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Mathematical modeling of the uptake of curing salts in pork meat

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ABSTRACT

A mathematical model was developed in order to represent the uptake of curing salts ($NaNO_2$, KNO_3, and NaCl) in pork meat pieces with the purpose of determining immersion times and suitable salt concentrations in the brine of wet curing processes. The partial differential equations of mass transfer under unsteady-state conditions were solved numerically, in three-dimensional geometry (finite cylinders), considering the diffusive and also the convective contributions of the different solutes, due to water uptake by the tissue. The variation of the diffusion coefficients of the curing salts with NaCl concentration was also considered. The numerical model was validated using results obtained from experiments of salt diffusion in pork meat cylinders of different diameters immersed in curing brines.

The model was applied to predict the time necessary for an industrial piece of meat to be immersed in brine without exceeding the maximum permitted nitrite value of 200 ppm and the recommendable sodium chloride concentration.

1. Introduction

In food processing, mass transfer between solid and fluid is used for preservation and to modify characteristics of flavor, color, and nutritional value. Pork meat curing can be conducted by immersion of meat tissues in NaCl brines, which is known as brine curing procedure. It is used in several countries by small processors for certain pork cuts. Pickle cure usually gives a product with a milder flavor than dry curing and requires less labor (Pearson and Gilett, 1996). An example of the application of this process is the Wiltshire bacon, a generic term for traditional tank-cured bacon in the UK. Similar processes are also used elsewhere, especially for ham curing.

In cured meat it is necessary to maintain the microbiological safety by controlling the amounts of incorporated salts to achieve an adequate water activity thus avoiding the growth of microorganisms, without adding amounts of chemical preservatives that exceed the allowed values of nitrite and nitrate, and without exceeding the level of NaCl accepted by consumers.

According to the effective regulations the use of sodium nitrite, potassium nitrate or its combination must not exceed 200 ppm (0.2 mg/g) expressed as sodium nitrite in the final product (USDA-FSIS, 1999). Besides a NaCl concentration acceptable by the consumer is between 3% and 4% (30 mg/g meat–40 mg/g meat, Pearson and Gilett, 1996).

Diffusion of salts in solid foods such as pork, beef, or fish has been studied by many workers (Djelveh and Gros, 1988; Dussap and Gros, 1980; Fox, 1980; Graiver et al., 2006; Gros et al., 1984; Pinotti et al., 2001; Sabadini et al., 1998; Schwartzberg and Chao, 1982; Siró et al., 2009; Turhan and Kaletunç, 1992; Wang et al., 2000; Wood, 1966). Wet curing process requires a thorough understanding of the effects that salts ($NaNO_2$, KNO_3, and NaCl) have on the tissue microstructure. In a previous work, Graiver et al. (2005) reported that sodium chloride affects the microstructure of meat tissues and that the diffusion coefficients of brine salts depend on NaCl concentration. Similar results were reported by Wang et al. (2000) and Pinotti et al. (2000).

In many foodstuffs the incorporation of salt is accompanied by water loss (Gerla and Rubiolo, 2002; Vestergaard et al., 2005). Graiver et al. (2006) found that in the case of pork meat wet curing, water movement (co or counter current) depends on NaCl content of the brine. At long contact times that is, under equilibrium conditions, meat tissue treated with increasing concentrations of NaCl showed important modifications. For NaCl concentrations in the solution ranging between 5 and 200 g/L the tissue gained water and incorporated great amount of solutes ("salting in"). Swelling of the fibers, and high values of water holding capacity of the myofibrillar proteins were observed in agreement with the results reported by Offer and Trinick (1983) and Belitz and Grosch (1997). The increase in water holding capacity might be attributed to the lateral expansion of myofibrils, which is coupled to protein solubilization. According to Xiong et al. (2000) and Cheng and Sun

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Nomenclature

A	cylinder area, m^2
C	total concentration, g/L
C_i	solute concentration, g/L
C_{if}	solute concentration of external solution, g/L
C^w	water concentration, g/g
C^w_{max}	maximum water concentration in the meat, g/g
C^w_0	initial water concentration in the meat, g/g
D	salt diffusion coefficient in water, m^2/s
D_m	effective diffusion coefficient, m^2/s
H	cylinder height, m
j_i	diffusive mass flux of solute, g/(m^2 s)
k	water mass transfer coefficient, m/s
k'	water mass transfer coefficient, s^{-1}
k_c	mass transfer coefficient, m^2/s
L	equivalent length, m
n_i	mass flux of solute i, g/(m^2 s)
R	cylinder radius, m
r	radial coordinate, m
t	time, s
v	global average velocity of the solution, m/s
v_∞	velocity of the fluid, m/s
V	cylinder volume, m^3
x_{NaCl}	average concentration of NaCl uptake in the tissue, g/g
x_{NaNO_2}	average concentration of $NaNO_2$ uptake in the tissue, g/g
x_1	immersion time, s
x_2	NaCl concentration in the brine, g/L
x_3	$NaNO_2$ concentration in the brine, g/L
x_4	KNO_3 concentration in the brine, g/L
z	axial coordinate, m

Greek symbols

ρ	solution density, kg/m^3
μ	solution viscosity, kg/(m s)
ω_i	mass fraction of solute i

Subscript

i	related to NaCl, $NaNO_2$, or KNO_3

Dimensionless numbers $j_m = \frac{Sh}{ReSc^{1/3}}$
Reynolds number $Re = \frac{\rho v_\infty L}{\mu}$
Schmidt number $Sc = \frac{\mu}{\rho D}$
Sherwood number $Sh = \frac{k_c L}{D}$

(2008), an increase in water binding and hydration in salted meat and muscle fibers are generally attributed to enhanced electrostatic repulsion between myofibrillar filaments, the protein structure matrix unfolds and the swelling occurs, causing the filament lattices to expand for water entrapment. The maximum water uptake was observed for NaCl concentrations ranging between 70 and 100 g/L; above 200 g/L NaCl in the brine the water holding capacity decreased showing water loss at 330 g/L (“salting out”) (Graiver et al., 2006). Salt has, in fact, been shown to cause a significant displacement of water from the outside to the inside of the myofibrillar matrix (Bertram et al., 2001).

Mathematical models can help to a better understanding of the transport phenomena and to control the variables involved in the process, such as immersion times and suitable salt concentrations in the brine.

The uptake of solutes cannot be interpreted as a simple Fickean diffusion process with a constant diffusion coefficient. The diffusion coefficient is suggested to be affected by changes in NaCl concentration, swelling, and degree of water movement (Vestergaard et al., 2005). Therefore, an additional contribution for the “salting in” process due to electrostatic repulsion forces between myofibrillar filaments in meat tissue can be represented as a pseudo-convective flux in which the driving forces are not pressure differences but electrostatic contributions. This phenomena lead to a formulation in which Fick’s law is used for the modeling of the diffusion process and “convective” terms are included to consider the global flux of brine due to electrostatic forces (Graiver, 2006).

The aims of this work were:

- to develop a mathematical model to describe mass transfer of salts ($NaNO_2$, KNO_3, and NaCl) during curing in pork meat pieces of similar dimensions to those used in the industry in order to simulate the operating conditions of the process, determining adequate immersion times and salt concentrations in the brine,
- to solve numerically the unsteady-state mass transfer differential equations considering the diffusive and convective contributions in a three-dimensional system and the variation of salt diffusion coefficients with NaCl concentration,
- to validate the proposed mathematical model by comparing predicted $NaNO_2$, KNO_3, and NaCl concentrations at different contact times with experimental data of salt concentration in pork tissue cylinders (free of visible fat) immersed in curing brines, and
- to determine operating conditions for industrial curing processing such as immersion times, $NaNO_2$, KNO_3, and NaCl concentrations in the brine.

2. Mathematical model

In a previous work Graiver et al. (2006) reported that there was a significant water uptake when NaCl concentration ranged between 5 and 200 g/L. This phenomenon implies that the convective contribution to the salt uptake has to be considered. Therefore in addition to a diffusive process of incorporation of solutes (j_i) a convective process of addition of water and solute ($C_i v$), is proposed.

The flux n_i includes both diffusive (j_i) and convective ($C_i v$) contributions as follows:

$$\underline{n_i} = \underline{j_i} + C_i \underline{v} = -C D_m \underline{\nabla} \omega_i + C_i \underline{v} \quad (1)$$

where i corresponds to each solute (NaCl, $NaNO_2$, or KNO_3), n_i is the total mass flux of a solute with respect to fixed coordinates, j_i the diffusive mass flux of solute that is replaced by Fick’s law, v the global average velocity of the solution, C_i the mass concentration of solute, D_m the effective coefficient of diffusion of the solute in the matrix, ω_i the mass fraction of solute i, and C the total concentration.

Microscopic mass balances for each of the solutes were used in order to analyze the incorporation of the solutes in a piece of meat, in the absence of chemical reaction. Considering that D_m is variable with the concentration of solute, which implies a non-linear problem and that the flux is incompressible ($\underline{\nabla} \cdot \underline{v} = 0$), with a constant total concentration the following is obtained:

$$\frac{\partial C_i}{\partial t} + \underline{v}.(\underline{\nabla}.C_i) = \underline{\nabla} D_m \underline{\nabla} C_i \quad (2)$$

In order to simulate the incorporation of curing salts in a finite cylindrical piece of meat, like those generally used under industrial conditions (e.g., whole *Longissimus dorsi* muscle). Eq. (2) was written in cylindrical coordinates with radial and axial diffusive and convective fluxes. D_m was considered variable with the concentration of solute and convective terms were added to consider v_r and v_z, being:

$$\frac{\partial C_i}{\partial t} + v_r \frac{\partial C_i}{\partial r} + v_z \frac{\partial C_i}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_m \frac{\partial C_i}{\partial r}\right) + \frac{\partial}{\partial z}\left(D_m \frac{\partial C_i}{\partial z}\right) \tag{3}$$

where z is the axial coordinate and r is the radial coordinate.

The convective flux from the immersion solution takes place in opposite direction to axes r and z, therefore: $v_r = -v$, $v_z = -v$, being v the apparent convective contribution. The detailed calculation of v is described in Section 4.2. Then:

$$\frac{\partial C_i}{\partial t} = \frac{\partial D_m}{\partial r}\frac{\partial C_i}{\partial r} + \frac{D_m}{r}\frac{\partial C_i}{\partial r} + D_m \frac{\partial^2 C_i}{\partial r^2} + \frac{\partial D_m}{\partial z}\frac{\partial C_i}{\partial z} + D_m \frac{\partial^2 C_i}{\partial z^2} + v\left(\frac{\partial C_i}{\partial r} + \frac{\partial C_i}{\partial z}\right) \tag{4}$$

The industrial curing process is not carried out under conditions of strong agitation, then a mass transfer coefficient k_c was considered, being the boundary conditions:

$$z = \pm\frac{H}{2}; \quad \forall r; \quad -D_m \frac{\partial C_i}{\partial z} = k_c(C_i - C_{if}) \tag{5}$$

$$r = R; \quad \forall z; \quad -D_m \frac{\partial C_i}{\partial r} = k_c(C_i - C_{if}) \tag{6}$$

where H is the cylinder height, R the cylinder radius, C_{if} solute concentration of the external solution, k_c mass transfer coefficient at the interface.

The initial condition was expressed as:

$$C_i = 0 \quad \text{at} \quad t = 0 \tag{7}$$

It was considered that the initial concentration of NaCl in the tissue could be neglected since it is about 0.17 g NaCl per 100 g of fresh meat (USDA Nutrient Data Laboratory, Agricultural Research Service, 2002).

Symmetry boundary conditions were:

$$\frac{\partial C_i}{\partial r} = 0 \quad \text{at} \quad r = 0; \qquad \frac{\partial C_i}{\partial z} = 0 \quad \text{at} \quad z = 0 \tag{8}$$

Eq. (4), initial and boundary conditions were discretized according to an explicit finite differences scheme and a computer code in Fortran 90 (version 4.0 Microsoft) was developed to solve these equations.

2.1. Calculation of the average concentrations in the model

To compare the numerical predictions of the model with experimental data, average concentrations in different regions of the cylinder (Fig. 1) were calculated by numerical integration (Dahlquist and Björck, 1974):

$$\overline{C} = \frac{2\pi \iint Cr\, dr\, dz}{2\pi \iint r\, dr\, dz} \tag{9}$$

3. Materials and methods

To validate the mathematical model, different experiments were carried out using *L. dorsi* pork tissue, free of visible fat. The initial water and protein contents determined according to AOAC methods (1984, 1980) were 74.10 ± 1.85 and 20.32 ± 0.21, respectively. Fat content was determined on previously dried samples by Soxhlet method, using ethyl ether and petroleum ether (Bp: 35–60 °C) in a 1:1 relationship as extraction solvent (Andrés et al., 2006); the obtained value was 2.13 ± 0.12.

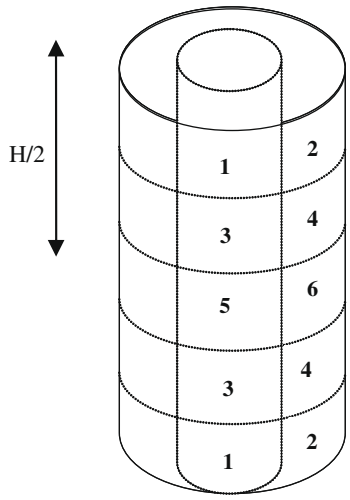

Fig. 1. Scheme of the different portions of meat tissue in which the concentrations of the solutes were determined to validate the numerical model experimentally.

3.1. Experiments to validate the mathematical model

Seven cylinders of 6 cm diameter and 12 cm height cut from pork whole muscle (*L. dorsi*) from different animals were used. They were immersed in a brine solution containing (NaCl 140 g/L, $NaNO_2$ 3 g/L, and KNO_3 2.5 g/L) at 4 °C. At each immersion time (3.66, 5, 8, 13, 24, 48, and 75 h) one of the cylinders was removed from the solution and cut perpendicular to the axial axis in five cylindrical sections of 2.4 cm thickness. The center of each section was removed with a borer of 2.6 cm of internal diameter (Fig. 1) and each of the rings and internal cylinders were used to determine the concentrations of nitrite, nitrate, and chloride anions. All experiments were performed in duplicates using 14 different animals to consider biological variability.

In Fig. 1, numbers 2, 4, and 6 correspond to the external ring at different heights whereas 1, 3, and 5 are the internal cylinders.

Besides, another set of similar experiments were carried out using five cylinders 5 cm diameter and 12 cm height of pork whole muscle from different animals to validate the mathematical model, with reference to the analysis of the effect of cylinder size on salt uptake.

3.2. Analytical techniques

For nitrite determination, meat tissue was homogenized in an Omnimixer equipment (Sorvall Omni-Mixer 17106, DuPont Instruments, Newtown, CT, USA); bidistilled water at 90 °C and 10 mL $HgCl_2$ saturated solution to denature proteins were added. The suspension was stirred during 10 minutes, diluted with water and filtered; 25 mL of the final solution were taken and Hach kit Nitriver 3, (method 371) was used for nitrite determination. After reacting for 15 min, nitrite concentration was measured at 507 nm in a Hach spectrophotometer (DR/2000).

This method is based on the reaction between nitrite in the sample and sulfanilic acid forming an intermediate diazonium salt according to AOAC method (2000). This couples with chromotrophic acid to produce a pink colored complex (Griess reaction), proportional to the amount of nitrite present (Girard, 1991).

Similar extraction procedures were followed for nitrate determination. The nitrate in the final solution was reduced to nitrite

using cadmium (Hach kit Nitraver 6, method 351), and then nitrite was measured as explained previously.

To measure the amount of NaCl present in the tissue after each immersion period, meat tissue was homogenized in an Omnimixer equipment with bidistilled water at 90 °C. The suspension was stirred, diluted with water, and filtered. NaCl was determined by measuring chloride content on a 100 mL aliquot, using a previously calibrated ion-selective electrode (Cole–Parmer 27502-12) with 2 mL of $NaNO_3$ solution (5 M) added to regulate the ionic strength (Graiver et al., 2006).

Each method was validated by injecting known amount of $NaNO_2$, KNO_3, and NaCl in small pieces of meat, and comparing those quantities with the values obtained following the extraction and determination procedure described above.

4. Results and discussion

In order to simulate the uptake of the different solutes by the tissue, the following information has been incorporated to the mathematical model: diffusion coefficients of the solutes as functions of sodium chloride concentration, convective contribution, and mass transfer coefficient in the immersion brine.

4.1. Effect of NaCl concentration on the diffusion coefficients of the curing salts in the meat tissue

To solve the concentration profiles of curing salts in the meat, the simulation was done using diffusion coefficients depending on the NaCl concentration contained in the product.

In previous works the effect of NaCl concentrations on the diffusion coefficients of NaCl, $NaNO_2$, and KNO_3 were obtained. A radial (unidirectional) diffusion system was adopted, using long cylinders of pork tissue (10 cm height and approximately 1.5 cm diameter) that were immersed in brines of sodium chloride (Pinotti et al., 2001; Graiver et al., 2006).

Experimental values of D_m (m^2/s) for NaCl, $NaNO_2$, and KNO_3 at different NaCl concentrations (C_{NaCl} expressed as mg NaCl/g meat) (Pinotti et al., 2001; Graiver et al., 2006) were used to obtain the following linear regressions:

$$D_{mNaCl} = (-0.00004C_{NaCl}^2 + 0.058C_{NaCl} + 1.72)10^{-10}\ m^2/s \quad (r^2 = 0.951) \tag{10}$$

$$D_{mNaNO_2} = (0.016C_{NaCl} + 2.66)10^{-10}\ m^2/s \quad (r^2 = 0.975) \tag{11}$$

$$D_{mKNO_3} = (0.028C_{NaCl} + 2.63)10^{-10}\ m^2/s \quad (r^2 = 0.995) \tag{12}$$

4.2. Convective contribution

The water uptake by the meat tissue as a function of immersion time was analyzed from independent previous experiments, in which small meat cylinders (2 cm height × 1.5 cm diameter) were immersed in well-agitated brine solutions with different NaCl concentrations ranging between 10 and 330 g/L at 4 °C and immersion times between 15 and 150 min (Graiver et al., 2006). Mass balances were proposed in order to analyze changes in the water, proteins, and NaCl content in the tissue. The ratio between the water uptake by the meat tissue (m_{water}) and the initial mass of the meat sample (M_0) was plotted as a function of immersion time for different NaCl content (Fig. 2a and b). When NaCl concentration in the brine was lower than 100 g/L, water uptake increased with salt concentration (Fig. 2a), while for higher NaCl concentrations (140 and 200 g/L) the opposite behavior was observed (Fig. 2b).

The water convective flux varied with immersion time. The water macroscopic balance in the small cylinders led to:

$$V\frac{dC^w}{dt} = k(C^w_{max} - C^w)A \tag{13}$$

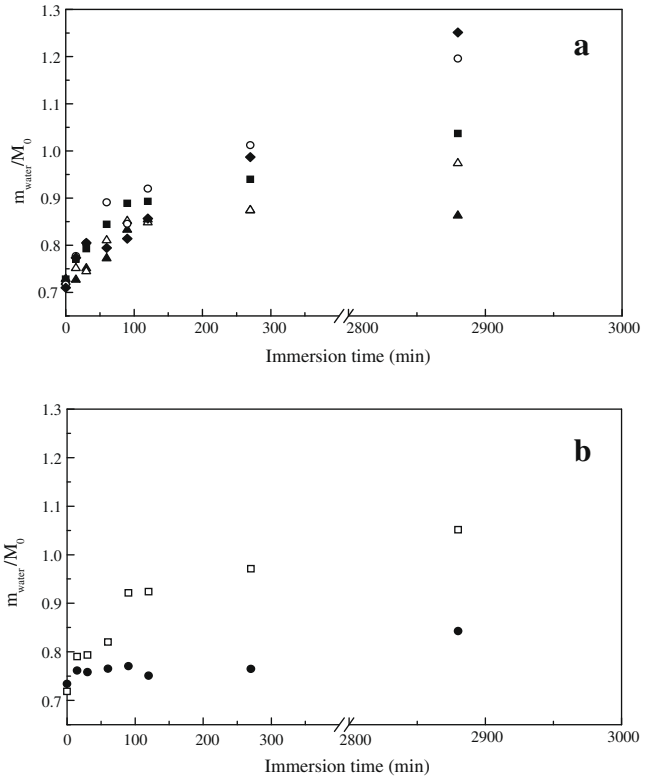

Fig. 2. Mass of water/initial mass of tissue (M_0) as a function of time for different brine concentrations: (a) (▲) 5, (△) 10, (■) 30, (○) 70, (♦) 100 g NaCl/L and (b) (□) 140, (●) 200 g NaCl/L.

where V is the volume of small cylinder used in the mass balance, A is the cylinder area, C^w the mass water concentration (g water/g dry tissue), k the mass transfer coefficient (m/s) and C^w_{max} the maximum water concentration in the tissue reached at each NaCl concentration in the brine. Rearranging the previous equation the following is obtained:

$$\frac{dC^w}{dt} = k'(C^w_{max} - C^w) \quad \text{where} \quad k' = \frac{kA}{V} \tag{14}$$

Integrating Eq. (14) and considering that initially: $C^w = C^w_0$ where C^w_0 is the initial concentration of water for each NaCl concentration, the obtained equation is:

$$\ln C^*_w = \ln\left(\frac{C^w_{max} - C^w}{C^w_{max} - C^w_0}\right) = -k't \tag{15}$$

where C^*_w is the dimensionless water concentration.

Experimental water content data of C^w were expressed as dimensionless values C^*_w. From the linear regressions of $\ln C^*_w$ as a function of the immersion time t, the value of k' was determined. An average value of $k' = 6 \times 10^{-5}$ 1/s ($r^2 = 0.7431$) was calculated for the different assayed NaCl concentrations ranging between10 and 200 g NaCl/L.

Combining Eqs. (13) and (15) the modulus (absolute value) of the velocity of water uptake in the tissue ($\underline{v}$) was calculated according to:

$$|v| = \frac{V}{A}\frac{dC^*_w}{dt} = ke^{(-k't)} \tag{16}$$

This velocity was introduced in the microscopic mass balance to represent the convective term.

4.3. Mass transfer coefficient in the immersion solution

The mass transfer coefficient k_c defined in Eqs. (5) and (6) was determined from the j_m correlation as a function of the dimensionless numbers Reynolds, Schmidt, and Sherwood for immersed cylinders (Sherwood et al., 1975).

The diffusion coefficients (at infinite dilution) of the salts in water at 25 °C (Lide, 1997), were used to calculate the corresponding values at 4 °C using the Stokes–Einstein equation. The obtained values at 4 °C were: $D_{NaCl} = 8.5 \times 10^{-10}$ m^2/s, $D_{NaNO_2} = 8.29 \times 10^{-10}$ m^2/s, $D_{KNO_3} = 10.18 \times 10^{-10}$ m^2/s. A low Reynolds number (Re = 3) was adopted for the stagnant solution obtaining a value of $j_m = 0.3$ that led to $k_c = 1.3 \times 10^{-7}$ m/s, as an average value for the three curing salts.

4.4. Validation of mathematical model

To validate the model against experimental results the computer code was run to simulate the experimental conditions described in Section 3.1.

Figs. 3a–c and 4a–c show the experimental data of the average concentrations of NaCl, $NaNO_2$, and KNO_3 corresponding to different zones of the tissue cylinders (6 cm diameter and 12 cm height) as a function of immersion time. Results for the external rings (zones 2, 4, and 6) and for the internal cylinders (zones 1, 3, and 5) are presented in Figs. 3 and 4, respectively.

Figs. 3 and 4 allow to compare experimental data with the values predicted by the numerical model (expressed as mg NaCl/g meat, mg $NaNO_2$/g meat, mg KNO_3/g meat) as a function of immersion time. A good agreement for the three analyzed salts was observed, with an average error of 9% that includes the biological variability of the samples. The satisfactory prediction of experimental values was achieved due to the convective term introduced in the numerical model.

The effect of cylinder diameter on sodium chloride uptake (average values in the whole meat sample) is observed in Fig. 5. Experimental data obtained for tissue samples of 5 and 6 cm diameter, both 12 cm height, were compared with model predictions, as a function of immersion time; a satisfactory agreement was observed, showing that to reach the same average sodium chloride concentrations in the cylinders, higher immersion times are necessary for the cylinder with a smaller diameter.

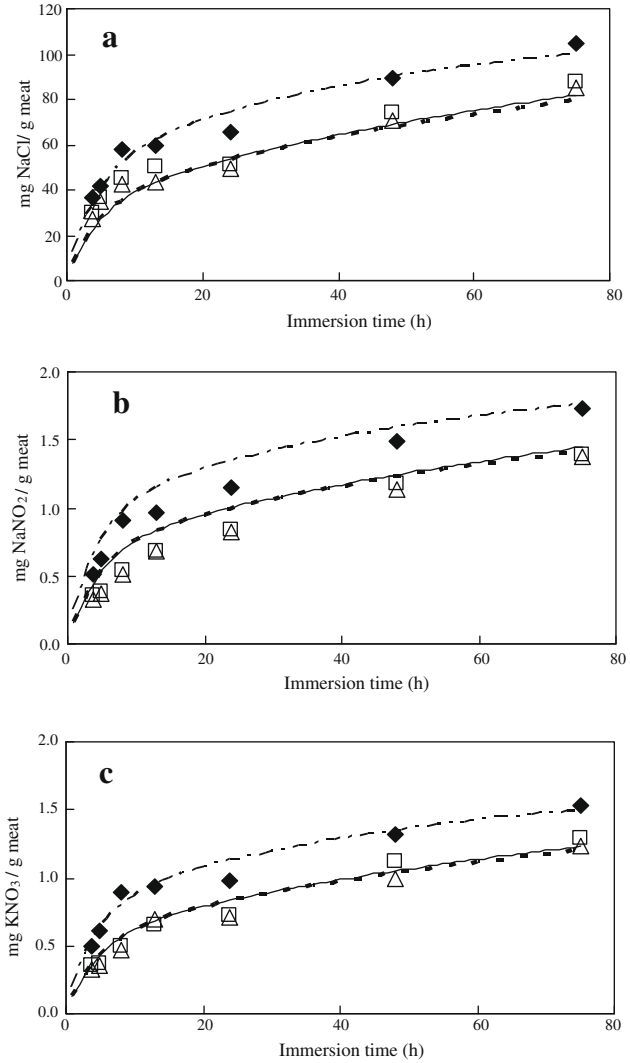

Fig. 3. Comparison of the amount of (a) mg NaCl/g meat, (b) mg $NaNO_2$/g meat, (c) mg KNO_3/g meat as a function of the immersion time in external rings: experimental (♦) 2, (□) 4, (Δ) 6 and predicted values (- · - · -) 2, (——) 4, (- - - -) 6 by the numerical model. Key numbers of the zones are shown in Fig. 1.

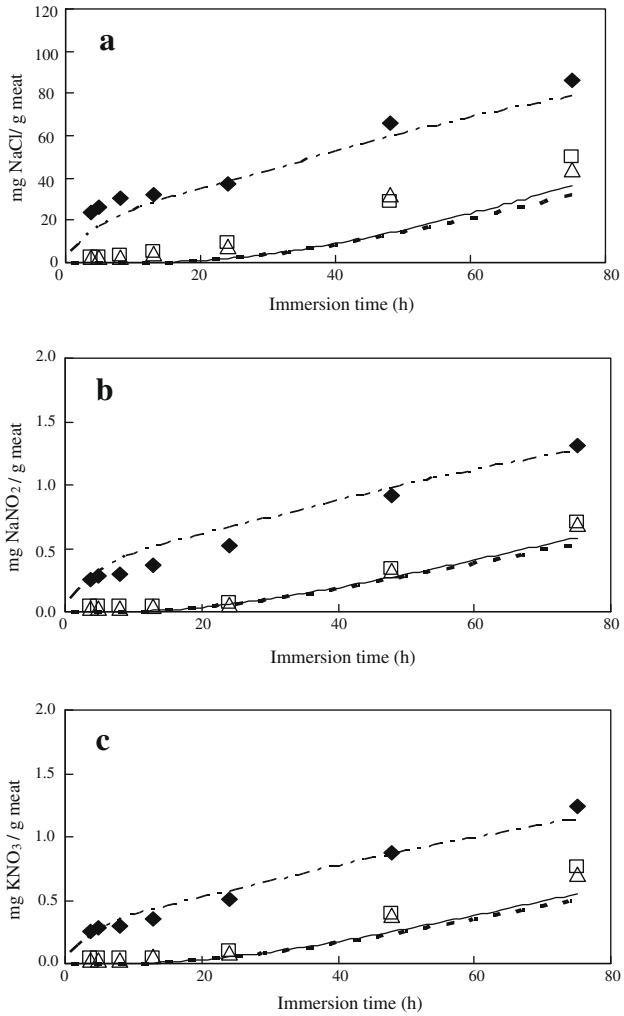

Fig. 4. Comparison of the amount of (a) mg NaCl/g meat, (b) mg $NaNO_2$/g meat, (c) mg KNO_3/g meat as a function of the immersion time in internal cylinders: experimental (♦) 1, (□) 3, (Δ) 5 and predicted values (- · - · -) 1, (——) 3, (- - - -) 5 by the numerical model. Key numbers of the zones are shown in Fig. 1.

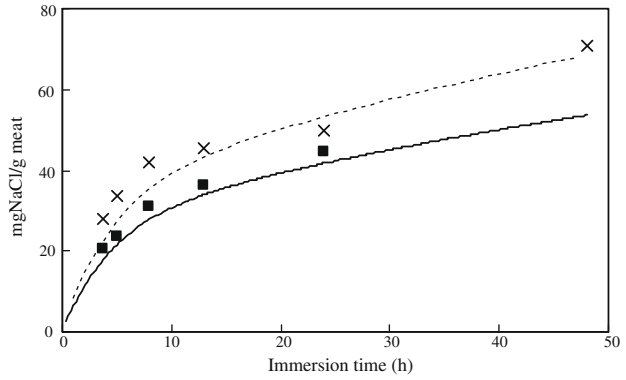

Fig. 5. Total sodium chloride uptake as a function of immersion times, for two cylinders with the same height (12 cm) and different diameters D: $D = 5$ cm experimental (■), predicted (——); $D = 6$ cm experimental (×), predicted (- - - -). Brine concentration: 140 g NaCl/L, 3 g $NaNO_2$/L, and 2.5 g KNO_3/L.

4.5. Predicted profiles

Once the computer code was validated, it was used to predict NaCl, $NaNO_2$, and KNO_3 concentrations in meat tissue for different operating conditions. The input sizes of the pork meat cylinders varied from 5 to 12 cm diameter and from 12 to 28 cm height; concentrations of sodium chloride, sodium nitrite, and potassium nitrate, ranged from 20 to 80 g/L, 0 to 0.20 g/L, and 0.05 to 0.25 g/L, respectively.

Fig. 6a shows the predicted changes in the average NaCl uptake in the tissue as a function of immersion time for cylinders of 26 cm height and diameters ranging between 9 and 12 cm, immersed in a brine of NaCl 70 g/L, $NaNO_2$ 0.1 g/L, and KNO_3 0.15 g/L. Fig. 6b exhibits a similar behavior for the average ($NaNO_2 + KNO_3$) concentrations expressed as $NaNO_2$ concentration.

In both figures it can be observed an increase of the salt concentrations in the meat tissue when the cylinder diameter increases, in agreement with the experimental data shown in Fig. 5.

Besides, from simulations keeping a constant diameter (10 cm) and varying the height of the cylinders between 28 and 25 cm, concentrations of NaCl and $NaNO_2 + KNO_3$ slightly decreased with decreasing height (data not shown).

Fig. 7 shows the simulated concentration profiles of NaCl corresponding to a cylinder of 6 cm diameter and 12 cm height during 8, 24, and 72 h of immersion time for a brine concentration of NaCl 140 g/L, $NaNO_2$ 3 g/L, and KNO_3 2.5 g/L. Fig. 7a corresponds to the concentration profile along the half height of the cylinder at a fixed radius of 1.45 cm, whereas Fig. 7b shows the concentration profile as a function of the radius for an axial position of 2.90 cm. Similar results were observed for $NaNO_2$ and KNO_3 salts.

4.6. Application of the model to determine operating conditions for an industrial curing processing

After the immersion process sodium chloride, sodium nitrite and potassium nitrate continue to diffuse through the meat, and concentration profiles tend to become uniform. These phenomena

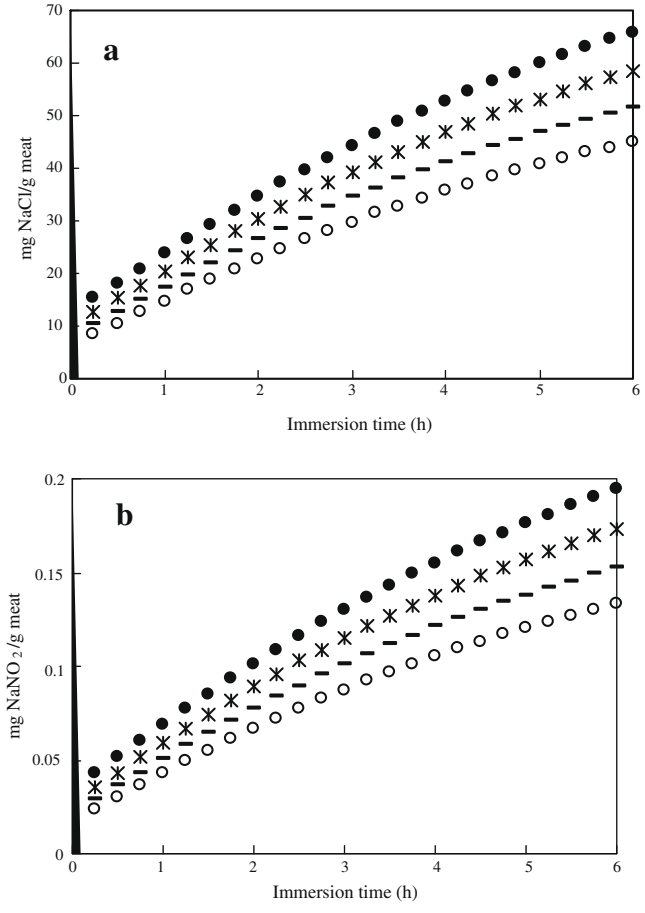

Fig. 6. Predicted concentrations of curing salts in the tissue as a function of immersion time in finite cylinders. (a) NaCl concentration (mg NaCl/g meat), (b) concentration of nitrite and nitrate ($NaNO_2 + KNO_3$) expressed as nitrite (mg $NaNO_2$/g meat). Pork meat cylinders of 26 cm height and different diameters (○) 9, (–) 10, (∗) 11 and (♦) 12 cm. Brine concentration: 70 g NaCl/L, 0.1 g $NaNO_2$/L, and 0.15 g KNO_3/L.

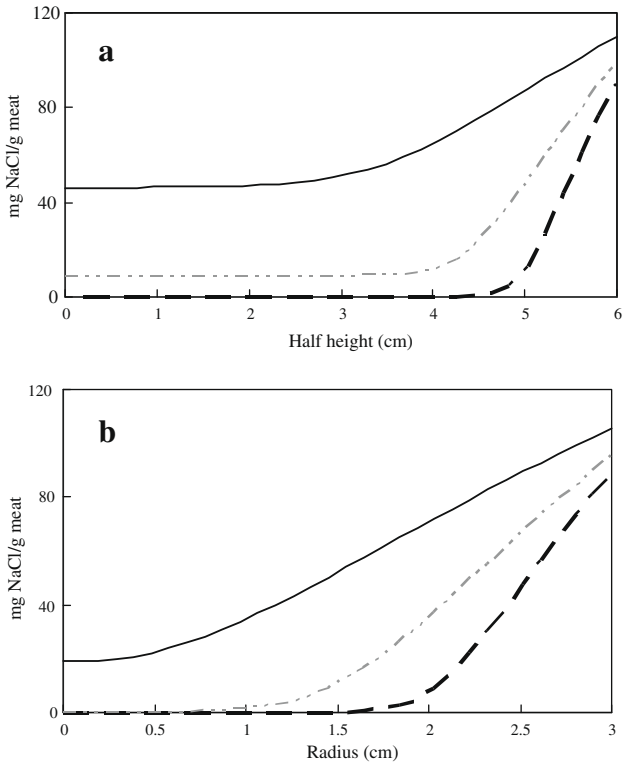

Fig. 7. Concentration profiles of NaCl in a pork meat cylinder ($D = 6$ cm, $H = 12$ cm) for different immersion times as a function of: (a) cylinder half height (fixed radial position: 1.45 cm) and (b) cylinder radius (fixed axial position: 2.90 cm). Immersion times: 8 (- - - -), 24 (- · - · -) and 72 h (——). Brine concentration: 140 g NaCl/L, 3 g $NaNO_2$/L, and 2.5 g KNO_3/L.

are accomplished during the drainage and drying steps, reaching an equalization of the concentration of curing ingredients through the meat with a simultaneous loss of water. All these processes have to be considered to comply with regulations (Varnam and Sutherland, 1995). To establish the average salt concentrations required after the immersion process, changes in water content from 75% to 50% due to the further maturation and drying process must be taken into account. The final product (water content 50%) must not exceed 0.2 mg/g of $NaNO_2$, KNO_3 or their mix expressed as $NaNO_2$ (Borchert and Cassens, 1998) and a desirable NaCl content would be about 40 mg/g which is the standard NaCl content in the commercial product available in Argentina. Therefore the following target values for the wet curing process may be considered: 0.1 mg/g of $NaNO_2$, KNO_3 or their mix expressed as $NaNO_2$ and 20 mg/g NaCl.

The numerical code was run considering different brine concentrations (NaCl ranging between 20 and 80 g/L, $NaNO_2$ between 0 and 0.20 g/L, and KNO_3 between 0.05 and 0.25 g/L) for a cylinder of 10 cm diameter and 26 cm height with immersion times between 1 min and 24 h. This information is necessary to obtain a final product with the organoleptic and microbiological required conditions that complies with the regulations.

From the results computed by the code, simple regression equations were obtained to represent the salt concentrations in the tissue: sodium chloride uptake (Eq. (17)) and the sum of nitrite and nitrate concentrations (expressed as sodium nitrite) (Eq. (18)).

As can be observed the following equations represent functions of immersion time and sodium chloride, nitrite, and nitrate concentrations in the brine.

$$x_{NaCl} = -1.61 + 2.64 \times 10^{-2} x_1 + 0.18 x_2 - 8.89 \times 10^{-5} x_1^2 - 7.00 \times 10^{-4} x_2^2 + 1.92 \times 10^{-3} x_1 x_2 \quad (r^2 = 0.993) \tag{17}$$

$$x_{NaNO_2} = 0.027 + 5.16 \times 10^{-4} x_1 + 0.20 x_3 - 0.14 x_4 - 1.15 \times 10^{-3} x_2 - 4.72 \times 10^{-7} x_1^2 + 1.86 \times 10^{-3} x_1 x_3 + 1.43 \times 10^{-3} x_1 x_4 + 5.40 \times 10^{-3} x_2 x_4 + 4.50 \times 10^{-6} x_2^2 \quad (r^2 = 0.991) \tag{18}$$

where x_{NaCl} is the average concentration of NaCl uptake in the tissue, x_{NaNO_2} is the average concentration of $NaNO_2$ uptake in the tissue, x_1 is the immersion time, x_2 is the NaCl concentration in the brine, x_3 is the $NaNO_2$ concentration in the brine, x_4 is the KNO_3 concentration in the brine.

Fixing in both equations the required conditions for the average concentrations in the wet tissue (0.1 mg/g of $NaNO_2$, KNO_3 or their mix expressed as $NaNO_2$ and 20 mg/g NaCl) the times to conform with the target values were determined for different salt concentrations in the brine. The obtained immersion times that accomplished the required conditions are shown as contour lines considering a fixed value of KNO_3 0.20 g/L in the curing solution (Fig. 8). The plot permits to determine adequate immersion times (contour lines) fixing NaCl and $NaNO_2$ concentrations in the brine. As expected, while NaCl or $NaNO_2$ increased in the brine, immersion times decreased.

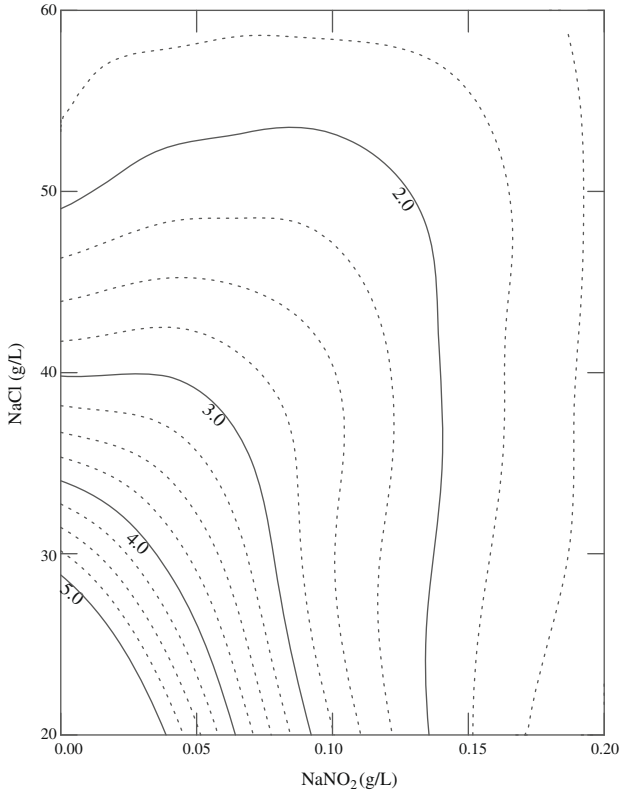

Fig. 8. Contour plot to determine immersion times expressed in hours necessary to reach 0.1 mg/g of $NaNO_2$, KNO_3 or their mix expressed as $NaNO_2$ and 20 mg/g NaCl in meat tissue. Concentrations of NaCl and $NaNO_2$ in the brine are given in the axes for a fixed value of 0.20 g KNO_3/L.

5. Conclusions

When the diffusion process of curing salts occurs in large pieces of meat, the NaCl concentration gradient affects progressively its microstructure and increases the diffusion of salts. In this work a mathematical model that represents a tridimensional complex non-linear problem was numerically solved and experimentally validated. This model incorporates salt diffusion coefficients that vary with the concentration of solute, and a convective contribution of the brine.

The model was applied to predict the time necessary for an industrial piece of meat must be immersed in a brine without exceeding the maximum permitted nitrite value and the recommendable sodium chloride concentration; therefore the model permits to determine the industrial operating conditions, such as salt concentrations in the brine and immersion times, in order to improve the curing process.

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