

The Sodium Diffusion during the Debittering of Green Table Olives. Elliptical Coordinates Model

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Abstract – Many models had been develops in order to study the diffusion process in fruits. All they were consistent, but they none fits exactly to the shape of the geometry of the fruit.

We had developed a new model into elliptical coordinates in order to can study the diffusion process in ovoid fruits. Its results has a very good agree with the experimental measure that we had made to table olive.

It has an annex benefit: when the model is used, the diffusion coefficient value at different time can to calculate to pulp of the ovoid fruits.

Keywords – Diffusion, Debittering, Elliptical Coordinates, Olives.

I. INTRODUCTION

Improper handling of the debittering operation it can to cause economics lost on the final product. So, it is very important to understand debittering process. Maldonado y Zuritz [1] study the olive diffusion phenomenon submerged in sodium using the green olives of the Arauco variety. They had considered that the diffusion process take a place into the isotropic fruit and that the diffusion coefficient is constant in all its pulp, justifying a quasi-stationary state through to its epidermis.

II. OBJECTIVE

The olives can be classified to its geometry in spherical, ovoid and elliptical forms; we want to develop the elliptical coordinates model in order to can to describe the olives behavior it having in consideration the geometrical forms mentioned, fundamentally to calculate the concentrations and diffusion coefficients under these conditions.

III. METHOD AND MATERIALS

In the Avena e Hijos S.A factory of the Maipú department, we made the experience with debittering olives, where the fruits were placed into the industrial recipients with capacity to the 4000 liters. In the inner of the recipient, we had collocated 2100 kg. of olives and it was completed the volume with 1900 liters of sodium at a concentration of 2.5 % in NaOH.

The sodium concentration variation on the time function was evaluated through of the treatment by titration at different time rank of the debittering solution. To each

experience, we had collected ten samples at regular periods, until the sodium arrive at an approximate depth like as a 75% of the total think of the pulp

The analysis samples were processed in according with establish for Maldonado and Zuritz (2003) on this way: It must to get samples at different deep value from the recipients using a punch. The analysis sample (on the debittering and washing process) were extracted and processed according to the established for Maldonado and Zuritz (2003) on this way: in order to can extract samples at different depth from the olive pulp it was used a glass punch of 0.5 cm of internal diameter with frosted tip. This tool must be inserted a perpendicular on the olive longitudinal axis. When the tool had been introduced, with the help of a thin blade, the olive must be sectioned until the pit. This procedure has allowed us extract a cylindrical sample of the approximately 4.6 mm of length and 4.8 mm of radius. After of this processing, we sectioned the cylinder with the thin blade in fourth portions of approximately 1.16 mm of thickness each (measured with a gauge of a resolution of 1:50).

A. Sodium determination

Between steps of the debittering, washing, include and keeping into the brine, we had studied approximately 6000 solid samples and 300 liquid samples.

All the samples extracted using this methodology had been weighed with a precision of 0.0001 g and they were conserved at -18°C until its process on the next way: Into the porcelain crucible with a lid we had placed the samples, in order to prevent liquid losses to thawing.

On the heater, the samples had been dried during 24 hours at 100°C ± 5°C and they were calcined at 550°C ± 25°C until that we had obtained withe ash, according to it established for Maldonado and Zuritz (2003).

The ash were collected quantitatively with 2 ml of HCL 50% solution (Sodium free) and 10 ml of deionized water in a test tube. The sodium content was measured with a flame photometer Metrolab 315, it was calibrated with standar patron of 0.7 meq. Na/l. Also we had constructed a calibration curve with 0.35, 0.15 and 0 meq. Na/l.

B. Theoretical Considerations

Elliptical coordinate definition

They are a two-dimensional system of the elliptical lines (μ, ν) whose definition is:

$$\begin{cases} x = a \cosh \mu \cos \nu \\ y = a \sinh \mu \sin \nu \end{cases}$$

Where μ is a positive real number and $\nu \in [0, 2\pi)$, these definitions corresponding to ellipses and hyperbolas whose equations are:

$$\frac{x^2}{a^2 \cosh^2 \mu} + \frac{y^2}{a^2 \sinh^2 \mu} = \cos^2 \nu + \sin^2 \nu = 1$$

That corresponding to an ellipses curves with μ value constant, while the equation:

$$\frac{x^2}{a^2 \cos^2 \nu} - \frac{y^2}{a^2 \sin^2 \nu} = \cosh^2 \mu - \sinh^2 \mu = 1$$

These equations corresponding to hyperbolas curves with the μ value constant. These curves can be observed in the figure 1.

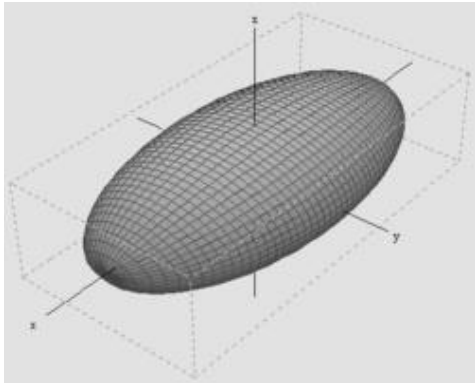


Fig.1. Body with a elliptical system coordinate associated.

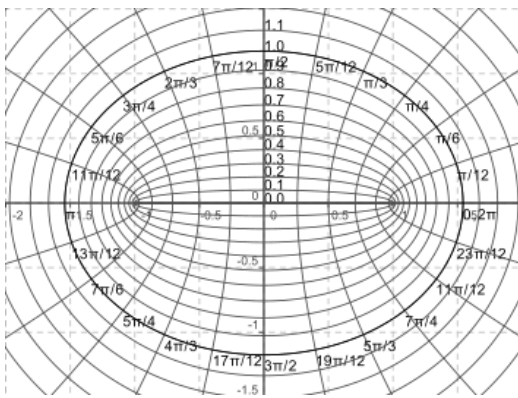


Fig.2. Elliptical System coordinate.

The diffusion equation is:

$$\nabla^2 c = D \frac{\partial c}{\partial t} \quad (1)$$

The concentration Laplacian into elliptical coordinate is:

$$\nabla^2 c = \frac{4}{R^2(\mu^2 - \nu^2)} \left\{ \frac{\partial}{\partial \mu} [(\mu^2 - 1)] \frac{\partial c}{\partial \mu} \right\} + \frac{\partial}{\partial \nu} [(1 - \nu^2)] \frac{\partial c}{\partial \nu} + \left(\frac{1}{\mu^2 - 1} + \frac{1}{1 - \nu^2} \right) \frac{\partial^2 c}{\partial \varphi^2} \quad (2)$$

Where $R^2 = 4(a^2 - b^2)/a^2$ is the ellipse eccentricity, a and b are the ellipsoidal major and minor semi-axes. If the fruit present isotropic properties, then $\frac{\partial^2 c}{\partial \varphi^2} = 0$ and the diffusion differential equation will be:

$$\nabla^2 c = \frac{4}{R^2(\mu^2 - \nu^2)} \left\{ \frac{\partial}{\partial \mu} [(\mu^2 - 1)] \frac{\partial c}{\partial \mu} \right\} + \frac{\partial}{\partial \nu} [(1 - \nu^2)] \frac{\partial c}{\partial \nu} \quad (3)$$

In order to resolve the equation 3, we use the separation variable method, and we propose as solution function:

$$c(\mu, \nu, t) = M(\mu) \cdot N(\nu) \cdot T(t) \quad (4)$$

Replacing the equation 4 into the equation 3 and if we operate, we can obtain:

$$\frac{4}{R^2(\mu^2 - \nu^2)} \left\{ \frac{1}{M} \frac{\partial}{\partial \mu} [(\mu^2 - 1)] \frac{\partial M}{\partial \mu} \right\} + \frac{1}{N} \frac{\partial}{\partial \nu} [(1 - \nu^2)] \frac{\partial N}{\partial \nu} \left\} = \frac{D}{T} \frac{\partial T}{\partial t} \quad (5)$$

We can observe that the equation 5 describe that the single $M(\mu)$ differential equation added at the single $N(\nu)$ differential equation is equal to a single differential equation that depend only on the time t . This fact is possible only if its results of each differential equation are a constant value and its addition (of the left side) is equal a certain constant α . In other words

$$\frac{4}{R^2(\mu^2 - \nu^2)} \left\{ \frac{1}{M} \frac{\partial}{\partial \mu} [(\mu^2 - 1)] \frac{\partial M}{\partial \mu} \right\} + \frac{1}{N} \frac{\partial}{\partial \nu} [(1 - \nu^2)] \frac{\partial N}{\partial \nu} \left\} = \frac{D}{T} \frac{\partial T}{\partial t} = \alpha \quad (6)$$

If we resolve the last two members of the equation 6, we have that:

$$\frac{dT}{T} = \alpha D dt \quad (7)$$

Integrating the equation 7 between the initial time equal to zero and a final time t , we arrive to the solution:

$$T(t) = T_0 e^{m^t \int_0^t D(\epsilon) dt} \quad (8)$$

In the equation 8 T_0 is the initial value of the function $T(t)$. Also, we had considered that the diffusion coefficient $D(t)$ is a time function, because when the time passes, pulp fruit increase its concentration and becomes saturated, this fact produce that the decrease its concentration absorption capacity, and we assume that the decay behavior or the concentration diffusion coefficient on the time function is given to:

$$D(t) = D_0 / (t + b) \quad (9)$$

D_0 is the initial concentration diffusion coefficient value. Then we have that at $t=0$.

$$D(0) = \frac{D_0}{(t+b)} = D_0$$

This result is correct only if $b = 1$. Then, the equation 9 become in:

$$D(t) = D_0 / (t + 1) \quad (10)$$

In order to find the complete expression of the $T(t)$ function, we must to integrate the equation 10. So, we had obtained that:

$$\int_0^t D(t) dt = D_0 \alpha \ln[t + 1] \quad (11)$$

If we replace this result into the equation 8 obtain:

$$T(t) = T_0 e^{D_0 \alpha \ln[t+1]} = T_0 [t + 1]^{D_0 \alpha} \quad (12)$$

When we replace this result on the equation 4, we obtain the solution function of the temporal differential equation as:

$$c(\mu, \nu, t) = M(\mu) \cdot N(\nu) \cdot T_0 [t + 1]^{D_0 \alpha} \quad (13)$$

In order to obtain the complete solution of the differential equation 3, we clear the a parameter from equation 13 and we propose like as solution functions $N(\nu)$ y $M(\mu)$:

$$M(\mu) = \frac{1}{2} \ln(\mu^2 - 1) + M_0 \quad (14.a)$$

$$N(v) = \frac{1}{2} \ln(1 - v^2) + N_0 \quad (14.b)$$

Here M_0 and N_0 are integration constant, whole value must be determinate to boundary and initials conditions. We can derive the equations 14, on a way that we obtain:

$$\frac{dM}{d\mu} = \frac{\mu}{(\mu^2-1)} \quad (15.a)$$

$$\frac{dN}{dv} = \frac{-v}{(1-v^2)} \quad (15.b)$$

If the equations 15 are replacing into differential equation and we operating them, we obtain:

$$\left\{ \frac{1}{\mu} \frac{\partial}{\partial \mu} \left[\mu \frac{\partial M}{\partial \mu} \right] + \frac{1}{N} \frac{\partial}{\partial v} \left[-v \frac{\partial N}{\partial v} \right] \right\} = \alpha \frac{R^2(\mu^2 - v^2)}{4} \quad (16)$$

Each member of the left side of the equation 16 is an independent differential equation that has the next partial derivatives:

$$\frac{\partial}{\partial \mu} \left[\mu \frac{\partial M}{\partial \mu} \right] = \frac{\partial}{\partial \mu} [\mu^2] = 2\mu \quad (17.a)$$

$$\frac{\partial}{\partial v} \left[v \frac{\partial N}{\partial v} \right] = \frac{\partial}{\partial v} [-v^2] = -2v \quad (17.b)$$

We can replace these results into the equation 16 and we obtained:

$$2(\mu - v) = \alpha \frac{R^2(\mu - v)(\mu + v)}{4} \quad (18)$$

or

$$v = \frac{8}{\alpha R^2} - \mu \quad (19)$$

Replacing the equation 19 into the equation 14 (b) we have:

$$N(\mu) = \frac{1}{2} \ln \left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} \mu - \mu^2 \right) + N_0 \quad (20)$$

Using this result we can to express the equation 13 of the way:

$$c(\mu, t) = \left[\frac{1}{2} \ln(\mu^2 - 1) + M_0 \right] \left[\frac{1}{2} \ln \left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} \mu - \mu^2 \right) + N_0 \right] T_0 [t + 1]^{D_0 \alpha} \quad (21)$$

If we call r_0 at the position in order to calculate the μ variable value on the pit surface. In this position the concentration value is considered null, because we assume that there are not concentration flux through to it. Then to this position in the inner of fruit, when begin the diffusion process its initial value will be zero. In others words, we will have that

$$c(r_0, 0) = \left[\frac{1}{2} \ln(ro^2 - 1) + M_0 \right]$$

$$\left[\frac{1}{2} \ln \left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} ro - ro^2 \right) + N_0 \right] T_0 = 0 \quad (22)$$

and

$$M_0 = -\frac{1}{2} \ln(ro^2 - 1) N_0$$

$$= -\frac{1}{2} \ln \left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} ro - ro^2 \right)$$

$$c(\mu, t) = \left[\ln^2 \frac{(\mu^2 - 1)}{(ro^2 - 1)} + \ln^2 \frac{\left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} \mu - \mu^2 \right)}{\left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} ro - ro^2 \right)} \right]$$

$$T_0 [t + 1]^{D_0 \alpha} \quad (23)$$

Also, on the exterior fruit surface ($\mu = re$ at $t = 0$) will be $c(\mu, t) = C_0$. Then we have that:

$$c(re, 0) = C_0 = \left[\ln^2 \frac{(re^2 - 1)}{(ro^2 - 1)} \right] T_0 +$$

$$\left[\ln^2 \frac{\left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} re - re^2 \right)}{\left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} ro - ro^2 \right)} \right] T_0 \quad (24)$$

Then, we have:

$$T_0 = C_0 \left[\ln^2 \frac{(re^2 - 1)}{(ro^2 - 1)} + \ln^2 \frac{\left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} re - re^2 \right)}{\left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} ro - ro^2 \right)} \right]^{-1} \quad (25)$$

$$c(\mu, t) = C_0 [t + 1]^{D_0 \alpha} \frac{\left[\ln^2 \frac{(\mu^2 - 1)}{(ro^2 - 1)} + \ln^2 \frac{\left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} \mu - \mu^2 \right)}{\left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} ro - ro^2 \right)} \right]}{\left[\ln^2 \frac{(re^2 - 1)}{(ro^2 - 1)} + \ln^2 \frac{\left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} re - re^2 \right)}{\left(1 - \frac{64}{\alpha^2 R^4} + \frac{16}{\alpha R^2} ro - ro^2 \right)} \right]} \quad (26)$$

This model considered that the diffusion flux through of the pit surface to its inner is null, then at $\mu = r_0$ we have that:

$$|-D \nabla c|_{\mu=r_0} = 0 \quad (27)$$

Which is the same that:

$$|-D \frac{\partial c}{\partial \mu}|_{\mu=r_0} = 0 \quad (28)$$

From this boundary condition we had obtained that:

$$\alpha = \frac{4}{r_0 R^2} \quad (29)$$

Replacing the equation 29 into equation 26 we find that:

$$c(\mu, t) = C_0 [t + 1]^{\frac{4D_0}{r_0 R^2}} \frac{\left[\ln^2 \frac{(\mu^2 - 1)}{(ro^2 - 1)} + \ln^2 \frac{\left(1 - \frac{4ro}{R^2} + 4ro\mu - \mu^2 \right)}{\left(1 - \frac{4ro}{R^2} + 3ro^2 \right)} \right]}{\left[\ln^2 \frac{(re^2 - 1)}{(ro^2 - 1)} + \ln^2 \frac{\left(1 - \frac{4ro}{R^2} + 4ro re - re^2 \right)}{\left(1 - \frac{4ro}{R^2} + 3ro^2 \right)} \right]} \quad (30)$$

After, a posterior time t_1 , we did a new concentration measure c_1 on the fruit surface. For that instant the equation will be:

$$c(re, t_1) = c_0 [t_1 + 1]^{\frac{4D_0}{r_0 R^2}} = c_1 \quad (31)$$

From the equation 31 we can to find an expression of initial diffusion coefficient D_0 , so clearing it can obtain:

$$D_0 = \frac{r_0 R^2 \ln(c_1/c_0)}{4 \ln(t_1 + 1)} \quad (32)$$

IV. AN EXAMPLE: RESULTS AND DISCUSSION

The media olives dimension used were: weight = 7.433×10^{-3} kg, $r = 0.915 \times 10^{-3}$ kg; equatorial diameter = 20.50×10^{-3} m, $r = 1.59 \times 10^{-3}$ m; length = 31.38×10^{-3} m, $r = 2.20 \times 10^{-3}$ m, skin thickness = 4.0×10^{-5} m.

The results of the applications of the elliptical coordinate model can see on the table 1. There to values of $a = 1.4$ mm.; $b = 0.89$ mm. With $R = 5.84$, $r_0 = 0.6$ mm. and $r_e = 4.2$ mm. The table1 show sodium concentration sample value to different times and deeps from the model used.

We can observe also that the initial sodium concentration value is 0.0045 meq Na/g to all μ value. Near of the pit ($\mu=0.06$) when the debittering had finished, the sodium concentration value had increased at 0.044 meq Na/g, while near of the skin ($\mu = 0.21$) the sodium concentration value was 0.703 meq Na/g. These facts show that at the skin level the sodium concentration value increase two magnitude order, and on the near pit level, the concentration value increase only one magnitude order.

Table 1 Theoretical concentrations value in meq/Na/g of olive. The times value are in seconds.

Tiempo/ μ	0,06	0,075	0,125	0,1725	0,21
0	0,0045	0,0045	0,0045	0,0045	0,0045
9000	0,02	0,035	0,11	0,22	0,36
16200	0,03	0,053	0,16	0,33	0,49
23400	0,039	0,068	0,21	0,42	0,64
27000	0,043	0,075	0,24	0,47	0,70

The figure 3 show the graphic of the sodium diffusion coefficient value vs. the time, we can observe its hyperbolic behavior: The diffusion coefficient decrease when the time increase, with a value of the 9×10^{-10} m²/s at 1000 seconds and an asintotico behavior at the value 1×10^{-10} m²/s to times bigger than 8200 seconds.

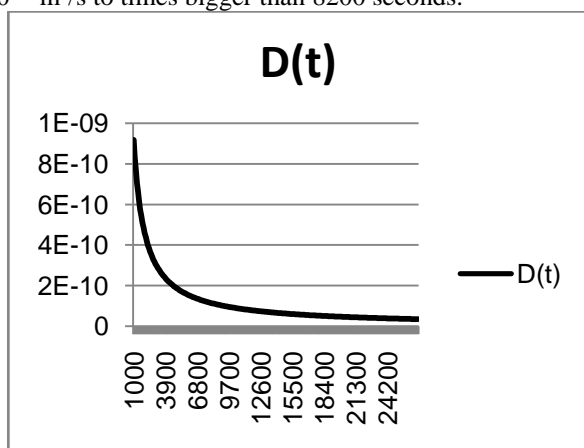


Fig.3. Sodium Diffusion coefficient in m²/s vs the time (seconds)

In the figure 4 we can see how change the sodium concentration on the concentric ellipsoidal surface to constant value of μ . For example, when $\mu=0.075$ the concentration values on this surface are smaller than for

$\mu=0.0125$. This fact explain the behavior to whole a surface that are more near of the pit, mayor is its concentration growth. This is the fundament that justified a previous size classification before of the debittering process.

V. SYNTHESIS AND CONCLUSIONS

We had cant to develop a mathematical model, it describe with a good approximation the solution diffusion process into ovoid fruits pulp. We had used elliptical coordinate in order to resolve the diffusion differential equation and we get a good solution to it.

In order to can validate the model, we apply it to an experimental case, and we saw that the theoretical result have a good agree whit the experimental measure.

We think that is a good tool in order to describe the diffusion process in all fruits with ovoid geometry.

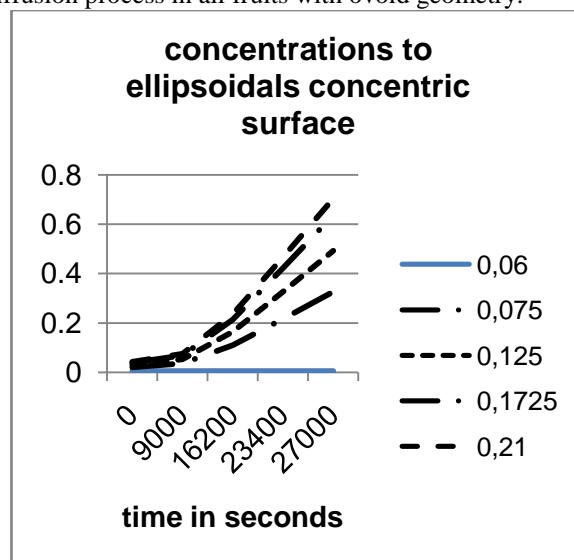


Fig.4. sodium concentrations of the ellipsoidal concentric surface.

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Before, Maldonado & col. [2] had developed a theoretical model that allow calculate the inner concentration of the isotropic fruit pulp substance with spherical geometry to any submerge time into the debittering solution.

Drusas & col. [3] quantified the sodium chloride diffusivity during the green olives brine treatment of the Konservolea variety. They had measured different concentrations of titration with silver nitrate (Morb method) at room temperature (20°) and they had considered that the brine is stable at the fifty treatment days. The diffusion of the compound was calculated to different liquid concentration on the time function. In one of their essays, they placed the olives submerged into bleach solution at the 1,8% during six hours after the debittering process and they find that the diffusion velocity increase respected the others treatment. The

authors, in order to resolve its models, had assumed that the geometry of olive is a hollow sphere.

Maldonado & Zuritz [1]-[4] had calculated the effectiveness diffusion coefficient of sodium during the green olives debittering with the Aloreña variety modeling themselves like as a hollow spheres. Before these experiences, they studies the sodium diffusion process during the debittering of the Arauco green olives using a thin plate model that is composed for an external wall (epidermis) exposed to a constant concentration, the pulp in the inner and other impermeable internal wall (pit). Also they had considered to your model an isotropic and quasi-stationary conditions. Also they had used a hollow semi-infinite cylindrical model in order to adjust the experimental data about the debittering process of the table green olives. They obtained the diffusion coefficient value (DL & DS) to 1.50%, 2.25% y3.00% of NaOH concentrations, the results were into the rank between 7.18×10^{-11} y 1.18×10^{-09} m²/s, and they can observed that its value increase with the temperature and sodium concentration increase.

Until now, many models had been used in order to study the table green olives diffusion process; all them had been consistent to determinate the order of magnitude of the diffusion coefficient effectiveness, but none them describe with precision the effects of its geometry.

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