

Effect of drying on the nutritional and colorimetric properties of quelite leaves (*Amaranthus* spp.)

Efecto del secado en las propiedades nutricionales y colorimétricas de hojas de quelite (*Amaranthus* spp.)

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Abstract

Objectives

Determine the influence of air temperature on the water loss from quelite leaves (*Amaranthus* spp.), model drying kinetics and measuring of post-drying functional properties effect.

Methodology

The kinetics of drying quelite leaves were carried out in an oven at 45, 55 and 65 ° C and in a direct cabinet-type solar dryer. Several models from the literature were evaluated, also colorimetry, phenolic content, chlorophyll and antioxidant activity pre and post drying were also determined.

Contribution

The solar dryer reached a maximum of 60 ° C with a minimum indoor moisture of 17%. The solar dryer and oven at 65 ° C reached equilibrium moisture in 270 min. At 45 ° C the drying oven time was 510 minutes. The Modified Page model best fits all thin layer drying curves, with greater than 96.7 values. The drying oven at 55 ° C better conserved the color and the functional properties concerning the fresh leaves with 73, 41 and 24% of the chlorophylls a, b, and c respectively. The residual antioxidant activity was between 38-42% with respect to the fresh content. There was no difference between the drying oven treatments ($\alpha = 0.05$).

Drying kinetics, Mathematical model, Nutritional properties

Resumen

Objetivos

Determinar la influencia de la temperatura del aire sobre la pérdida de agua de hojas de quelite (*Amaranthus* spp.), modelar el secado y medir la afectación de las propiedades funcionales post secado.

Metodología

Se realizaron las cinéticas de secado de hojas de quelite en horno a 45, 55 y 65 ° C y en un secador solar directo tipo gabinete. Se evaluaron varios modelos de la literatura y se determinó colorimetría, el contenido de fenoles, clorofila y actividad antioxidante pre y post secado.

Contribución

El secador solar alcanzó 60 ° C como máximo con humedad mínima interior de 17%. El secador solar y en horno a 65 ° C alcanzaron la humedad de equilibrio en 270 min. A 45 ° C el tiempo de secado fue de 510 minutos. El modelo Page Modificado dio mejor ajuste a todas las curvas de secado en capa delgada, con un valor mayor a 96.7. El secado en horno a 55 ° C conservó mejor el color y las propiedades funcionales respecto de las hojas frescas con 73, 41 y 24% de las clorofilas a, b, y c respectivamente. La actividad antioxidante residual fue entre 38-42% respecto al contenido en fresco. No hubo una diferencia entre los tratamientos de secado en horno ($\alpha=0.05$).

Cinéticas de secado, Modelo matemático, Propiedades nutrimentales

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Introduction

Endemic Mexican plants are losing popularity in their consumption, among some native varieties, edible plants “quelites, quintoniles” or amaranths (*Amaranthus* spp.) with 8 main species reported are included [R.A. Bye Boettler, E.L. Mazari, 2011]. Quelites have been shown to have different essential of nutrients such as protein, fiber, calcium. In addition, quelites have an important portion of bioactive compounds such as chlorophyll, antioxidant activity related to its content of polyphenolic compounds, flavonoids and polyunsaturated fatty acids, so they can be considered functional foods [Y.O. Santiago-Saenz, A.D. Hernández-Fuentes, C.U. López-Palestina, J.H. Garrido-Cauich, J.M. Alatorre-Cruz, R. Monroy-Torres, 2019]. Most of the time, quelites are consumed after heat treatments made to reduce or avoid their toxicity as cooking, boiling, blanching, frying or roasting. A peculiarity of most quelites is that they are consumed by harvesting during rainy season since they appear from the seeds self-deposited in soil, so their availability throughout the year is not constant, making preservation methods such as drying a need to possibility their storage, with appropriate conditions to preserve their nutraceutical properties. In advantage with other preservation methods, drying reduces transportation and packaging costs, since drying decreases product volumes. Unfortunately, conventional drying consumes a large amount of energy during the process, impacting on environmental pollution [F. Lagunes, I. Estrada, J. Guerrero, R. Navarrete, 2013], that is why solar drying represents a feasible and sustainable option for solar food drying [G. Lopez-García, 2017]. Drying characteristics of a food and thin layer mathematical models are necessary to design, build and operate drying systems [E.C. López-vidaña, A. L. César-Munguía, O. García-Valladares, I. Pilatowsky Figueroa, 2020]. Mathematical modeling in drying procedures is a powerful tool for improving the product quality by reducing energy consumption and the operational performance optimization [V. Tomar, G. N. Tiwari, and B. Norton, 2017], [D. V. N. Lakshmi, P. Muthukumar, A. Layek, and P. K. Nayak 2018]. The objective of this study was to evaluate and analyze the thin layer mathematical model on quelite drying, as well as to determine the color changes and nutritional properties in post drying.

Methodology

Sample origin: Fresh quelites were collected in non-human disturbed areas around the municipality of Colotlán, Jalisco, México. The leaves were separated from the stem and it was discarded. Next, the leaves were washed to eliminate any residual soil that could interfere with the methodologies to be used. After drying, samples were milled in a grain mill to 80 U.S. STD. Sieve.

Drying: Conventional oven drying under controlled conditions was carried out in an electric oven, (eco-shell, Mexico) under triplicate for each experiment at 45, 55 and 65 ° C. Solar drying was carried out in a cabinet direct solar dryer. The solar dryer is made with transparent polycarbonate, and included three different levels to place the samples with a total area of 0.30 m².

Sample extraction: Acetone extracts: 0.6 g of dry sample were run in triplicate, 25 mL of 90% (V/V) in water acetone solution were added and recipients were put in orbital 100 rpm shaking for 24 h at room temperature in the absence of light. After that, the supernatant was separated by centrifugation at 10000 rpm for 15 min and room temperature. The extracts were stored at -4 ° C in the dark until they were used for chlorophyll determination.

Phenolic extracts: 0.6 g of dry sample were orbital 100 rpm mixed with 40 mL of methanol 90% in water (V/V) for 24 h. After that, the supernatant was separated by centrifugation at 10000 rpm for 15 min and room temperature. The extracts were stored at -4 ° C in the dark until they were used for phenolic and antioxidant capability determinations.

Determination of antioxidant activity: it was evaluated by the colorimetric decolorization radical capability of extracts on the 2,2-Diphenyl-1-picrylhydrazyl (DPPH) at 517 nm, and 2,2-azinobis (3-ethylbenzothiazolin) -6-sulfonic acid (ABTS) at 732 nm. A gallic acid standard curve was used for equivalents calculation. The results were expressed as μmol gallic acid equivalent / 100 g of sample (dry basis).

Determination of phenolic content: The Folin-Ciocalteu method [8] was used for free polyphenols quantification. For this methodology a 25% (V/V) in water solution, of the Folin-Ciocalteu reagent were used and 0.5 M Na_2CO_3 . Sample triplicates in appropriated water dilution were placed in a 96 cell microplate, 125 μL of 0.5 M Na_2CO_3 solution and Folin-Ciocalteu reagents were added, after mixing, plate was incubated at 40 ° C for 15 minutes, and read at 690 nm in a microplate reader. A standard curve with gallic acid was made for calculations.

Chlorophyll determination: it was carried out by colorimetric spectrophotometric method. The absorbance of the acetonetic extracts obtained, was read at 665, 645 and 630 nm in a Biotek EPOCH2 spectrophotometer.

Statistical treatment: MINITAB17 was used to perform the statistical analysis by the Tukey test in a one-way ANOVA and t-student test with a 95% confidence.

Thin layer models: The mathematical function to calculate the humidity ratio (MR) is shown in equation (1) [G. Lopez-García, 2019]. The humidity radius MR is a function of the drying time and is calculated as in [9]:

$$MR = \frac{M_c - M_e}{M_0 - M_e} \quad (1)$$

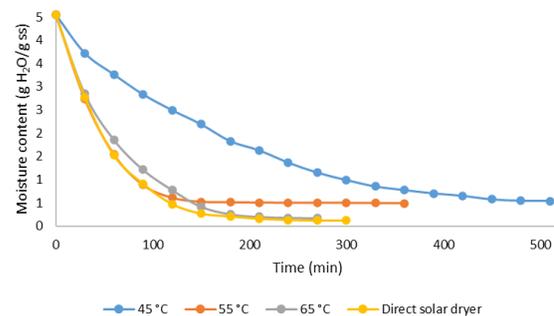
M_c es the moisture content, M_e is the equilibrium moisture, and M_0 is the initial moisture.

Regression and correlation statistical methods for modeling were used. The statistical analysis was made with DataFit 9.1 software. The determination coefficient R^2 was used as primary criterion to select the best model for data fit with experimental data. Additionally, the reduced chi-square, χ^2 and the root mean square error (RMSE) were calculated. The best data fit is the one with the highest R^2 and the lowest χ^2 and RMSE. [I. T. Togrul and D. Pehlivan, 2020].

Results

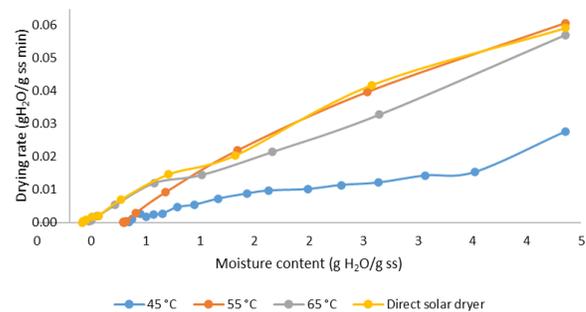
The final moisture content represents the equilibrium moisture between the samples and the drying air under the experimental conditions. The initial humidity of the sample was 82%.

In Graphic 1, it is observed that equilibrium humidity is reached in the less time in the oven at 65 ° C drying at 270 min, practically at the same time as with the direct solar dryer, which reached a maximum drying chamber temperature of 63 ° C. The longest kinetics are observed with the oven drying at 45 ° C. It can be assumed that the drying time, depends on the drying temperature.



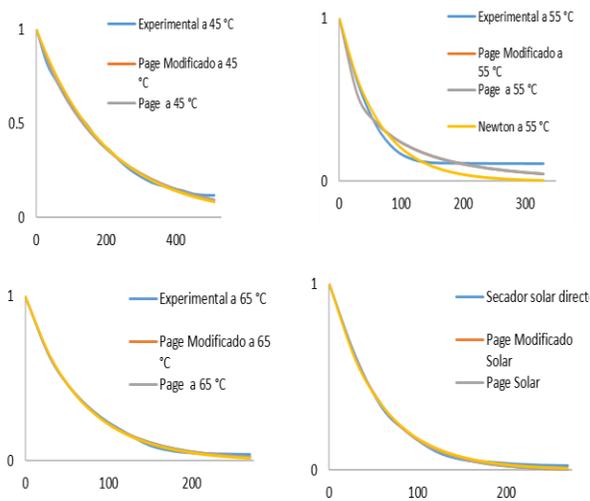
Graphic 1 Moisture content versus drying time

In Graphic 2, the drying rate of overall experiments can be observed. It is noticeable that only in drying at 45 ° C a constant drying rate is observed, while in the other kinetics there are no such periods. The maximum drying rates are similar for the oven at 55, 65 ° C and for solar drying (about 0.06 g H_2O / g ss min).



Graphic 2 Drying speed with depending on the drying time

The graphs shown in Graphic 3 show the adjustments to the experimental results. It can be seen that the data fit is high, with R^2 greater than 0.96 for all cases, as shown in Table 1. The model that better predict the drying behavior of Quelite is the Modified Page model, which can be used to sizing and design of dryers for similar cases.



Graphic 3 Best three data fit adjustment with experimental data

Model	Parameter	45 ° C value	55 ° C value	65 ° C value	Direct solar drying
Modified Page	k	0.00502	0.01747	0.01511	0.01761
	n	0.91464	0.65694	0.97702	0.65694
	R ²	0.99770	0.96710	0.99880	0.99850
	RMSE	0.01247	0.04816	0.01015	0.54317
	X ²	0.00017	0.00278	0.00013	0.00017
Page	k	0.00788	0.07002	0.01663	0.01481
	n	0.91464	0.65694	0.97702	1.04287
	R ²	0.99770	0.96710	0.99880	0.99860
	RMSE	0.01247	0.04816	0.01015	0.01164
	X ²	0.00017	0.00278	0.00013	0.00017
Newton	k	0.00496	0.01590	0.01502	0.01777
	R ²	0.99948	0.93920	0.99870	0.99830
	RMSE	0.01881	0.06552	0.01061	0.01264
	X ²	0.00037	0.00468	0.00013	0.00018

Table 1 Best fit models, their coefficients and fit parameters

The functional properties (Table 2) of quelite leaves were negatively affected by heat treatments, especially chlorophyll, when exposed to light, decomposes into its brown-colored phenolic derivatives. The loss of chlorophyll with respect to fresh material ranges between 26 to 76% for drying in the cabinet, while solar drying favors at least 93%. These results agree with that obtained for the antioxidant activity, which is also decreased after the treatments, in statistical terms, for the antioxidant activity there is no statistical difference ($\alpha = 0.05$) for the oven drying treatments, while solar drying decreases 85 % activity with respect to fresh quelite. Authors who have previously worked on drying and heat treatments for quelite report concordant results regarding to the loss of functional nutrients [F. Lagunes, I. Estrada, J. Guerrero, R. Navarrete, 2019, G. Lopez-García, 2019]. Finally, even with de chlorophyll and antioxidant loss, the ΔE indicates acceptable color lost for the samples.

Sample	Chlorophyll a,b,c (mg/100 g)	DPPH antioxidant activity (Gallic Acid equivalents/100 g)	ABTS antioxidant activity (Gallic Acid equivalents/100 g)	ΔE
Fresca	539,227,139	3926.8±62.7	211.42±3.0	0
45 °C	203,49,50	1695.8±41.7	208.553±3.3	1.32
55 °C	395,94,34	1733.0±63.5	206.74±20.0	1.28
65 °C	148,67,43	1670.7±31.7	325.32±9.6	1.44
Solar Drying	34,11,17	391.85±0.0	35.58±9.4	-

*Results are dry basis expressed.

Table 2 Functional properties of quelite *Amaranthus* spp before and after drying

Conclusions

A comparison of both the kinetics of conventional drying at various temperatures and direct solar drying, as well as an analysis of the organoleptic and nutritional properties of the dried product were made. The results show that Quelite solar drying is an adequate and sustainable option, with very competitive drying times compared to conventional oven drying (270 min in oven at 65 ° C versus 300 min in direct dryer). The Modified Page Model was the best adjusted to the kinetics of Quelite drying in all cases, so this model can be used for future predictions. The monitoring of the functional properties during the drying kinetics is required to improve the drying conditions, as well as to the establish the cost-benefit analysis regarding with the solar drying technologies to preserve this plant.

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