**0.92**	**Random**
Oswin	**16.80642**	**-0.165721**	**0.26921**	**-**	**-**	**4.25**	**0.61**	**Random**
Halsey	6.074901	-0.031444	2.25793	-	-	7.19	1.72	Non - random
Henderson	0.000168	2.104682	2.01878	-	-	12.65	2.37	Non - random
GAB	7.981194	0.031613	1274.42	7616.816	1184.732	13.17	1.68	Non - random
	Sample № 8							
Chung-Pfost	**340.6437**	**27.2859**	**0.17667**	**-**	**-**	**5.98**	**0.91**	**Random**
Oswin	**15.18153**	**-0.098736**	**0.28583**	**-**	**-**	**6.51**	**0.98**	**Random**
Halsey	5.641867	-0.022798	2.16973	-	-	6.63	1.95	Non - random
Henderson	0.000173	3.814607	1.96361	-	-	15.7	3.17	Non - random
GAB	10.30602	0.181426	0.00041	3009.263	26329.82	6.32	0.97	Random

Table 3. Coefficients of the models (*A*, *B*, *C*, h_1, h_2), Mean relative error (*MRE*, %), Standard error of estimation (*SEE*) and *Residuals* for adsorption process.

Model	*A*	*B*	*C*	h_1	h_2	*MRE*	*SEE*	Residuals
	Sample № 2							
Chung-Pfost	**275.5714**	**6.164**	**0.21732**	**-**	**-**	**1.74**	**0.80**	**Random**
Oswin	**16.24571**	**-0.164634**	**0.26927**	**-**	**-**	**0.23**	**0.64**	**Random**
Halsey	6.707673	-0.037202	2.50774	-	-	4.28	0.86	Non - random
Henderson	0.000152	2.786643	2.08047	-	-	10.92	1.79	Non - random
GAB	7.601109	0.026919	23882.1	8020.316	6995.23	11.47	1.50	Non - random
	Sample № 8							
Chung-Pfost	**615.7558**	**53.1007**	**0.2147**	**-**	**-**	**1.88**	**0.74**	**Random**
Oswin	**12.65355**	**-0.051013**	**0.2983**	**-**	**-**	**0.014**	**0.62**	**Random**
Halsey	5.671833	-0.014142	2.36895	-	-	4.32	0.77	Non - random
Henderson	0.000128	4.773546	2.04930	-	-	18.78	3.89	Non - random
GAB	7.513814	0.377072	0.00049	1605.596	28009.4	4.02	0.58	Random

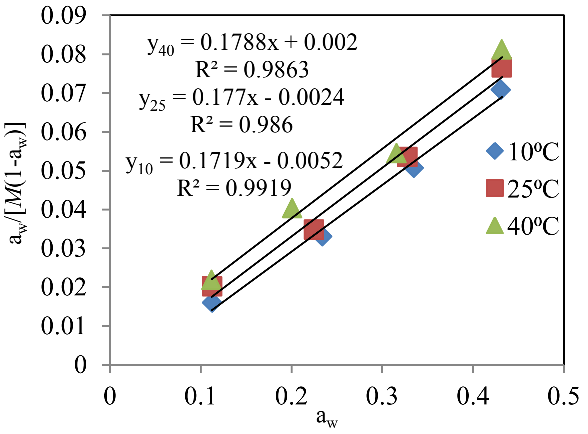

Fig. 6. Linearization of BET model for adsorption process of the extrudates (Sample № 8).

The monolayer moisture contents of the rest samples was determined by the same way and the experimental results were presented in Table 3.

Table 3. BET monolayer moisture content M_m (% d.b.) of wheat extrudates enriched with cocoa bean shells.

Sample	*t*, °C	adsorption	desorption
№ 2	10	7.63	7.80
	25	5.78	7.26
	40	5.08	5.35
№ 8	10	6.00	7.24
	25	5.73	7.08
	40	5.53	5.36

The values of the monolayer moisture content varies between 5.08 % d.b. and 7.8 % d.b., as well as the highest values were obtained for extrudates (Sample № 2) and the lowest temperature of 10 °C. It was established that at the higher temperatures the values of monolayer moisture content for the both extrudates (Sample № 2 and Sample № 8) were practically the same. The monolayer moisture content also shows a tendency to decrease it’s values with the increase of temperature and it can be seen a hysteresis effect (the

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values of desorption process were higher than these from adsorption process).

The adsorption of water molecules is performed on the so-called specific surface area of sorption S_m. This surface area determines the sorption potentialities and the kinetics of product moistening or drying. The values of the specific surface area of sorption for both extrudates (Sample № 2 and Sample № 8) for the three investigated temperatures 10 ºC, 25 ºC and 40 ºC, respectively are shown in Table 4.

Table 4. Specific surface area of sorption S_m (m^2/g) of wheat extrudates enriched with cocoa bean shells

Sample	t, ºC	adsorption	desorption
№ 2	10	272.75	278.82
	25	206.62	259.52
	40	181.59	191.24
№ 8	10	214.48	258.81
	25	204.83	253.09
	40	197.68	191.60

The specific surface area of sorption decrease with the increase of the temperature due to the reduction of polar centers caused from physical and chemical changes occurring at higher temperature [27]. The specific surface of sorption for wheat extrudates with 10 % cocoa bean shells content, 14 % moisture content, 160 °C temperature of the matrix varies between 214.48 (m^2/g) and 197.68 (m^2/g) for adsorption and from 258.81 (m^2/g) to 191.60 (m^2/g) for desorption respectively. According to the wheat extrudates with 5 % cocoa bean shells content, 20 % moisture content, 160 °C temperature the specific surface of sorption changes from 272.75 (m^2/g) to 181.59 (m^2/g) for adsorption and from 278.82 (m^2/g) to 191.24 (m^2/g) for desorption. It was found that the increase of temperature of the matrix from 10 °C to 40 °C decreases the values of the specific surface of sorption for both examined samples.

4 Conclusion

The equilibrium sorption isotherms of wheat extrudates enriched with cocoa bean shells had been determined by the static gravimetric method at different temperatures (10 ºC, 25 ºC and 40 ºC). The Oswin and Chung-Pfost models were the most suitable for describing the relationship between the equilibrium moisture content and the water activity. The monolayer moisture content ranged within 5.08 % d.b and 7.80 % d.b. The specific surface area of sorption for wheat extrudates enriched with cocoa bean shells varied between 181.59 (m^2/g) and 278.82 (m^2/g).

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