Moisture adsorption behavior of the banana flours (*Musa paradisiaca*) unmodified and modified by acid-treatment

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1. Abstract

Moisture equilibrium data (absorption) of untreated and acid treated banana flour were determined using the static gravimetric method of saturated salt solutions at temperatures of 30 ºC. The range of water activities (a_w) between 0.14 and 0.97. The equilibrium moisture content increased with the increase a^w. The experimental data were fitted to four mathematical models BET, GAB, Smith and Iglesias-Chirife. The BET and GAB model were compared because are the models that fit better la experimental data. Monolayer moisture content (X_0) for untreated banana flour (UBF) and acid traded banana flours (ATBFs) were found to be in the range of 4.06 to 5.47 (BET model) and 3.87 to 5.88 (GAB model). The GAB model was found to be the most suitable model to describe the isothermal water sorption of UBF and ATBFs in the evaluated intervals of a_w. This result suggests the mechanism of adsorption of water follows the GAB model and some structural evidence (SEM and X-ray diffraction) to account for the differences in water adsorption behavior in $ATBF_S$ in comparison with UBF.

2. Introduction

Starch is the main reserve of carbohydrate synthesized by superior plants that constitutes an essential source of energy to many living organisms, principally the man[1]. This represents the major component in a large number of agriculture products like cereals (corn, wheat and rice) and some fruits like banana, which can be content of starch from 70 to 80%.[2] (unripe based). Besides, banana is one of the fruits that grow pretty well in the tropical and sub-tropical regions of the world. These bananas are mainly transported to urban areas, where they would be eaten as fruit. However, unavoidable delay in transport, poor post harvest technology and fluctuating market demand result in overripe and senescence of fruits prior to market delivery. For this reason, large quantities of fruits are lost during commercialization as a consequence of deficient postharvest handling. For which nowadays they propose new economical strategies of banana use are now considered for banana use, such as the production of unripe banana flour (BF) due to its high starch content.[3] Nowadays, the new product development area in those industries is interesting in searching for starches with improved functional products such as viscosity, solubility, low retrogradation and syneresis tendency, etc. Since some years ago, the tendency is looking for alternative sources to obtain starches exhibiting better physicochemical and functional characteristics. The native starches present limitations that reduce their use at the industrial level. For which in recent years, it has been studied the acid-thinned starch, because due to the industries, Acid modification is widely used in the starch industry to produce thin boiling starches for use in food, paper, textile and other industries. Acid modification

could change the morphological properties, crystalline properties, gelatinization properties involving transition temperatures and gelatinization enthalpy. Acid modification of starch could be very helpful to understand the inner structure of starch granules. The objectives of this study was evaluate the behavior the sorption isotherms of acid-treated banana flours and some morphological and structural properties.

3.1 Materials and Methods

3.1 Preparation of banana flour

Commercial hard green (unripe) banana (Musa paradisiaca L.) fruits were purchased from the local market in Cuautla, Morelos, México. Fruits were cut into 1 cm slices and were immediately rinsed in citric acid solution (0.3% w/ v). The slices were dried at 50 ºC, ground with a commercial grinder (Mapisa Internacional Sociedad Anonima de Capital Variable, México, Distrito Federal) to pass a US 50 sieve, and stored at 25 ºC in sealed plastic containers until further analyses could be carried out.

3.2 Chemical composition of banana flour (BF)

Moisture content was determined gravimetrically; the sample (2–3 g) was heated (130 ± 1 ºC for 15 min.). The ash, protein, and fat contents were analyzed according to AACC methods (08-01, 46-13, 30- 25, and 32.05, respectively).[4] Total starch (TS) was determined by the method of .[5]

3.3 Chemical modification (Lintnerization) of banana flour (BF)

Acid hydrolysis of samples was obtained by hydrolysis of 100 g of BF in 400 mL of 1.6 M HCl at 38 °C for different reaction time (1, 5, 11, 16 and 20 days) with a stirrer operating at 200 rpm (Table 1). After the reaction, the blend was neutralized with NaOH at the same concentration of HCl used; the pH was adjusted to 7.0. Thereafter, the wet powder was washed with distilled water.

3.4 Determination of sorption isotherms

Water sorption isotherms were determined using a gravimetrical exposing the sample at different salts. Tree grams samples were placed in weighed sample dishes and dehydrated and vacuum oven at 70 °C for 8 h.[6] These salts were employed as saturated solutions to give constant water activity (a_w) values. The samples (3 g dry basis) of untreated banana flour (UBF) and acid-treated banana flours (ATBF). The optimum moisture content of flour samples were calculated from the equilibrium moisture data by using four mathematical models Brunauer-Emmett-Teller equation (BET), Guggenheim, Anderson and de Boer (GAB), Smith and Iglesias-Chirife.

3.5 Scanning electron microscopy (SEM)

For SEM studies, the samples were fixed to a conductive double glued tape of copper; which was covered with a 20 nm of thick coal layer. It was deposited under a vacuum using an evaporator in a JEOL JSMP 100 (Japan) electron microscope. Later on, samples were covered in the ionizer metals JEOL with a 50 nm thickness gold layer. A film piece was mounted on aluminium stubs using a double-sided tape and then coated with a gold layer

(40-50 nm), allowing surface and cross-section visualization. All samples were examined using an accelerating voltage of 5 kV.

3. X-ray diffraction analysis

X-ray diffraction allows the determination of crystallinity and composition of crystalline phases in starch samples.18–20. The samples were stored at room temperature before analysis. They were scanned in the angular range 3–378 (2y) with an Advance D8 Diffractometer from Bruker (Coventry, UK) at 35 kV with Cu Ka radiation (1.542 Å). The crystallinity percentage (%C) was determined form the diffractogram by calculation of the area corresponding to the crystalline peaks (Ap; from the difference between the area under the curve and the area of the amorphous halo), the total area under the curve (At), and the instrumental noise (N).

4. Results and discussion

4.1 Chemical composition

UBF had a moisture content of 12.64%, higher than those determined in BF obtained from the pulp (7.1%[3]) and However, the moisture content of UBF was similar to that obtained for commercial wheat flour (11.4%22). The difference might have been related to the time used in the drying process. The protein level of UBF (4.03%) resembled that reported previously for BF (3.8%[7]) but was slightly higher than that of BF prepared with pulp (3.27%3). The differences shown were related to the variety, cultivar, soil, altitude, agronomic trials, and procedure used for flour preparation. UBF exhibited a 4.64% ash content, which was similar to that reported for BF prepared with the pulp (4.70%3) and BF prepared with pulp and peel (4.4%4). Lower ash contents (2.6–3.5%) were determined in UBFs.[8]The UBF we analyzed had a lipid content of 3.24%, similar to the value (2.69%3) reported for BF.[8] The pulp of unripe bananas features a high starch content,2,3 and this was confirmed by our results (73.01%).

4.2 Equilibrium moisture content

The adsorption isotherms for UBF and ATBF at 30 °C are shown in Figure 1. The equilibrium moisture content at each water activity represents the mean value of three replications. The result of sample demonstrates an increase in equilibrium moisture content with increasing water activity (0.3-0.97), at constant temperature (30 °C). This behavior is manifested in the form of a sigmoidal shaped curve, thus reflecting a Type II isotherm which are the most frequent in foods as fruits and vegetables. The starch sorption isotherm is attributable mainly to hydrogen-bonding of water molecules to the available hydroxyl groups of chain amilosa and amylopectin, those in the amorphous regions and on the surfaces of the crystallites.[9]

Menkov and Durakova (2007) report moisture sorption isotherms of sesame flour at several temperatures, the GAB model was found to be the most suitable for describing the adsorption data, reporting value for X_0 of 5.178 . However, also the values X_0 (3.69-5.50) of BET model are in agreement with ours research.[10, 11] This difference in the between UBF and bananas flours modified ($ATBF_1$, $ATBF_2$, $ATBF_3$ and $ATBF_4$) suggest that the mechanism of water adsorption by chain starch involves factors other than the hydration affinity of the

characteristic groups. These are the availability of the polar groups in the molecule of the polysaccharide, the distribution and arrangement of these groups in the starch granule, conformation, the degree of crystallinity and packing of the chains.

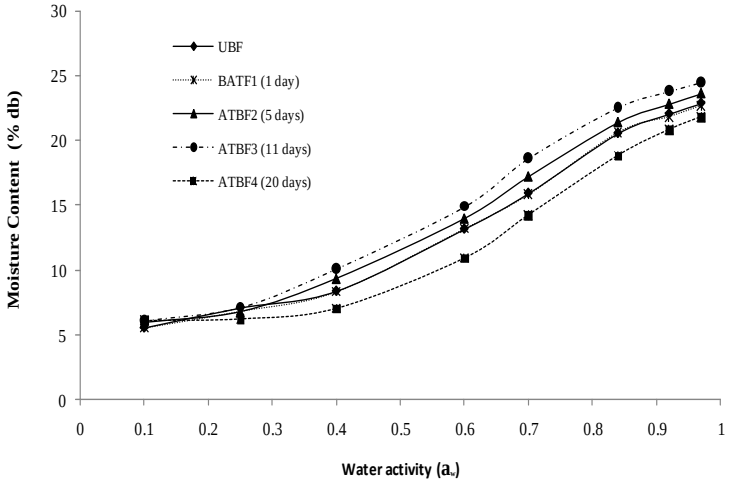

Figure 1. The adsorption moisture isotherms of untreated banana flour (UBF) and acid-treated banana flour (ATBF) observed data at 30 °C; ATBF1: modified for 1 day, ATBF2; modified for 5 days, modified for 11 days and ATBF; modified for 20 days.

4. Differential scanning calorimetry (SEM)

SEM micrographs of banana starch, UBF and $ATBF_S$ are displayed in Fig. 2. SEM of banana starch and UBF show the presence of large elliptic and oval or small spherical granules (Figure 2a and 2b). The surface of the granule appears to be smooth, with no evidence of any fissures. During 1days of the hydrolysis (Figure 2c), no obvious changes occur on the shape and size of the starch granules from the SEM photographs. However, after 5 days of hydrolysis (Figure 2d), some fissures and destruction could be observed on the surface of some starch granules. This effect becomes more evident at the 11 and 20 days of the hydrolysis (Figure 2e and 2f) after all amylose and amylopectin molecules on the outer layer had been destroyed.

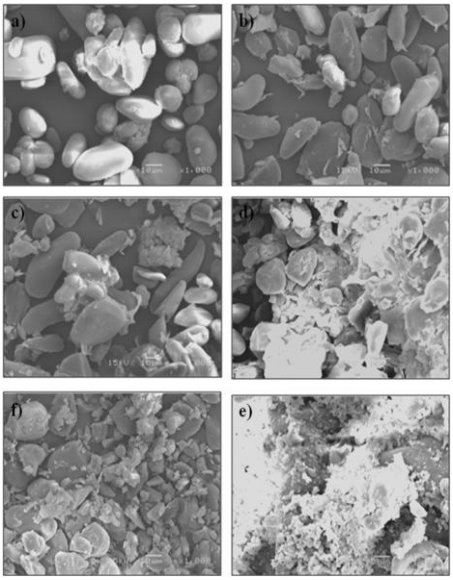

Figure 2. Scanning electron micrographs (magnification 1000x) of banana starch (a), untreated banana flour (b), acid-traded banana flour for 1 day (c), acid-traded banana flour 5 days (d), acid-traded banana flour for 11 days (e) and acid-treated banana flour for 20 days (f).

4.3 X-ray diffraction analysis

The results of crystallinity were 19.3% (UBF), 18.9% ($ATBF_1$), 20.5% ($ATBF_2$), 22.2% ($ATBF_3$) and 17.6% (ATBF4). This agreed with the result obtained in isotherm adsorption, because the acid treatment degraded the amorphous zones of the starch present in the UBF, which increased the crystallinity. However, the $ATBF_4$ present a value of less crystallinity compared to all the samples, due to time of modification.

5. Conclusions

Equilibrium moisture contents were found to increasing with increasing water activity. The values the equilibrium moisture content in ATBF3 was slightly higher than UBF. Calculations of the sorption areas from the monolayer moisture values obtained from the GAB equation were comparable with other sorption areas reported in the literature for various cereal grains and starch.

The granule morphology (SEM) and crystalline structure were significantly affected by the acid-treatment in $ATBF_s$, because the erosion and caused the breakdown in starch granules. The results presented conclude that acid hydrolysis efficiently increases the crystallinity of starch it may induce interconversion between crystalline types.

6. References

1. Buléon, A., Colonna, P. et Leloup, V. 1990. Les amidons et leurs dérivés dans les industries céréales. Industries alimentaires et agro-industrielles. Juin. 515-532.
2. Bello-Pérez L. A., Agama-Acevedo E, Sánchez-Hernández L. And Paredes-López. 1999. Isolation and partial characterization of banana starches. Journal Agricultural Food and Chemistry. 47: 854-857.
3. Juarez-Garcia, E., Agama-Acevedo, E., Sáyago-Ayerdi, S. G., Rodríguez-Ambriz, S. L y Bello-Pérez, L. A. 2006. Composition, digestibility and application in breadmaking of banana flour. Plant Foods Human Nutrition. 2006, 61, 131.
4. American Association of Cereal Chemists. 2000. Approved Methods of the ACCC, 10th Ed. The Association: St. Paul, MN.

5. Goñi, I., Garcia-Alonso A. and M and Saura-Calixto F. 1997. A Starch hidrolisis procedure to estimate glycemic index. Nutr Res. 17: 427-437.
6. Labuza T. P., Kaanane A and Chen J. Y. 1995. Effect of Temperature on the Moisture Sorption Isotherms and Water Activity Shift of Two Dehydrated Foods. Journal of Food Science. 50(2):385 – 392.
7. Faisant, N.; Gallant, D. J.; Bouchet, B.; Champ, M. Eur J Clin Nutr 1995, 49, 98.
8. Da Mota, R. V.; Lajolo, F. M.; Ciacco, C.; Cordenusi, B. R. Starch 2000, 52, 63.
9. Urquhart, A. R. (1959). Sorption of water by cellulose and starch. In J. Honeyman (Ed.), Recent advances in the chemistry of cellulose and starch (pp. 240–264). London: Heywood & Company.
10. McLaughlina C. P. and Magee T. R. A. 1998. The determination of sorption isotherm and the isosteric heats of sorption for potatoes. Journal of Food Engineering, 35 (3): 267-280.
11. Oyelade, O. J. Tunde-Akintunde, T. Y and Igbeka, J. C. 2008. Predictive equilibrium moisture content equations for yam (Dioscorea rotundata, Poir) flour and hysteresis phenomena under practical storage conditions. Journal of Food Engineering 87, 229–235.