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Calculation of the Effective Diffusion Coefficients in Drying of Chemical and Mechanical Pretreated Rosehip Fruits (*Rosa eglanteria* L.) with Selected Mass Transfer Models

Abstract: The aim of this work was to select models of mass transfer to estimate effective mass diffusion coefficients during the dehydration of *Rosa eglanteria* fruits with air at 70°C. Fruits were pretreated chemically and mechanically (dipping it in NaOH and ethyl oleate solutions and cutting or perforating the fruit cuticle). Selected models were those of Becker and Fick's second law, considering fruit shrinkage during drying. Both models satisfactorily predict the fruit drying, and the different pretreatments, to total or partially remove this waxen cuticle, noticeably improved water diffusion, reducing the time of processing from 28% (NaOH) to 52% (oleate and mechanical pretreatments). Mechanical pretreatments were the more effective, because oleate presents quality problems.

Keywords: rosehip, drying pretreatments, effective diffusion coefficients, experimental and models

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1 Introduction

Dehydration is one of the oldest methods of food preservation known to man. Drying reduces water content, preventing the development of microorganisms and a series of quality degradative reactions. Moreover, drying also reduces fruits weight and volume with the consequent reduction of costs in transport and storage. Dehydrated fruits are widely used as ingredients in elaborated food, as confectionary, dehydrated soups, powders to prepare ice creams and juices, and the elaboration of fruit teas [1]. During the last decades, the commercialization of rosehip fruit (*Rosa eglanteria* L), mainly as dehydrated fruit, markedly increased in the Andean Region of Argentina [2].

At present, the conventional hot air drying of fruits and vegetables is performed in a rapid manner and at low temperatures, as possible, to minimize energy consumption and thermal degradation of nutritional components and other attributes of quality [3]. However, one of the major reasons of quality loss of dehydrated rosehip fruit is the required long times of drying, taking from 10 to 20 h at industrial scale and more than 12 h at laboratory scale. In these fruits, as well as in cherries, plums and grapes, the control of water migration to the fruit surface through the fruit tissue was demonstrated to be controlled by an exterior very impermeable waxen cuticle [4, 5].

The waxy layer also affects the flow of moisture from inside the fruit to its surface, a crucial process in drying. Pretreatment methods employing chemical dipping, mechanical methods and thermal treatments have been used to overcome the wax barrier in several applications [6–10].

The implementation of different types of pretreatments on the skin of the fruits, both physical and chemicals, has the aim to total or partially remove this waxen cuticle, in order to improve water diffusion and reduce the time of processing [4, 11–14]. A number of authors have reported the effects of pretreatments on the drying rates and quality parameters of various foodstuffs. The chemical treatments basically consist in dipping the fruits in hot water solutions, breaking the cuticle and creating microscopic pores that facilitate the water permeability. Fatty acid ester emulsions have been used as chemical pretreatment before drying [15].

Grapes were surface treated by dipping in ethyl oleate, which greatly increases the drying rate by altering the waxy layer structure at the grape surface, thus reducing the internal resistance to water diffusion [16]. The treatment with hot dipping solution causes cracking and perforation in the waxy cuticle, increasing the drying rate. Dipping in hot water and the use of chemicals such as sulfur, NaOH and KOH solutions are some other pretreatments widely used for fruit drying.

The physical treatments are based on some type of mechanical cuts on the skin of the fruits, in order to break the waxy cuticle which hinders moisture transfer and makes dehydration rate very low. Based on an overall assessment of moisture removal and taste acceptability, halving cranberries provided the most practical pretreatment method prior to osmotic drying as compared to chemical and thermal methods [8]. Mechanical cutting of blueberries and tomatoes is not possible due to the softness of these fruits.

Another mechanical pretreatment, perforating the skin, had been tested on cranberries and on cherry tomatoes [6, 8]. Grabowski and Marcotte [8] had determined that the perforations should represent 20–30% of the total surface area of the cranberries for this method to be effective. Azoubel and Murr [6] washed and perforated cherry tomatoes with needles (1 mm in diameter) to a pin hole density of 16 holes/cm^2, prior to osmotic and air drying.

Although the method of skin abrasion is one of the most studied physical pretreatments, there exists very little information about superficial cuts and slightly deep perforations with needles of small diameter. Reductions of time of drying for fruits with mechanical pretreatments that range between 20% and 40% have been reported [6, 8].

The most widely used method industrially for dehydration of fruits is the convective air drying technology, such as cabinet or tray, fluidized bed and spouted bed.

Generally, the dehydration of a solid food takes place during the falling rate period [17]. During this period, the rate of drying is normally governed by factors that affect the movement of water inside the food. To properly study the drying phenomenon during the falling rate period several mathematical models have been proposed, both empirical and based on the hypothesis that a particular mechanism of movement of moisture inside the solid prevails. The most known hypothesis considers that water migrates inside the solid due to a concentration gradient between the surface and the interior of the fruit, satisfying the Fick's second law of diffusion.

Many of the proposed solutions for this law assume that water diffusivity is constant during the whole falling rate period. However, several authors suggested that the above-mentioned supposition is not totally satisfactory, since diffusivity is affected, among other factors, by the shrinkage suffered by solid foods during drying [18, 19].

In previous experiences, authors observed [20] that pretreated rosehip fruits required a significantly minor time for drying suffering, however, a considerable reduction of size during the dehydration. These two factors modify the effective diffusion coefficients (D_{eff}).

The aim of this work was to select simple models considering particle shrinkage, to determine D_{eff} during the drying of rosehip fruits with conventional convective air drying, with and without skin pretreatments.

2 Materials and methods

2.1 Raw material

Fruits of wild rosehip (*Rosa rubiginosa L.*) used in this work were harvested in El Bolsón, Province of Río Negro, Argentina. The fruits had an average water content of 1.07 (w/w), decimal dry basis and were kept refrigerated at 2°C and 90% relative humidity until use. Fruits were selected visually by superficial color and size. Fresh fruits are rounded, slightly elongated with longitudinal diameter of 0.015 ± 0.002 m and equatorial diameter of 0.018 ± 0.03 m. Dehydrated fruits are nearly spherical shape, diameter 0.008 ± 0.0015 m.

2.2 Pretreatments

Before drying, fruits were pretreated in order to speed up the drying process. Pretreatments were:

(a) *Chemical pretreatments*: Consisted in dipping the fruits in (a) 1% and (b) 1.5% NaOH solution at boiling (100°C) for 1.5 min and (c) 2% ethyl oleate and 2.5% potassium carbonate solution at 70°C for 2 min. After treatment, fruits were rinsed with tap water for 5 min and dried on paper.

(b) *Physical pretreatments*: The mechanical realized treatments were: (a) external longitudinal cuts (4 or 6 cuts, 0.2-mm deep) on the cuticle, made equidistantly with a scalpel and (b) slightly deep perforations at equidistant points (3, 6 or 12 perforations) along the equatorial plane of the fruit, manually made with a 0.001-m diameter metallic punch. Fruits without pretreatment were also dried as control.

2.3 Drying equipment

Experiments were carried out in a purpose-built pilot scale dryer, consisting basically of a closed system with forced air circulation and appropriate drying variables control, as presented by Ochoa et al. [21]. Weight loss was measured with an OHAUS (Ontario, Canada) digital balance (± 0.001 g). Air temperature was automatic controlled and measured with a copper constantan thermocouple connected to a digital thermometer Digi-Sense (Cole-Parmer Instrument Company, NY, USA), while air velocity was measured with a hot wire anemometer (Mini Vane CFM Termo Anemometers, EXTECH Instruments, Madison, USA). The water vapor content of drying air was determined with a Hygro Palm Hygrometer (Rotronic Instruments, New York, USA). All variables were measured at the drying chamber inlet. Fruits were placed in a single layer on a 0.225-m diameter and 0.10-m-high perforated shelf. The process was stopped, when the fruits reached constant weight. Processing parameters were as follows:

Drying air temperature: 70°C
Air relative humidity at entrance (RH): 5%
Air flow rate: 5 m/s

Samples' weights were obtained with a OHAUS (Ontario, Canada) digital balance (± 0.001 g). Dried fruits were packed in water impermeable plastic bags and stored at 2°C until analysis.

The drying experiences were performed in duplicate for each pretreatment in the same drying condition. The differences between duplicates were minimum $-$ 6.9% and maximum $+4.8\%$.

2.4 Mathematical models

Dehydration is a coupled phenomenon of heat and mass transfer, so it is necessary to maintain mass and energy balances, to evaluate dehydration kinetics of individual particles. However, the literature has shown that as the rate of relaxation of the heat transfer potential is by far faster than that for mass transfer, the temperature profile inside the food can be considered flat, especially if compared with the steep moisture content gradient [22]. In this regard, thermal diffusivity of rosehip fruits vary between 1.196×10^{-7} and 2.009×10^{-7} m^2/s [23], while mass diffusivities – the effective diffusion coefficient in solids – according to Zogzas et al. [24], lie between 10^{-10} and 10^{-11} m^2/s in most foods. By taking an average of the values published by these authors (more than 100 diffusion coefficients from 61 foods with diverse moisture contents), a value of 1.45×10^{-10} m^2/s is found, with which the relationship of thermal to mass diffusivity varies around 824 and 1,386, that is, that heat transfer is some 1,000 times faster than mass transfer. According to Márquez et al. [17], this guarantees heat transfer to be instantaneous against mass transfer, therefore can be considered isothermal drying and allows isothermal drying to be used as a reasonable simplification to accept that mass transfer occurs with internal control. Therefore, it can be resorted to the analytical solution for unsteady state diffusion with prescribed condition on the surface [25] and diffusion coefficient independent of particle moisture during drying.

The analytic solution, obtained after integrating local moisture contents in the particle volume, considering spherical particle and moisture diffusivity constant for this work, is [17, 23, 25]:

$$X^* = \frac{X - Xe}{Xo - Xe} = \frac{6}{\pi^2} \sum_{n=1}^{n=\infty} \frac{1}{n^2} Exp\left[-n^2 \pi^2 \left(\frac{D_{eff}\, t}{R_p^2} \right) \right] \tag{1}$$

where X^* is the dimensionless moisture; X is the mean moisture content of the particle at time t; Xo and Xe are the initial and equilibrium particle moisture, respectively; D_{eff} is the effective diffusion coefficient and Rp is the particle radius. Particle radius is a variable due to the volume shrinkage of the fruit [26] and will be evaluated by the following equation [27]:

$$\frac{R_p}{R_0} = \left[0.2437 + 0.7537 \frac{X}{X_0} \right]^{\frac{1}{3}} \tag{2}$$

where Ro is the initial fruit radius (m). According to the article published by Márquez and De Michelis (2009), the Heywood shape factors would allow the assumption of spherical geometry, rose hip fruits were considered as spheres with the same volume of the particle [17], and the variable radius was calculated as the average between the value for the fresh fruit (i.e. $t = 0$) and the value for the radius at the moisture content corresponding to the time t.

The diffusive equation developed by Becker [28] has been used successfully for grain and fruit drying [17]. The equation for spherical geometry predicts:

$$X^* = \frac{X - Xe}{Xo - Xe} = 1 - \frac{2}{\sqrt{\pi}} a_v \sqrt{D_{eff}\, t} + 0.331 a_v^2 D_{eff}\, t \tag{3}$$

where a_v is the surface area of particle per unit particle volume. In spheres, $a_v = 3/Rp$, where R_p is the particle radius. Analytic solutions, as well as semi-empirical and empirical expressions, have been used in most cases with constant particle radius. However, in eq. (3), variable radius was also considered.

3 Results and discussion

3.1 Drying curves

Figure 1 presents the experimental results of drying curves as *X/Xo* vs time, for pretreated and control rosehip samples.

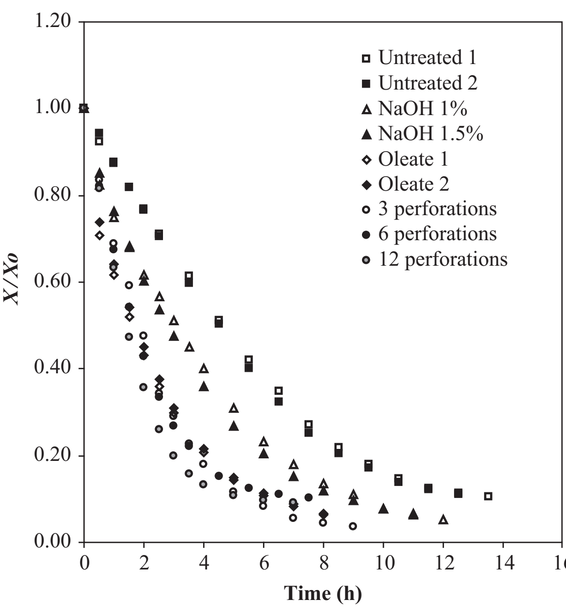

Figure 1 Comparison of experimental drying curves as a function of rosehip fruit pretreatment, for 70°C, 5% RH and 5 m/s drying conditions

As Figure 1 shows, water content continuously decreases with time, and drying practically occurs only during the falling rate period. It was assumed from this behavior that diffusion was the mechanism of water transport during the dehydration of rosehip fruits, with or without previous treatments.

On the other hand, all the applied treatments significantly diminished the drying process time. It was assumed that pretreatments increased the drying rate, due to a significant reduction in moisture transport resistance through the impermeable fruit skin. Those fruits mechanically treated by cutting the cuticle dried at a higher velocity. The least effective pretreatment was the dipping in NaOH's solution. In any case, the drying time necessary to reduce pretreated fruit's water content from 1.07 (w) to ~0.15 (w) was 28–52% lower as compared with the control sample.

As can be seen from Figure 1, experiments of the same type of treatments provide very close results. From the experimental data shown in Figure 1, authors found that drying time was practically independent of the different mechanical pretreatments (ANOVA, 1%, $p > 0.67$) applied to rosehip fruit. Similar results were obtained, when fruits were pretreated prior to drying with different concentrations of NaOH solution (ANOVA, 1%, $p > 0.75$). Therefore, only average drying curves were considered for effective diffusivity coefficients (D_{eff}) evaluation.

3.2 Effective diffusivity coefficient (D_{eff})

Effective diffusivity coefficients (D_{eff}) were evaluated both by the model of Becker and the analytical solution derived from the second Fick's law, represented by eqs (1) and (3), respectively. In both cases, the non-dimensional moisture content predicted by the model was compared with the moisture values obtained from the experimental drying curves, using an iterative approximation procedure. The validity of models' fitting was evaluated maximizing the coefficient of correlation R^2 and *minimizing the relative percentage mean error* (RME, %) between experimental and simulated curves [29, 30].

Figures 2 and 3 compare the experimental non-dimensional water content with the models estimated

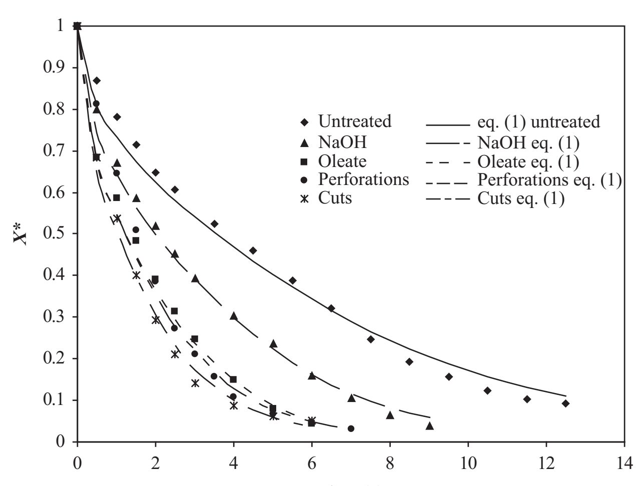

Figure 2 Comparison of experimental drying curves (symbols) and predictions by eq. (1), for pretreated rosehip fruit and control. Drying conditions: $T = 70°C$, RH $= 5\%$ and air velocity $= 5$ m/s

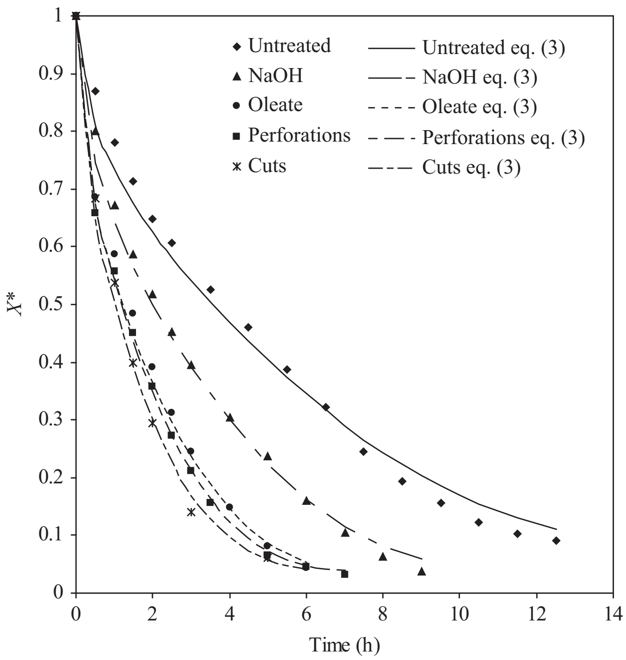

Figure 3 Comparison of experimental drying curves (symbols) and predictions by eq. (3), for pretreated rosehip fruit and control. Drying conditions: $T = 70°C$, RH = 5% and air velocity = 5 m/s

values during the drying of pretreated and control rosehip fruit, with particle shrinkage considered. Results indicate that applied diffusion models appropriately described the studied phenomenon.

Table 1 lists effective diffusion coefficients obtained both with Becker's model and the analytical solution, including the correlation coefficients (R^2) and relative mean errors (RME, %). Higher D_{eff} values were obtained when fruits were treated mechanically, and all pretreatments resulted in higher diffusivity values, as compared with those obtained during the drying of fruit control. Fruits with surface cuts and perforations presented the higher D_{eff} (approximately four times higher than control) and differing less than 2% among them. On the other hand, the alkaline solution of ethyl oleate shows the higher D_{eff}, among chemical treatments, but this treatment reduces the brightness of the dried fruit, having a negative impact on visual quality.

4 Conclusions

Effective diffusion coefficients (D_{eff}) changed between 1.076×10^{-10} and 4.58×10^{-10} m^2/s when estimated with Becker's model and between 1.086×10^{-10} and 4.561×10^{-10} m^2/s when the analytical solution of Fick's second law of diffusion was applied. These values are consistent with the *range* of *reported values* for several fruit products. In all cases, $R^2 > 0.97$ and RME (%) was in the order of 10^{-5}, indicating both models satisfactorily fit experimental data. As supposed, D_{eff} increased with pretreatments, the major values obtained when the mechanical treatments were applied prior to rosehip fruit drying, which improved about four times diffusion coefficients, when compared with the control sample. Times reductions obtained using mechanical pretreatments as comparable with of using dip oleate pretreatment (52%), but oleate pretreatments produce a strong reduction of surface brightness of the dried fruit, so its use is not recommended. The least effective pretreatment was dipping with NaOH solution (reduces 28% the drying times). There was practically no difference between coefficients obtained with the models studied in this work, and both models appropriately fit the experimental data when the models are used considering variable particle radius due to volume shrinkage that occurs during the drying of fruits.

Table 1 Effective diffusivity coefficient (D_{eff}) and statistical parameters for goodness of fit, valid for the convective air drying of rosehip fruit

Pretreatment	D_{eff} (m^2/s) $\times 10^{10}$		R^2		RME (%) $\times 10^5$	
	Becker	Fick's second law	Becker	Fick's second law	Becker	Fick's second law
Control	1.08	1.09	0.98	0.98	1.84	0.01
NaOH solution	2.42	2.44	0.99	0.99	1.45	0.02
Ethyl oleate solution	3.84	3.87	0.99	0.99	0.02	0.94
Mechanical (cuts on cuticle)	4.58	4.56	0.99	0.99	2.59	0.47
Mechanical (equidistant perforations)	4.09	4.01	0.98	0.98	5.90	0.08

Nomenclature

X^*	Dimensionless moisture
X	Mean moisture content of the particle at time t (decimal db)
Xo	Initial particle moisture (decimal db)
Xe	Equilibrium particle moisture (decimal db)
D_{eff}	Effective diffusion coefficient (m^2/s)
Rp	Particle radius (m)
Ro	Initial fruit radius (m)
a_v	Surface area of particle per unit particle volume (m^{-1})
t	Time (s)

References

1. Barta J. Fruit drying principles. In: Hui YH, editor. Handbook of fruit and fruit processing, 1st ed. Oxford: Blackwell, 2006:81–93.
2. Vullioud M, Pirone B, Ochoa M, Kesseler A, Márquez CA, De Michelis A. Avances durante el secado de frutos de la rosa mosqueta. Rev Presencia 2007;51:5–7.
3. Devic E, Guyot S, Daudin JD, Bonazzi C. Kinetics of polyphenol losses during soaking and drying of cider apples. Food Bioprocess Technol 2010;3:867–77.
4. Doymaz I. Influence of pretreatment solution on the drying of sour cherry. J Food Eng 2007;78:591–6.
5. George SD, Cenkowski S, Muir WE. A review of drying technologies for the preservation of nutritional compounds in waxy skinned fruit. Written for presentation at the 2004 North Central ASAE/CSAE Conference, Canada. Paper Nº MB04–104, 2004.
6. Azoubel PM, Murr FE. Effect of pretreatment on the drying kinetics of cherry tomato (*Lycopersicon esculentum* var. *cerasiforme*). In: Welti-Chanes J, Velez-Ruiz F, Barbosa-Cánovas GV, editors. Transport phenomena in food processing. New York: CRC Press, 2003:137–51.
7. Feng H, Tang J, Mattinson DS, Fellman JK. Microwave and spouted bed drying of frozen blueberries: the effect of drying and pre-treatment methods on physical properties and retention of flavour volatiles. J Food Process Preservation 1999;23:463–79.
8. Grabowski S, Marcotte M. Pretreatment efficiency in osmotic dehydration of cranberries. In: Welti-Chanes J, Velez-Ruiz F, Barbosa-Cánovas GV, editors. Transport phenomena in food processing. New York: CRC Press, 2003:83–94.
9. Grabowski S, Marcotte M, Poirier M, Kudra T. Drying characteristics of osmotically pretreated cranberries: energy and quality aspects. Drying Technol 2002;20:1989–2004. Available at: http://cetcvarennes. nrcan.gc.ca/eng/publication/r2002083e.html. Accessed:12 June 2003.
10. Yang AP, Wills C, Yang CS. Use of a combination process of osmotic dehydration and freeze drying to produce a raisin-type lowbush blueberry product. J Food Sci 1987;52:1651–3, 64.
11. Erenturk S, Gulaboglu MS, Gultekin S. The effects of cutting and drying medium on the vitamin C content of rosehip during drying. J Food Eng 2004;68:513–8.
12. Femenia A, Sánchez E, Simal S, Rosselló C. Effects of drying pretreatments on the cell wall composition of grape tissues. J Agric Food Chem 1998;46:271–6.
13. Gambella F, Piga A, Agabbio M, Vacca V, D'hallewin G. Effect of different pre-treatments on drying of green table olives (*Ascolana tenera* var.). Grasas Y Aceites 2000;51:173–6.
14. Tarhan S. Selection of chemical and thermal pretreatment combination for plum drying at low and moderate drying air temperatures. J Food Eng 2006;79:255–60.
15. Petrucci V, Canata N, Bolin H, Fuller G, Stafford A. Use of oleic acid derivatives to accelerate drying of Thompson seedless grapes. Paper presented in the Symposium "Novel Uses of Agricultural Oils" at the AOCS Spring Meeting, New Orleans, 1973.
16. Di Matteo M, Cinquanta L, Galiero G, Crescitelli S. Effect of a novel physical pretreatment process on the drying kinetics of seedless grapes. J Food Eng 2000;46:83–9.
17. Márquez CA, De Michelis A, Giner SA. Drying kinetics of rose hip fruits (*Rosa eglanteria* L). J Food Eng 2006;77:566–74.
18. Brennan JG. Evaporation and dehydration. In: Brennan JG, editor. Food processing handbook, 1st ed. Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA, 2006:71–121.
19. Saraceno A, Aversa M, Curcio S. Advanced modeling of food convective drying: a comparison between artificial neural networks and hybrid approaches. Food Bioprocess Technol 2010;5:1694–705.
20. Ohaco EH, Mabellini A, Márquez CA, De Michelis A, Lozano JE. Aceleración del secado de frutos de la *rosa rubiginosa* mediante el empleo de pretratamientos químicos y mecánicos. Proceeding of (Trabajo 13.13, publicado en CD, 5 pp) XII Congreso CYTAL – AATA. Facultad de Ciencias de la Alimentación, UNER, Entre Ríos, Argentina, 7–9 de octubre, 2009.
21. Ochoa MR, Kesseler AG, Pirone BN, Márquez CA, De Michelis A. Volume and area shrinkage of whole sour cherry fruits (*Prunus cerasus*) during dehydration. Drying Technol 2002;20:147–56.
22. Giner SA, Mascheroni RH. Diffusive drying kinetics in wheat. Part.1. Potential for a simplified analytical solution. J Agric Eng Res 2001;80:351–62.
23. Marquéz CA. Deshidratación de frutos no tradicionales: *Rosa mosqueta* (rose hips). Tesis doctoral. Universidad Politécnica de Valencia. España, 2003.
24. Zogzas NP, Maroulis ZB, Marinos-Kouris D. Moisture diffusivity data compilation in foodstuffs. Drying Technol 1996;14:2225–53.
25. Crank J. The mathematics of diffusion, 2nd ed. Oxford: Oxford University Press, 1975.
26. Burmester K, Eggers R. Heat and mass transfer during the coffee drying process. J Food Eng 2010;99:430–6.
27. Márquez CA, De Michelis A. Comparison of drying kinetics for small fruits with and without particle shrinkage considerations. Food Bioprocess Technol 2009;2:1–7.
28. Becker HA. A study of diffusion in solids of arbitrary shape, with application to the drying of the wheat kernel. J Appl Polym Sci 1959;1:212–26.
29. Barbosa-Cánovas GV, Vega-Mercado H. Dehydration of foods. New York: Chapman & Hall, 1996.
30. Mabellini A, Ohaco E, Márquez CA, De Michelis A, Lozano JE. Coeficientes de difusión efectivos durante el secado con aire caliente de rosa mosqueta pretratada y sin pretratar. Proceeding of III Congreso Internacional de Ciencia y Tecnología de Alimentos. Córdoba – Argentina. 15 al 17 de Abril de 2009. Libro 3: Avances en Ingeniería y Tecnología, 2009:126–34.