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Moisture sorption isotherms and other physicochemical properties of nixtamalized† amaranth flour

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This study reports the moisture sorption isotherms of lime-cooked amaranth flour processed under combinations of the following parameters: temperature (°C), cooking time (min) and calcium hydroxide (%, w/w). Monolayer moisture content (M_1) from a Brunauer-Emmett-Teller (BET) model were obtained. Also, the following physicochemical properties were determined: water activity, water absorption index, water solubility index, Hunter colour, and particle size index. Amaranth flour processed at 90°C, 15 min, and 1% calcium hydroxide showed the highest monolayer moisture content (83·7 mg water/g dry flour). All these physicochemical properties correlated with temperature. Moisture sorption isotherms were found to belong to BET type II. The moisture-sorptive capacity of nixtamalized amaranth flours was affected by processing conditions.

INTRODUCTION

Previous studies carried out at our laboratory showed that amaranth can be cooked with calcium hydroxide to produce nixtamalized flour possessing the basic functional properties for tortilla making (Vargas-López *et al.*, 1990). This promising use led to a study of the thermodynamic behaviour of amaranth lime-cooked flour in moistened atmospheres. There is a close relationship between moisture sorption isotherms and the chemical, physical, and microbiological stability of dehydrated foods (Scott, 1957; Paredes—López & Mora-Escobedo, 1983; Hsieh *et al.*, 1990). The interaction of water with food components can be studied by thermodynamic, kinetic, spectroscopic, and diffraction techniques (Kuntz & Kauzmann, 1974), but in the food area a majority of such studies has been done by the thermodynamic method of moisture sorption isotherms. This method measures the degree of hydration of a material as a function of water activity (A_w) at constant temperature and pressure (Van den Berg & Bruin, 1981). Moisture sorption studies on most cereal and starchy flours have already been compiled (Iglesias & Chirife, 1982; Lomauro *et al.*, 1985).

The aim of the present research was to assess the effect of the processing conditions, temperature, cooking time and calcium hydroxide concentration, on the moisture sorption isotherms, and on other physicochemical properties, of nixtamalized amaranth flours.

MATERIALS AND METHODS

Flour preparation

Samples of *Amaranthus hypochondriacus*, Mercado type, were harvested at a local experimental farm; this cultivar is high yielding with some other outstanding agronomic traits. The lime-cooked flour was prepared (Vargas-López *et al.*, 1990) by varying temperature, cooking time and calcium hydroxide concentration (Table 1). Raw amaranth seed flour, and a commercial nixtamalized maize flour commonly known as Maseca (Maseca SA, Zamora, México) were used as control.

Moisture sorption isotherms

Water sorption isotherms were determined gravimetrically in the A_w range from 0·115 to 0·841. Predried flour samples (in a convection oven at 50°C for 24 h) of

† *Nixtamalized* means the addition of 1 part of whole amaranth, 0·6 to 1% (based on previous weight) of calcium hydroxide or lime, and two parts of water. The mixture is heated at 50 to 90°C for 15 to 25 min. Then, the cooking liquor is decanted and the sample, now referred to as nixtamalized amaranth, is washed two or three times with water. The cooked amaranth is then ground to flour.

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Table 1. Treatments applied for lime-cooking of amaranth

Treatment	Temperature (°C)	Cooking time (min)	$Ca(OH)_2$ (g/100 g seeds)
1	50	15	1·0
2	70	15	1·0
3	70	25	1·0
4	80	20	0·6
5	90	15	1·0

1 g were placed in aluminium pans and stored over saturated salt solutions (Resnik *et al.*, 1984) in desiccators, which were maintained at 25 ± 0·2°C in a thermostatic chamber (Nieto, SA, Celaya, México). The salts (J. T. Baker, Xalostoc, México) used were: lithium chloride, potassium acetate, magnesium chloride, sodium chloride, sodium nitrite and potassium chloride. Samples were weighed periodically until attaining headspace equilibrium (10–14 days) (Gevaudan *et al.*, 1989). To avoid fungal spoilage, the desiccators were closed in a laminar flow chamber with ultraviolet light.

Moisture and A_w

Moisture was measured by weighing 2 g flour samples in aluminium dishes and hand shaking until contents were evenly distributed. The dishes were placed in a forced air oven for 2 h at 135°C according to AACC method 44—19 (AACC, 1983). A_w was determined in 5 g flour samples, tempered at 25°C, using a hygrometer Rotronic Hygroskop DT (Rotronic AG, Huntington, NY), which was calibrated with potassium chloride saturated solution (A_w = 0·841 at 25°C). After leaving the samples 1 h, the headspace equilibrium was attained, and then readings taken.

Monolayer moisture content

This property was calculated from the experimental data moisture content versus A_w, by applying the linearized BET model (Brunauer *et al.*, 1938) shown below:

$$A_w/[M(1 - A_w)] = 1/M_1C + (C - 1)\,A_w/M_1C$$

where A_w = water activity, M = moisture content (mg water/g dry flour), M_1 = monolayer moisture content (mg water/g dry flour), and C = model constant.

Water absorption and solubility indices

Water absorption (WAI) and water solubility (WSI) indices were assessed as described by Anderson *et al.* (1969). Each flour sample of 4·5 g was suspended in 30 ml of water in a tared 60 ml centrifuge tube. The slurry was shaken with a glass rod for 1 min at room temperature and centrifuged at 3000 × *g* for 10 min. The supernatant was poured carefully into a tared evaporating dish. The WAI was calculated from the weight of the remaining gel and expressed as grams of gel per gram of solid. The WSI, expressed as gram of solids per gram of original (2·5 g) solids, was calculated from the weight of dry solids recovered by evaporating the supernatant overnight at 110°C.

Hunter colour

Surface colour of samples was measured using a HunterLab D25-2 Color Difference Meter (Hunter Associates, Inc., Reston, VA). L, a and b colour values were recorded and compared with the standard with the following values: L_s = 91·2, a_s = −1·0, and b_s = −1·7. Total colour difference (ΔE), was calculated (Clydesdale, 1976) by using the equation:

$$\Delta E = [(L_s - L)^2 + (a_s - a)^2 + (b_s - b)^2]^{1/2}$$

Particle size index

Flour samples of 100 g were placed in a series of US standard sieves (W. S. Tyler, Inc., Mentor, OH) with the following sizes: No. 40 = 420, no. 70 = 212, no. 80 = 180 and no. 100 = 150 μm. Sieves were shaken by a Ro-Tap machine (W. S. Tyler, Inc.) for 10 min. Material retained on the different sieves and in the pan was weighed and expressed as per cent overs. To compute the particle size index (PSI) of flours, the following formula was used (Bedolla & Rooney, 1984):

$$PSI = \Sigma\, a_i b_i$$

where a_i = percentage of overs on sieve i, and b_i = coefficient relative to sieve i.

The b_i values for sieves numbers 40, 70 and 80 were 0·4, 0·7 and 0·8, respectively. Overs from the sieve No. 100 and from the pan were added and an overall b_i = 1·0 was assumed. The greater the PSI value, the finer was the flour.

Bulk density

Four samples were placed in a known-volume stainless steel cylinder until topped at 25°C. The device was topped five times and the flour density obtained by dividing the sample mass by the cylinder volume.

Statistical analysis

The M_1 and the other physicochemical data obtained from duplicated determinations were treated by simple regression analysis and by the Duncan's multiple range test ($p < 0·05$) for comparison among means.

RESULTS AND DISCUSSION

Table 2 shows the physicochemical properties of nixtamalized flours. A_w was an experimentally determined quantity which ranged from 0·221 to 0·305 for the flours processed at 50 and 90°C, respectively. This

Table 2. Physicochemical properties of the lime-cooked amaranth flours[a]

Treatment (°C/min/ $Ca(OH)_2$)	A_w	M_1	WAI	WSI	ΔE	PSI
50/15/1·0	0·221d	73·3c	2·43b	12·2a	17·2d	98·3b
70/15/1·0	0·261c	76·3b	2·57a	8·8b	18·8c	99·1a
70/25/1·0	0·264c	72·7c	2·49b	8·8b	19·0c	99·0a
80/20/0·6	0·283b	72·5c	2·51a	8·9b	19·9b	99·1a
90/15/1·0	0·305a	83·7a	2·47b	8·5b	20·8a	99·3a

[a] Means with the same letter are not significantly different ($p < 0·05$).
A_w = water activity; M_1 = monolayer moisture content (mg H_2O/g dry flour); WAI = water absorption index; WSI = water solubility index; ΔE = total colour difference; PSI = particle size index.

property showed a significant ($p < 0·05$) correlation with temperature ($r = 0·99$) (Table 3). Amaranth flour nixtamalized at 90°C displayed the highest M_1 and the lowest value corresponded with that at 80°C. Processing conditions affected this physicochemical property, probably due to changes of the native structure of macromolecules (e.g., starch, proteins), as suggested by other workers (Mannheim & Passy, 1982). M_1 is considered equivalent to the amount of water held adsorbed on specific sites of the adsorbent (flour). This is the moisture content at which each polar and ionic group has a water molecule bound to it, to form the start of a liquid-like phase (Labuza, 1984). The M_1 values of nixtamalized amaranth flours ranged from 73·3 to 83·7 mg water/g dry flour (Table 2). Aguerre *et al.* (1989) reported M_1 values of 84 and 85 mg water/g dry flour for corn and sorghum starches, respectively.

It has been reported that there is a low amylose content in amaranth grain when compared with maize and wheat (Paredes-López & Hernández-López, 1991). M_1 data for amylopectin and amylose were 52·2 and 61·1 mg water/g dry flour as found by Mannheim and Passy (1982) which agree with the M_1 values for amaranth lime-cooked flours. M_1 can be used as a factor of comparison among sorption isotherms of different starchy materials because it is a parameter obtained from the BET model. Thus, isotherms from experimental flours were similar to starches reported above.

Table 3. Regression equations for the physicochemical properties of the lime-cooked amaranth flours

Function	r
$A_w = 0·116 + 0·0021\ T$	0·99
$M_1 = 59·56 + 0·26\ T$	0·86
$WAI = 2·42 + 0·001\ T$	0·55
$WSI = 16·43 - 0·0942\ T$	−0·91
$\Delta E = 12·69 + 0·09\ T$	0·99
$PSI = 96·99 + 0·026\ T$	0·72

A_w = water activity; M_1 = monolayer moisture content (mg H_2O/g dry flour); WAI = water absorption index; WSI = water solubility index; ΔE = total colour difference; PSI = particle size index; T = temperature.

WAI was affected by cooking temperature in all the nixtamalized amaranth flours. WAI values for lime-cooked amaranth flour ranged from 2·43 to 2·57 g gel/g dry flour (Table 2). Increases of WAI for alkaline treated samples might be related to flour starch damage (Vargas-López *et al.*, 1990). Anderson (1982) reported that cooking temperature increased WAI for several grains. Results of this study agree with those findings. It may be suggested that WAI is mainly influenced by the affinity of the flour particles for water because finer particles form a greater gel matrix with water trapped into it (Anderson *et al.*, 1969).

WSI correlated negatively ($r = -0·91$) with temperature (Table 3). Low cooking temperatures stimulated the migration of certain solutes which can be leached out on contact with water; this behaviour led to high WSI values. A similar trend was obtained from roll-cooked wheat grits values as reported by Anderson (1982). However, further studies on this effect are needed.

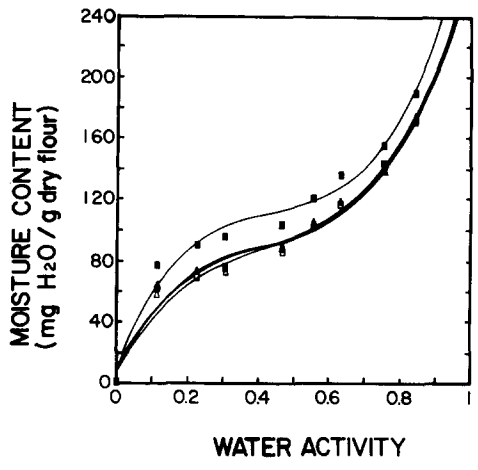
ΔE represents the total colour difference in relation to a white standard; higher ΔE values mean darker flours. The ΔE for the experimental flours varied from 17·2 to 20·8, with a strong dependence on cooking temperature ($r = 0·99$) (Tables 2 and 3). Colour of amaranth flours became slightly brownish yellow after lime cooking (Vargas-López *et al.*, 1990). This effect could be due to the reaction of the amaranthin pigment, which is present in amaranth seeds, with other flour components (Sánchez-Marroquín, 1980). However, all samples appeared to have a pleasant colour at tested conditions.

PSI is a measurement of flour finesse; higher values of PSI mean smaller flour particles. The experimental flours showed PSI values from 98·3 to 99·3 under described conditions (Table 2). Bedolla and Rooney (1984) found that PSI for nixtamalized maize flour was positively correlated with temperature; this correlation was also found for nixtamalized amaranth flour ($r = 0·72$) (Table 3).

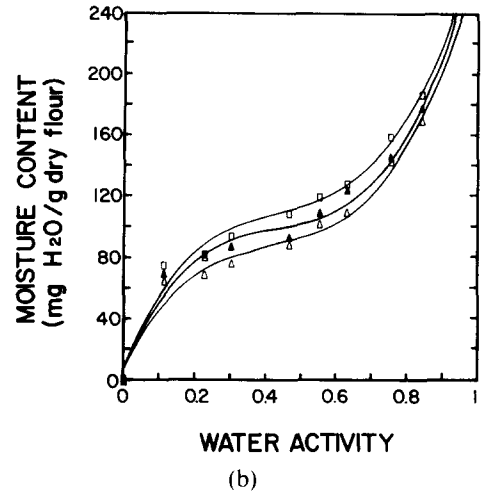
Bulk density (0·5 g/cm³) measurements showed insignificant differences ($p > 0·05$) for all samples (data not shown).

The flour physicochemical parameters of Table 3 were mostly dependent on temperature followed by cooking time and calcium hydroxide. All the regression equations showed positive correlation with temperature, except WSI which showed a high negative coefficient. The highest correlation coefficients were exhibited by A_w and ΔE, and the lowest by WAI.

Moisture sorption isotherms of nixtamalized amaranth flours, plus raw amaranth and Maseca flours studied here, belong to BET type II, as demonstrated by Figs 1a and b. Changes in the isotherm behaviour reflect the effect of treatments applied to amaranth seeds, as observed for the M_1 values as well. At all A_ws, equilibrium moisture content of both nixtamalized (70°C/25 min/1·0% calcium hydroxide) and raw amaranth flours was higher than that of samples processed under less strong conditions (Fig. 1a). Figure 1b shows that lime-cooked amaranth flour at 90°C tended



(a)



(b)

Fig. 1. Moisture-adsorption isotherms of nixtamalized amaranth flours at 25°C. (a) Temperature, °C/cooking time, min/calcium hydroxide concentration, %: Δ, 50/15/1·0; ▲, 70/15/1·0; □, 70/25/1·0; and control ■, raw amaranth flour. (b) Δ, 80/20/0·6; ▲, 90/15/1·0; and control □, commercial nixtamalized maize flour (Maseca).

to have a higher equilibrium moisture content at all A_ws tested than did the sample cooked at 80°C, whereas the commercial nixtamalized maize flour had the highest values. It has been suggested that between 0 and 0·1 A_w water is strongly and directly bonded on polar sites of the flour macromolecules; between 0·1 and 0·65 A_w, water molecules are bonded either on those previously bound or on polar sites previously hidden inside the structure and now accessible due to swelling. Above 0·65 A_w, water molecules accumulate in small capillaries and intermacromolecule spaces (Multon *et al.*, 1980; Mok & Dick, 1991). The number of exposed polar sites and spaces available for water accommodation are somehow changed by the amaranth nixtamalization conditions, consequently affecting the moisture-sorptive capacities of flours. In general, very complex reactions might be influencing trends followed by isotherms; in lime-cooking of amaranth seeds, gelatinization and 'pasting' phenomena generated by various processing temperatures, and by different water and ion concentrations (Paredes-López & Hernández-López, 1991) also occur.

In summary, the amaranth lime-cooked flour processed at 90°C showed the highest M_1. Lime-cooking temperature positively correlated with the physicochemical properties studied here, except WSI. All the moisture sorption isotherms belonged to BET type II.

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