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ACTIVITY WATER AND SORPTION BEHAVIOR AFTER CITRIC ACID PRETREATMENT IN DRIED SCALLOP MEAT (*Nodipecten subnodosus*)

EFECTO DEL ÁCIDO CÍTRICO COMO PRETRATAMIENTO SOBRE LA ACTIVIDAD DE AGUA Y COMPORTAMIENTO DE SORCIÓN EN CALLO DE ALMEJA SECO (*Nodipecten subnodosus*)

Pacheco-Aguilar R[1], Ocaño-Higuera VM[2], Maeda-Martinez AN[3], Garcia-Sanchez G[1] Jimenez-Ruiz EI[2], Ruiz-Cruz S[2], Marquez-Rios E[4]*

[1]Centro de Investigación en Alimentación y Desarrollo, A.C. Carretera a La Victoria. Km. 0.6. Hermosillo, Sonora 83000, México. [2]Departamento de Ciencias Químico Biológicas, Universidad de Sonora. Rosales y Niños Héroes S/N. Hermosillo, Sonora 83000, México. [3]Centro de Investigaciones Biológicas del Noroeste. Mar Bermejo. La Paz, BCS, 23090, México. [4]Departamento de Investigación y Posgrado en Alimentos, Universidad de Sonora. Rosales y Niños Héroes S/N. Hermosillo, Sonora 83000, México.

ABSTRACT

In this study was applied an acid pre-treatment to scallop with the aim of reducing drying times of Pacific Lion's Paw Scallop meats. The samples were immersed in 0.1M citric acid for zero (control), one, and three hours. Pretreatment in acid solution and drying temperature (50, 60 and 70 ºC) were evaluated on the a_w and the sorption phenomenon in dried scallop. Both, acid pre-treatment and drying temperature, showed a significant effect ($P<0.05$) on the a_w. The sorption phenomenon was similar for every drying temperature as well as for the pre-treatment. Sorption behaviour was well explained by means of the BET equation, founding values for monolayer from 0.04 to 0.05g of moisture (water/g of dry matter).

Keywords: drying**,** sorption phenomenon, a_w, scallop

RESUMEN

En presente estudio se aplicó un tratamiento de inmersión en ácido cítrico a callo de almeja, con el objetivo de reducir el tiempo de secado de la almeja mano de león. Las muestras se sometieron a inmersión en ácido cítrico 0.1 M, durante cero (control), una y tres h. Se evaluó el efecto del pre-tratamiento de inmersión en solución ácida y la temperatura de secado (50, 60 y 70 °C), sobre la a_w y el fenómeno de sorción en el callo seco. Ambas variables mostraron un efecto significativo ($P<0.05$) sobre la a_w. El fenómeno de sorción fue muy similar en cada una de las temperaturas de secado, así como para el pre-tratamiento de inmersión ácida. El comportamiento de sorción fue bien explicado por medio de la ecuación BET, encontrando valores de monocapa de 0.04 a 0.05 g de humedad (g de agua/g de materia seca).

Palabras clave: secado, fenómeno de sorción, a_w, callo

INTRODUCTION

Pacific Lion´s Paw Scallop (*Nodipecten subnodosus*) is a bivalve mollusk harvest in the Pacific coast of the Baja California Peninsula, Mexico and it is an important marine resource (Massó-Rojas *et al*., 2001). The only commercial fishery is found in the Laguna Ojo de Liebre in Baja California Sur (Barrios-Ruiz *et al*., 2003) where the scallop is harvested by Hooka divers. The yearly production of adductor muscle increased from 5 tonnes in 1991 to a peak of 216 tonnes in 2005 (Marquez-Rios *et al*., 2009). This scallop fishery is still underdeveloped and is a good candidate for production through aquaculture. The product has a high economic value and the scallop rapidly grows (Koch *et al*., 2005). From 2001 to 2002, several Mexican enterprises cultivated and produced ~3.2×10^6 specimens in the Laguna Manuela. The scallop can reach commercial size of 7cm in 8 months. Production and culture of scallops are considerably increasing worldwide promoting the diversification of the product lines of these organisms by means of the development of a wide variety of fresh ready-to-eat and fresh-frozen products, this has led to a major increase in the consumption of scallops (Ocano-Higuera *et al*., 2006).

The most common processed presentations of scallops are the traditional tinned, and the semi dried ones (Pacheco-Aguilar *et al.,* 2001). It has had great acceptance, even there is little information about drying conditions and sample pre-treatments of the scallops (Tanikawa *et al.,* 1985). Drying provides a very useful preservation. It is one of the oldest methods of food preservation, and it represents a very important aspect of food processing. The main aim of drying products is to allow longer periods of storage, minimise packaging requirements and reduce shipping weights. The quality of these products depends on the drying times (Cohen and Yang, 1985; Strumillo and Adamiec, 1996). This fact has renewed the interest of food technologists who are trying to reduce the drying time. Variables such as temperature, air flow, and relative humidity have been used with this purpose but they have had little effect on the drying rate. The use of certain pre-treatments has given good results. One example is the osmotic dehydration of a great variety of vegetables, which allows the starting the drying process with less moisture.

A common pretreatment for dried scallop meats is the precooked (Tanikawa *et al*., 1985), which decreases the drying time and gives the product a better appearance. The pretreatment in acid solutions showed better results in the

*Autor para envío de correspondencia: Enrique Márquez Ríos
Correo electrónico: emarquez@guayacan.uson.mx
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drying process of lion's paw scallop, it decreased drying times when the scallop was immersed in citric acid at pH 3.0, moreover this pretreatment reduced darkening inhibiting the Maillard reaction and this improved the appearance (Marquez-Rios *et al*., 2009). Nevertheless, it is important to study the pretreatment in acid solution on a_w and sorption behavior. In consequence the present research focus on the effect of immersion in citric acid (0, 1and 3 h) and drying temperature (50, 60 and 70 °C) on the water activity and the sorption behaviour.

MATERIALS AND METHODS

Samples

To carry out this study, we used the abductor muscle of the Pacific lion's paw scallop (*Nodipecten subnodosus*), which was commercially bought in Guerrero Negro, Baja California Sur, Mexico and stored at -20 °C until use.

Treatment

The average weight was 70g. Due to the big size of the abductor muscle the frozen meats were cut, perpendicularly to muscle fibers into 1.2 cm thick slices. The slices were immersed in 0.1M citric acid solution, at pH 3, for 1 and 3 h at 4 ºC with the control no immersed. Scallop slices were left to drain off the excess of solution for 5 minutes at 4 ºC. The pre-treatment and the whole process were repeated three times. After immersion and draining, the slices were cooked for 5 min in a separate solution containing 5% salt and 3% sugar.

Dried

Scallop meat slices were dried in an oven, Enviro-Pack (Micro-Pack series MP500, E.U.) at 50, 60 and 70 °C to allow the product to have a final moisture content of 20%.

Water Activity

Water activity of scallop was measured with a digital moisture analyzer Aqualab CX-2 (Decagon devices, Inc. Pullman Washington 99163, U.S.A.).

Sorption Isotherms

Sorption isotherms were prepared in duplicate according to the gravimetric method (AOAC, 1996). The scallop was put in small containers with controlled relative humidity by means of saturated salt solutions (drierite, LiCl, CH_3CO_2K, K_2CO_3, $Mg(NO_3)_2$, $SrCl_2$, KCl, and K_2SO_4 corresponding to a_w levels of 0.11, 0.22, 0.43, 0.52, 0.70, 0.84 and 0.97 respectively). Samples exposed to relative humidities higher than 50% were irradiated by UV rays for 30 minutes to prevent the appearance of fungi. For adsorption, the samples were subjected to vacuum drying at 30 °C for 21 days (Sheldon Manufacturing Inc., Cornelius, OR). Containers were kept at constant temperatures of 25 and 45 °C until the sample was in equilibrium with the relative humidity of its chamber. The grams of water per grams of solid were plotted against the relative humidity.

Experimental Design

In this experiment a 2^3 factorial arranged with two main effects was used. The main effect A, drying temperature, had three levels (50, 60 and 70 ºC) and the main effect B, time of immersion in acid solution, also with three levels (0, 1 and 3 h). Multiple comparisons were made according to the Tukey method when it was necessary using a significant level of 5%. The data was analyzed using the NCSS program version 5.1.

RESULTS

Water Activity

The acid pre-treatment and drying temperature in our study showed a significant effect ($P<0.05$) on a_w (Figure 1). For control and scallop submitted to acid immersion a slight decrease in a_w was observed when increased the drying temperature. The immersion in citric acid caused a reduction of pH in the abductor muscle from 6.20 (control) to 5.99 (1 h) and 5.80 (3 h). Water activity in dry meats ranged from 0.62 to 0.78, which is considered relatively high for dry products (Stencl, 1999).

Sorption Isotherms

The sorption isotherms obtained in this work resemble the typical behaviour of most food rich in protein (Tsami *et al.,* 1990). This phenomenon was similar for every drying temperature at different relative humidity (RHs) and expectedly the equilibrium moisture content increased when the water activity increased (Figures 2-4). We found the monolayer water value from 0.04 to 0.05 without any reduction in moisture when the temperature increased. This happens because in our study we were unable to note the apparent effect in the sorption at 25 and 45 °C. We observed a reduction in the heat of sorption in meats subjected at 45 °C that is connected with the ease of removing moisture at that temperature. The adsorption and desorption isotherms showed a hysteresis phenomenon, where the moisture content in equilibrium for a particular water activity was higher in desorption than adsorption (Figures 5-7).

DISCUSSIONS

Water Activity

The a_w is one of the most important properties of dry food because it largely determines the chemical, biochemical, microbiological, and physical changes that could present a product during its storage (Giese, 2000). The formation of a dry film on the surface of the meat could have caused the reduction of a_w while the drying temperature increased. So, the highest temperatures used during desiccation, the lowest a_w obtained. This was possibly caused by the formation of a more dried surface in the scallop. On the other hand at the same temperature scallop treated with citric acid showed higher a_w regard the control. This result suggested that during desiccation of scallop treated with citric acid the formation of a dried surface is unlikely regard the control, due to the removal of moisture from them was facilitated by the pH effect. The pH effect on the water-holding capacity of myofibrilar proteins has been extensively studied. The physical changes that occurs in these proteins when the pH in the muscle is lower causes a decrease in the water-holding capacity because the pH is nearer the isoelectric point (pI) of this protein, then its total net charge tends to zero as close the pH is to the pI (Huidoro and Tejeda, 1993).

At the a_w level in this study showed that bacterial deterioration is not possible, but fungi can be formed during storage. Studies made by Rahman *et al.* (2000) reported that dried mackerel with a_w levels from 0.72 to 0.74 showed no bacterial or fungal deterioration. Our results indicated that a greater stability in dried scallop was achieved at higher temperature by getting lower a_w values both for control scallop and scallop immersed in citric acid, moreover the pH reduction can also provide better stability to these products (Chirife and Favetto, 1992). Similary, the darkening caused by the Maillard reaction can be also controlled.

Sorption Isotherms

The characteristic shape of moisture isotherms depends upon the variety and total amount of hygroscopic materials present in the particular heterogeneous mixture of the hydrophilic substances. Many models have been proposed to describe moisture sorption isotherm including kinetic models based on a multilayer. The BET isotherm is a good model used to interpret the multilayer sorption isotherms, particularly for Type II isotherm characteristics (Anderson, 1946). The American Society of Agricultural Engineers has adopted the BET and GAB models as equations to describe sorption isotherms (ASAE, 1985). These models have been widely used in literature (Pahlevanzadeh and Yazdani, 2005). In this research we only used the BET equation to study the sorption phenomenon. This model establishes the minimum moisture content for the product to be more stable. It determines the monolayer water content (X_m) as well as the constant C required for the estimation of heat of sorption. Dried scallop is a food that is preserved in dry environment and stored using a good film impermeable to prevent water vapour. In consequence, it is important to know the sorption behaviour.

Normally, moisture content is expected to decrease while temperature increases at any given water activity. Temperature dependence of the monolayer value has been linked to the reduction of sorption active sites as a result of the physiochemical changes induced by temperature. In our study the monolayer water content was similar for all the products at both 25 and 45 ºC (Table I). Labuza *et al.* (1985) found that the monolayer water of fishmeal was 0.0433g of moisture (water/g of dry matter) and decreased when temperature was increased. Adam *et al.* (2000) reported monolayer water values of 0.064g of moisture, which also decreased with a rise of temperature.

Since temperature affected the mobility of water molecules and the dynamic equilibrium between water vapour and adsorbed phases, the water vapour pressure of moisture within the product increased and hastened the transfer of moisture from the product to the surrounding air (Kapsalis, 1987). The product was more hygroscopic in water activities > 0.5 (Figures 2-4). This type of behaviour has been attributed to the presence of low energy sites in food biopolymeric constituents that bind water molecules (Caurie, 2007), therefore this product is less hygroscopic in low a_w. The reduction of low energy sites able to retain water molecules is probably caused by the damage in proteins and carbohydrates in the abductor muscle due to dehydration caused by heating as well as lowering the pH caused by the acid pre-treatment.

Adsorption behaviour of control meats and those immersed in acid solution showed a high degree of simi-

Table 1. Effect of drying temperature and acid pretreatment on BET equation parameters of dry scallop meats
Tabla 1. Efecto de la temperatura de secado y pre-tratamiento de inmersión ácida sobre los parámetros de la ecuación BET en callo seco

Drying temperature (ºC)	Pretreatment (immersion h)	25 ºC		45 ºC	
		X_m (g water/g dry matter)	Sorption heat (Kcal/mol)	X_m (g water/g dry-matter)	Sorption heat (Kcal/mol)
50	0	0.044 ± 0.012	27.4 ± 1.2	0.036 ± 0.009	12.3 ± 1.5
50	1	0.047 ± 0.015	30.0 ± 2.3	0.049 ± 0.011	14.2 ± 1.2
50	3	0.052 ± 0.013	43.3 ± 2.6	0.039 ± 0.005	13.0 ± 1.2
60	0	0.058 ± 0.009	18.3 ± 1.6	0.048 ± 0.012	5.0 ± 0.7
60	1	0.060 ± 0.014	15.2 ± 0.8	0.044 ± 0.010	9.6 ± 0.9
60	3	0.053 ± 0.016	13.6 ± 1.0	0.043 ± 0.008	7.5 ± 0.7
70	0	0.047 ± 0.011	32.4 ± 1.3	0.031 ± 0.007	10.5 ± 1.5
70	1	0.055 ± 0.012	20.5 ± 1.6	0.045 ± 0.009	7 .0 ± 0.4
70	3	0.060 ± 0.019	32.5 ± 1.8	0.045 ± 0.010	19.1 ± 0.9

Values are the mean ± standard deviation of three replicates.

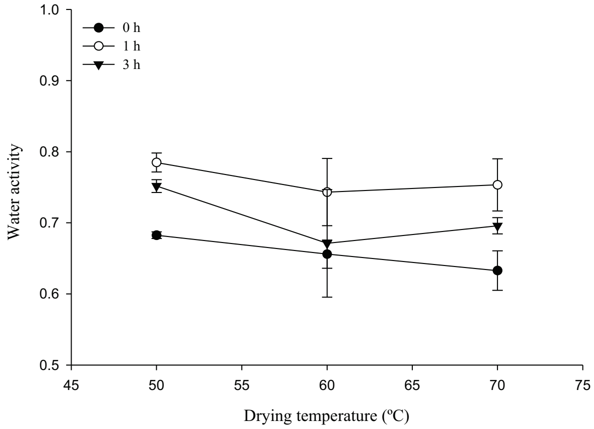

Figure 1. Effect of drying temperature and immersion in acid solution on water activity in dried scallop meats
Figura 1. Efecto de la temperatura de secado e inmersión en solución ácida sobre la actividad de agua en callo seco

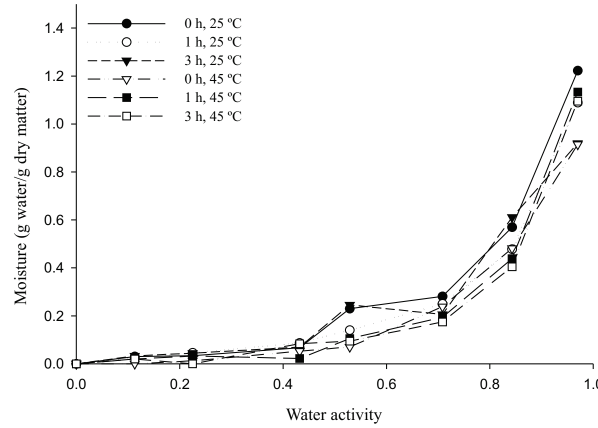

Figure 2. Effect of drying temperature and immersion in acid solution on adsorption isotherms of dried scallop meat at 50 °C
Figura 2. Efecto de la temperatura de secado e inmersión en solución ácida sobre las isotermas de adsorción de callo secado a 50 °C

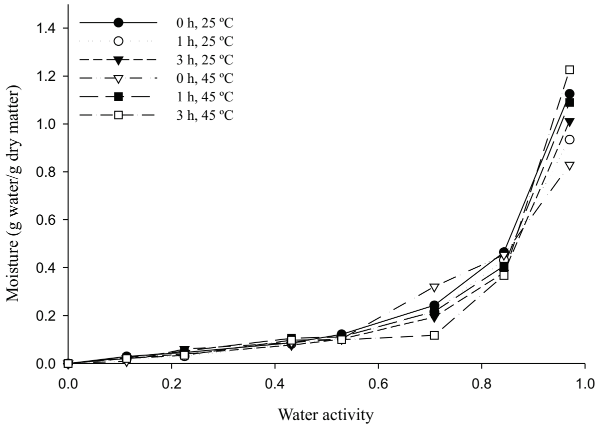

Figure 3. Effect of drying temperature and immersion in acid solution on adsorption isotherms of dried scallop meat at 60 °C
Figura 3. Efecto de la temperatura de secado e inmersión en solución ácida sobre las isotermas de adsorción de callo secado a 60 °C

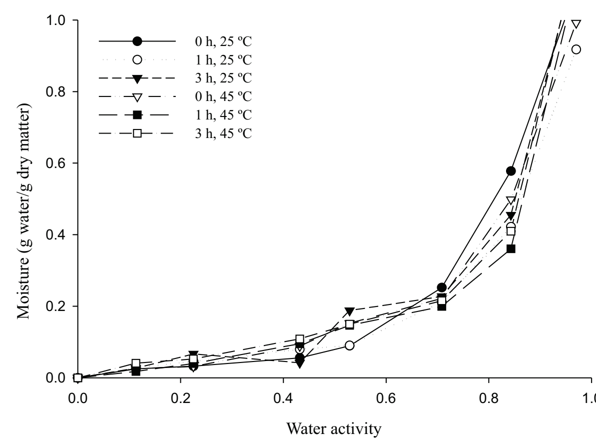

Figure 4. Effect of drying temperature and immersion in acid solution on adsorption isotherms of dried scallop meat at 70 °C
Figura 4. Efecto de la temperatura de secado e inmersión en solución ácida sobre las isotermas de adsorción de callo secado a 70 °C

larity although pre-treated scallop meats were expected to be affected less by thermal effect because the drying time was less (Marquez-Rios *et al*., 2009) and as a consequence less damage in biopolymeric constituents of the abductor muscle. This would lead to greater hygroscopic and low a_w. In addition the pH could have played a key role because it altered the net charge of the myofibrilar proteins.

Bettelheim and Erhlich (1963) as well as D´Arcy and Watt (1981) pointed out that in swelling polymers, hysteresis seems to depend on relaxation of cohesive forces within the absorbent matrix. This means that the substrate has a different form for desorption regard to desorption, this due to physical damage caused at the active sites of biopolymers during dehydration. This shows that under our experimental conditions the decrease of pH in the abductor muscle is the primary cause for the hysteresis. Kaya and Oner (1996) obtained a sharp hysteresis in cheese at 20 °C where there was never an overlap of isotherms. They reported that for mois-

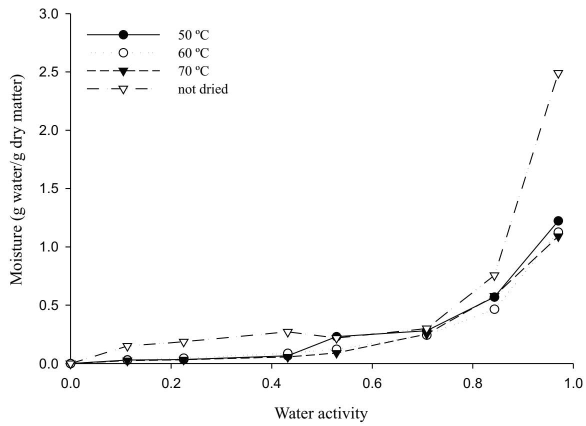

Figure 5. Effect of drying temperature on desorption behaviour in control scallop meat
Figura 5. Efecto de la temperatura de secado sobre el comportamiento de desorción en callo control

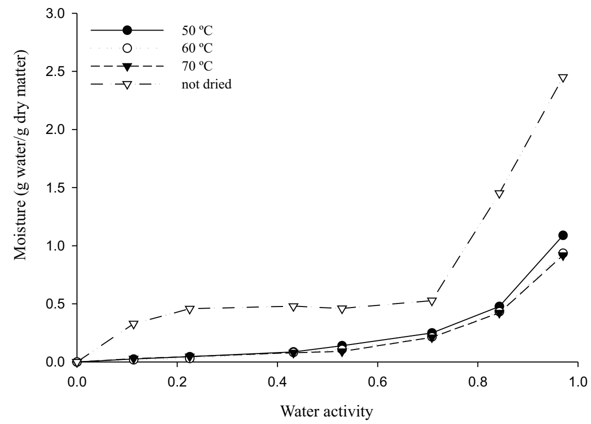

Figure 6. Effect of drying temperature on desorption behaviour in scallop meat immersed in acid solution for 1 h
Figura 6. Efecto de la temperatura de secado sobre el comportamiento de desorción en callo sujeto a inmersión en solución ácida por 1 h

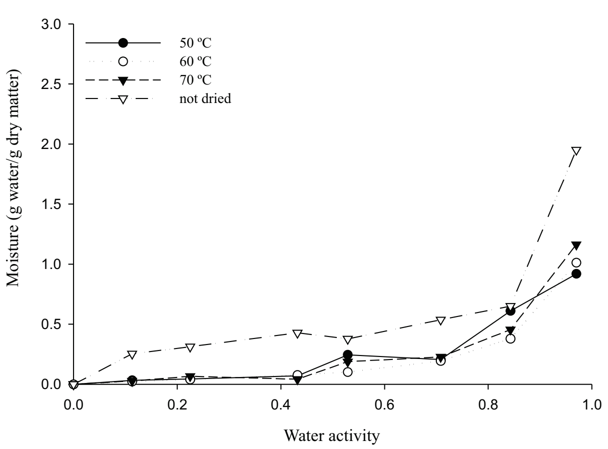

Figure 7. Effect of drying temperature on desorption behaviour in scallop meat immersed in acid solution for 3 h.
Figura 7. Efecto de la temperatura de secado sobre el comportamiento de desorción en callo sujeto a inmersión en solución ácida por 3 h

ture content of 1% in the adsorption, desorption showed 10% moisture at the same water activity.

Some researchers that studied the sorption heat behaviour during adsorption and desorption phenomena have pointed out that due to the reduction of active sites during adsorption the product became less hygroscopic (Adam, 2000). During the desorption processes the sorption heat was greater than for adsorption in the whole moisture range, understanding that more energy is required to remove water during desorption than in adsorption. In desorption, the active sites of biopolymers such as proteins and carbohydrates were virtually untouched, whereas in adsorption these active sites suffered physical and chemical changes that altered or modified the ability to bond again water molecules.

CONCLUSIONS

The use of an acid pre-treatment in the production of dried products can be a good alternative for processing efficiency, improved organoleptic qualities, and food stability. In this study was evaluated the effect of the immersion in acidic solution and the drying temperature. It seems to be that drying scallop at 70 °C provides better stability because this temperature offers the lower a_w. Furthermore, the acid treatment helps to inhibit the Maillard browning, which sometime can be a problem in dried products. The adsorption behaviour does not seem to be affected by drying temperature or immersion in acidic solution. However, the study of desorption revealed protein damage in the abductor muscle as a result of immersion in citric acid solution.

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