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Effect of a moderate electric field on the salting of Atlantic Salmon (*Salmo salar*): An experimental study and phenomenological understanding

H. Núñez[a,*], G. Cavada[a], C. Ramírez[a,b], J. Moreno[c], G. Cornejo[a], A. Jaques[a], M. Pinto[a], O. Vega[d], R. Simpson[a,b]

[a] *Departamento de Ingeniería Química y Ambiental, Universidad Técnica Federico Santa María, Avenida España 1680, Valparaíso, Chile*
[b] *Centro Regional de Estudios en Alimentos Saludables (CREAS), CONICYT-Regional GORE Valparaíso Proyecto R17A10001, Avenida Universidad 330, Placilla, Curauma, Valparaíso, Chile*
[c] *Departamento de Ingeniería en Alimentos, Universidad del Bío-Bío, P.O. Box 447, Chillán, Chile*
[d] *BIOALI Research Group, Department of Food, Faculty of Pharmaceutical Sciences and Food, Universidad de Antioquia, Medellín, Colombia*

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ABSTRACT

Salting is one of the oldest methods of preserving food. The main limitation of salting is its extended processing time due to slow salt diffusion. A moderate electric field (MEF) can improve the mass transfer rate through electroporation. Regularly, mass transfer processes are modeled with Fick's second law. However, due to the anisotropic nature of food microstructures, it might be more appropriate to use an anomalous model.

The main objective of this study was to search for a phenomenological explanation for salt and water diffusion in the salmon brining process coupled with MEF.

Salmon fillets were cut into finite cylinders (0.025 × 0.025 m) and brined in two salt concentrations (6 and 24% w/w NaCl) at 6 °C for 20 h. MEFs were applied in the range of 0 to 2 V/cm. The salt and water contents of the salmon were measured during the process. Fick's second law and anomalous model based on fractional calculus were used to describe the diffusion phenomena.

The results showed that an MEF tended to reduce the brining processing time and increase the salt content of salmon. This effect is predominantly due to an increase in the equilibrium salt concentration in the salmon tissue. Mathematical analysis shows that the anomalous diffusion model is more suitable for representing the brining process, exhibiting superdiffusion behavior ($\alpha > 1$).

An MEF accelerates the salt mass transfer into salmon tissue even at lower temperatures, significantly reducing the processing time. In addition, the diffusion process can be characterized with an anomalous model.

1. Introduction

Salting is a conventional and old process commonly used to incorporate salt into muscle tissue as a preliminary step in the smoking process to reduce water activity and to prevent microbial spoilage (Barat et al., 2003; Thorarinsdottir et al., 2004; Van Nguyen et al., 2010). Although salting controls food spoilage very effectively, one of its main drawbacks is that it is a very slow process that can take up to several days (Bampi et al., 2016).

Two main factors can affect the uptake and distribution of salt in fish muscle that has been exposed to brine: the salt concentration in the brine solution and the process temperature (Boudhrioua et al., 2009; Chiralt et al., 2001; Martínez et al., 2012; Sigurgisladottir et al., 2000; Van Nguyen et al., 2010). In general, the mass transfer involved in the salting process is rather slow, and it may take many hours to attain the required concentration and a homogeneous distribution of NaCl throughout the muscle tissue (McDonnell et al., 2014; Rinella, 2014). The slow diffusion rate is affected by microstructural elements, such as the presence of cell membranes and extracellular pathways that hinder the movement of salt into the cell (Janositz et al., 2011). Thus, treatments that modify the cell structure tend to favor mass transfer. Such treatments include the application of a pulsed electric field (McDonnell et al., 2014; Janositz et al., 2011), ohmic heating (i.e., a moderate electric field) (Hong et al., 2012; Moreno et al., 2011; Sensoy & Sastry 2004; Kusnadi & Sastry 2012; Simpson et al., 2007, Yildiz et al., 2016), and ultrasound treatment (Siró et al., 2009), in which electroporation or cavitation induces cell membrane damage, allowing and facilitating salt diffusion. Additionally, vacuum impregnation (Bampi et al., 2016;

* Corresponding author.
E-mail address: helena.nunez@usm.cl (H. Núñez).

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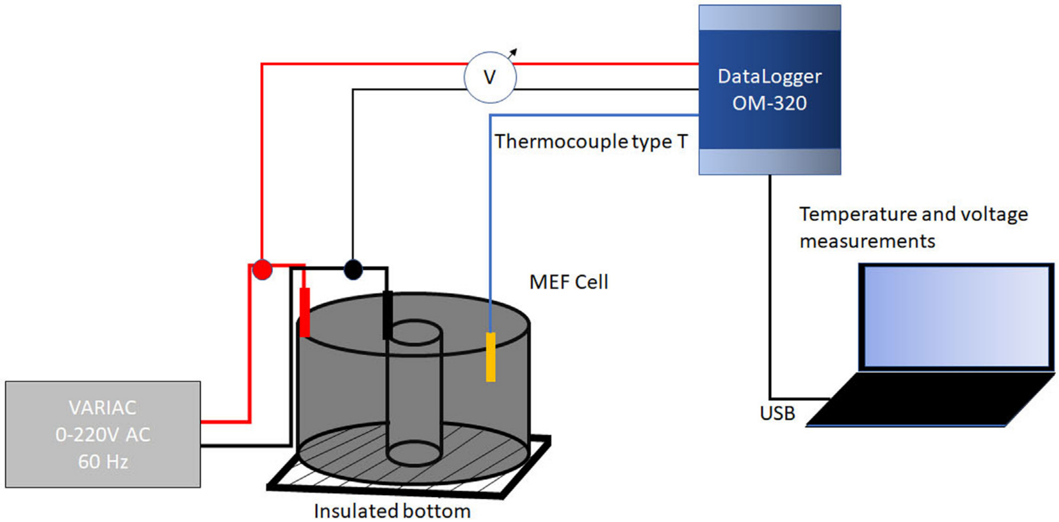

Fig. 1. Experimental setup of the salting process.

Chiralt et al., 2001; Martins et al., 2019) favors mass transfer through the replacement of the air occluded in the matrix with osmotic solution by means of pressure gradients and capillary effects (Deumier, 2004).

It has been shown that the use of moderate electric fields (MEFs, also called ohmic heating) in the osmotic dehydration of vegetable tissues accelerates mass transfer and thus significantly reduces the processing time (Allali et al., 2009; Lima et al., 2001; Moreno et al., 2012; Simpson et al., 2007; Simpson et al., 2015). However, the only report examining the application of this process to fish tissue is a study (Simpson et al., 2018) reporting the use of an MEF during the salting of Atlantic salmon (*Salmo salar*). It was concluded that the application of MEF produces a significant increase in the equilibrium salt concentration attained in the salmon muscle during salting. The salt concentration in these salmon tissue samples was higher than that in samples processed with the traditional salting process alone. However, the water holding capacity was not significantly affected by the MEF.

In addition, due to the complex nature of salmon tissue (Birkeland et al., 2004; Kong et al., 2007, Løje et al., 2007), the difficulties in diffusion make accurate predictions challenging because several of the assumptions of Fick's second law are not fulfilled in the heterogeneous muscle and connective tissue of salmon (Cranck, 1975). In addition, structural changes occur during the salting process coupled with an MEF. These effects are not truly considered by the traditional diffusion formulation through Fick's second law. Salmon tissue has a heterogeneous structure in which diffusion occurs across different paths (muscle fibers, fat globules and connective tissue). Under these condition, diffusion phenomena violate Fick's second law of diffusion. Anomalous, or non-Fickian, diffusion has been used successfully as mathematical model to treat complex food microstructures (de Souza et al., 2019; Flores et al., 2007; Franco et al., 2019; Simpson et al., 2015, Ramírez et al., 2017). In addition, although the mathematical resolution of this anomalous model is complex, several studies, mainly using infinite geometries, have been successfully implemented through efficient computer routines, including the use of fractional calculus (Del Nobile et al., 2003; Ghehsareh et al., 2019; Liang et al., 2018; Luchko, 2010; Simpson et al., 2013, Simpson et al., 2015; Wagner et al., 2017). An anomalous diffusion model based on the fractional calculus approach has been developed for infinite geometries and fitted using only one term of the sum (assuming a long time). However, this approach has not been developed for finite geometries or applied to the whole process.

Therefore, the objective of this study was to explore a phenomenological explanation based on a fractional calculus tool of the salt and water transfer process in a finite cylinder of salmon through an experimental study of the brining process coupled with the application of a moderate electric field (MEF).

2. Materials and methods

2.1. Sample preparation

Fillets of Atlantic salmon (*Salmo salar*) were purchased from a local market and transported in an insulated box to the laboratory under refrigeration (2 °C). Three fillets were used for each experiment. The fillets were cut into finite cylinders of 0.025 ± 0.001 m in diameter and 0.025 ± 0.001 m in height (0.0238 ± 0.0016 kg). Each sample was weighed, tagged and immediately processed.

2.2. Brining and sampling

The samples were randomly collected and salted by immersion in one of two different concentrations of brine (6 or 24% NaCl, w/w). The salting treatments were either conventional brine salting (BS) or brine salting coupled with the application of a moderate electric field (BS-MEF) at 6 ± 2 °C for 20 h. The temperature in the water bath was controlled with a thermostat. The ratio of brine to fish was 11:1 w/w to avoid dilution of the salt solution (Simpson et al 2018).

For both processes (BS and BS-MEF), the samples were immersed in an MEF cell formed by two concentric cylindrical stainless-steel covers with graphite to avoid corrosion of 0.037 and 0.19 m in diameter, fixed by means of a nonconducting plastic bottom with a distance (d) of 0.0765 m between the electrodes. The samples were kept submerged using a plastic grid that prevented them from floating during the experiments. For the BS-MEF case, the salting solution was subjected to an alternating current; the electrodes were connected by means of copper bridges to a 60 Hz voltage variator (Variac Slideup, Model SB-10, USA) and a 220 V alternating current (AC) input. Furthermore, voltage and current transducers were used to measure the voltage and current through the samples (Fig. 1). The temperature and voltage were measured with a thermocouple type T connected to a data acquisition system (OM-320 data logger, Omega Engineering, Stamford, CT, USA). The voltages used in this research were determined in preliminary tests and based on the capacity of MEF equipment. Then, in the case of brine at 6% w/w, electric field strengths (E) of 1 and 2 V/cm were applied, while in the case of 24%, the maximum electric field strengths were 0.8 and 1.2 V/cm, respectively. The electrical conductivity was measured with an electrical conductivity meter (Hanna model Hi 2003–02, Woonsocket, USA), and values of 8.89 and 45.14 S/m were obtained for concentrations of 6% and 24%, respectively. During salmon salting, samples (n = 3) were analyzed after drainage for 2–3 min on a grid at different sampling times (0, 0.5, 1, 2, 4, 8, 12, and 20 h). At each sampling time, three cylinders of salmon were randomly chosen, and their salt concentration and water content were separately determined.

2.3. Analysis of the sample composition

The moisture content (X_t^W) was determined by drying the samples (n = 3) to a constant weight at 105 °C according to the method defined by the Association of Official Analytical Chemists (AOAC, 1996). During brine salting, the salt concentration of each sample was measured in triplicate using a DiCromat II Salt Analyzer (PCL Control Instrument, Leicester, UK).

Changes in the salt and water contents (ΔM_t^W and ΔM_t^{NaCl}, respectively) were calculated using the following equations:

$$\Delta M_t^W = \frac{M_t^0 x_t^W - M_0^0 x_0^W}{M_0^0} \tag{1}$$

$$\Delta M_t^{NaCl} = \frac{M_t^0 x_t^{NaCl} - M_0^0 x_0^{NaCl}}{M_0^0} \tag{2}$$

where M_0^0 and M_t^0 represent the sample weight at times 0 and t, respectively; and x_0^w, x_t^w, x_0^{NaCl}, and x_t^{NaCl} are the water (W) and salt (NaCl) mass fractions in a given sample at times 0 and t, respectively.

2.4. Fick's second law (D_e)

Salmon tissue can be considered to have a heterogeneous structure in which the salt and water diffusion process varies according to the structure through which the solute passes: connective tissue, fat globules or muscle fibers (Sigurgisladottir et al., 2001). Therefore, the diffusion process can be represented by an effective diffusion coefficient (D_e) that describes the salting process as a diffusive process, where D_e is an observed average value for the diffusion process in the tissue. The geometry for the salmon sample used here is a finite cylinder. The average concentration progress of the sample can be modeled by combining the infinite cylinder and the infinite slab analytical solutions of Fick's second law. Then, the mathematical description of the diffusion process in a finite cylinder is given by Eq. (3):

$$\frac{\partial C}{\partial t} = D_e \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + D_e\left(\frac{\partial^2 C}{\partial z^2}\right) \tag{3}$$

where C is the solute concentration in salmon; r and z are the radial and axial directions (m), respectively; D_e is the effective diffusion coefficient (m^2/s) in the tissue; and t is time (s). The solution of Eq. (3) depends on the initial conditions,

$$C(r, z, 0) = C_0 \tag{4}$$

and boundary conditions,

$$C(r = R, z, t) = C(r, z = \pm L/2, 0, t) = C_e, t > 0 \tag{5}$$

where C_0 is the initial concentration and C_e is the equilibrium salt concentration (considered to be the surface condition). The previous expressions (Eqs. (3), (4) and (5)) represent the solute concentration distribution in the tissue, which must be averaged to obtain the observed mass and concentration changes.

The dimensionless average concentration for a finite cylinder is given by the integration of Eq. (3) (Cranck, 1975)

$$C^* = \frac{8}{\pi}\left[\sum_{n=0}^{50}\frac{1}{2n+1}\exp\left(-D_e\left(\frac{(2n+1)\pi}{L}\right)^2 t\right)\right]\left[\sum_{n=1}^{50}\frac{4}{\varepsilon_n^2}exp\left(\frac{\varepsilon_n^2 D_e t}{R^2}\right)\right] \tag{6}$$

where L is the half-thickness (m); ε_n is the nth root of the equation J0(ε) = 0, R is the cylinder radius (m) and n is the number of terms used for summation (for this study case, the number of terms corresponds to 50).

2.5. Anomalous diffusion model

In the case of anomalous diffusion, a particular generalization of the Fickian law of diffusion is used (Simpson et al. 2015) that is mathematically expressed through Eq. (7):

$$\frac{\partial^\alpha C}{\partial t^\alpha} = D_e^* \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + D_e^*\left(\frac{\partial^2 C}{\partial z^2}\right) \tag{7}$$

The temporal fractional calculus approach is followed, in which the value of α is associated with the anomalous order. The value of α indicates the transport mechanism that dominates the mass transfer process.When, if 0 < α < 1, the diffusion mechanisms can be assumed to be subdiffusive. In contrast, if α > 1, the mechanisms can be considered superdiffusive. If α converges to unity, the anomalous diffusion model converges to Fick's second law. D_e^* is the fractional diffusion coefficient (m/s^α), where the same boundary conditions (Eqs. (4) and (5)) for Fickian diffusion are applied.

For anomalous diffusion, another expression for the dimensionless average concentration is obtained using the fractional calculus approach (Simpson et al., 2015). In particular, the Mittag-Leffler function (Eq. (8)) is incorporated to adequately represent the fractional order.

$$E_\alpha(z) = \sum_{k=0}^{\infty}\frac{z^k}{\Gamma(\alpha k+1)} \tag{8}$$

Then, the solution of the differential equation is similar to that of Eq. (6). As shown in Agrawal 2006, the exponential terms are replaced by the Mittag-Leffler function.

$$C_f^* = \frac{8}{\pi}\left[\sum_{n=0}^{\infty}\frac{1}{2n+1}E_{\alpha,1}\left(-D_e^* t^\alpha\left(\frac{(2n+1)\pi}{L}\right)^2\right)\right]\left[\sum_{n=1}^{\infty}\frac{4}{\varepsilon_n^2 R^2}E_{\alpha,1}\left(-\frac{\varepsilon_n^2 D_e^* t^\alpha}{R^2}\right)\right] \tag{9}$$

Finally, to inversely solve Eq. (9), it is necessary to fit a nonlinear regression model while simultaneously adjusting the effective diffusion coefficient (D_e^*) and parameter α (detailed in section 2.5).

2.6. Optimization and statistical analysis

The D_e values are obtained from nonlinear regression analysis of experimental data by minimizing the least squares sum using MATLAB R2019a software, version 9.6 (The MathWorks, Inc., Natick, MA, USA), in which the following objective function was minimized:

$$F_{objective}(D_e) = \sum_{i=1}^{n}(C^*(t)_{calculated} - C^*(t)_{experiment})^2 \tag{10}$$

For anomalous diffusion (Eq. (9)), the same formula (Eq. (10)) is used. However, in this case, two parameters ($D_e^*$and α) are obtained from the fitted data.

$$F_{objective}(D_e^*, \alpha) = \sum_{i=1}^{n}(C_f^*(t)_{calculated} - C_f^*(t)_{experiment})^2 \tag{11}$$

The adjusted coefficients of determination (R^2)for both are calculated to account for the difference in the number of parameters

$$R^2 = 1 - (n-1)/(n-p)\cdot F_{objetive}$$

where p is the number of parameters and n is the sample size of the respective adjustment. Comparing the adjusted coefficient of determination allows us to account for overfitting. In this way, it is possible to compare the models with different numbers of parameters.

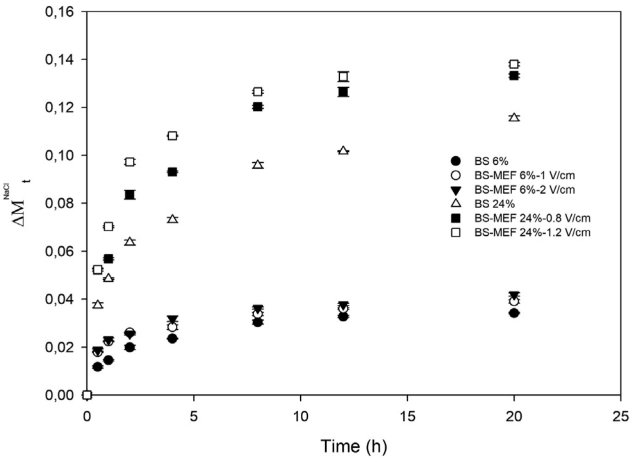

Fig. 2. Salt weight changes as functions of time and the brine concentration (• BS 6%, ° BS-MEF 6%-1 V/cm, ▼ BS-MEF 6%-2 V/cm, Δ BS 24%, ■ BS-MEF 24%-0.8 V/cm, □ BS-MEF 24%-1.2 V/cm).

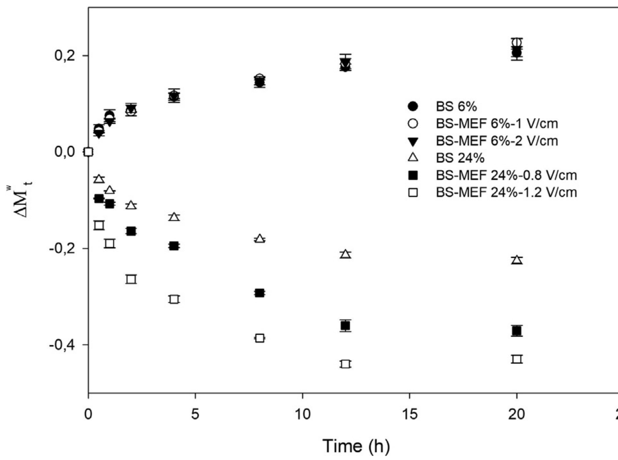

Fig. 3. Water weight changes as functions of time and the brine concentration (• BS 6%, ° BS-MEF 6%-1 V/cm, ▼ BS-MEF 6%-2 V/cm, Δ BS 24%, ■ BS-MEF 24%-0.8 V/cm, □ BS-MEF 24%-1.2 V/cm).

3. Results and discussion

3.1. Changes in composition

As depicted in Fig. 2, the mass of salt in the samples (ΔM_t^{NaCl}) in the samples increased as the brine concentration increased. Simpson et al. (2018) and Gallart-Jornet et al. (2007) obtained comparable results in their study, where the salt concentration increased as the brine concentration increased. Table 1 shows that treatments with an MEF resulted in products with higher salt concentrations. As an example, for a sample brined at 6%, the salt weight significantly increased from 3.5% for the control to approximately 4.3% when a field strength of 2 V/cm was applied ($p < 0.05$). The use of a higher electric field (2 V/cm) significantly affected the NaCl concentration in the samples from 4 h of brining, resulting in NaCl values ($p < 0.05$) higher than those produced by the 1 V/cm treatment. This tendency was observed until the end of the process. When brining was performed at 24%, the salt weight at the end of the process (20 h) increased significantly ($p < 0.05$) from 11.55% for the control to 13.8% when an electric field of 1.2 V/cm was applied. As reported in the literature, low electric fields, such as those used in this research, generate reversible electroporation effects on the cell membranes, facilitating the entrance of salt into the cell, which halts once the MEF is turned off, entrapping the salt inside the cells (Hong et al., 2012). Similar effects have been reported in salmon and pork by Simpson et al., 2018 and Hong et al., 2012, respectively. These results can be explained by the higher salt concentration favor protein denaturation affecting cell membrane permeability increasing the effect of electroporation. In addition, the same kind of effects have been reported in vegetables (potato and celery) (Kulshrestha and Sastry, 2006, Kusnadi and Sastry, 2012).

Fig. 3 shows changes in the mass of water (ΔM_t^{w}) in the salmon samples brined at 6% and 24%. In the case of salmon brined at 6%, the results showed a maximum increase of 23% with respect to the control. However, there were no significant differences between the electric fields applied. For samples brined at 24%, a dewatering effect along the brining process was observed. This effect was also reported by Nguyen et al. (2010). However, unlike those attained with brining at 6%, the changes in the mass of water attained with brining at 24% were significantly affected by the electric field applied. When electric fields of 0.8 or 1.2 V/cm were applied, dewatering increased significantly. A possible explanation for this result is that in the case of 6%, reversible electroporation allows salt to enter the cell, saturating the interior of the cell. In this way, water enters to reach an osmotic balance, allowing weight gain. However, for 24%, although reversible electroporation occurs, the high concentration of salt rapidly saturates the extracellular spaces, favoring dewatering from the cell, which supported by the formation of pores. Thus, electroporation coupled with a high salt concentration favored the movement of water from the cell into the medium.

3.2. Phenomenological analysis: Fick's second law and anomalous diffusion model

The results were analyzed by comparing both the Fickian and anomalous diffusion models. An important difference between these approaches for diffusion (Sokolov et al., 2002) is that the "tail" (the end part of the diffusion process) decays as either an exponential function (in the Fickian model) or as a power law function (in the anomalous model). This difference is depicted in Fig. 9, which compares both curves in a semilog plot. The Fickian plot converges to a straight line, whereas the anomalous plot converges asymptotically to 0, and the experimental data converge to the latter. The tail of the diffusion

Table 1
Mean values and standard deviations of mass of salt in the samples (ΔM_t^{NaCl}) at different salting treatment.

Concentration (%)	Time (h)						
	0.5	1	2	4	8	12	20
6-BS	0.0118 ± 0.0005 [a]	0.0146 ± 0.0004 [a]	0.0199 ± 0.0008[a]	0.0236 ± 0.0002[a]	0.0304 ± 0.0009 [a]	0.0328 ± 0.0004 [a]	0.0342 ± 0.0003 [a]
6-MEF 1 V/cm	0.0179 ± 0.0009[b]	0.0224 ± 0.0002[b]	0.0261 ± 0.0005[b]	0.0283 ± 0.0009[b]	0.0339 ± 0.0006[b]	0.0361 ± 0.0003[b]	0.0391 ± 0.0007[b]
6-MEF 2 V/Cm	0.0188 ± 0.0005[b]	0.0232 ± 0.0006[b]	0.0256 ± 0.0005[b]	0.0319 ± 0.0001[c]	0.0363 ± 0.0004[c]	0.0378 ± 0.0005[c]	0.0420 ± 0.0007[c]
24-BS	0.0374 ± 0.0009[c]	0.0486 ± 0.0004[c]	0.0636 ± 0.0001[c]	0.0731 ± 0.001[d]	0.0958 ± 0.001 [d]	0.1017 ± 0.0002 [d]	0.1155 ± 0.0001 [d]
24-MEF 0.8 V/cm	0.0522 ± 0.0004 [d]	0.0568 ± 0.0004 [d]	0.0836 ± 0.001[d]	0.0931 ± 0.0004[e]	0.1203 ± 0.0006 [e]	0.1264 ± 0.002 [e]	0.1333 ± 0.0008 [e]
24-MEF 1.2 V/cm	0.0523 ± 0.0006 [d]	0.0703 ± 0.0004 [e]	0.0973 ± 0.001[e]	0.1081 ± 0.0003[f]	0.1265 ± 0.0007[f]	0.1328 ± 0.002[f]	0.1380 ± 0.0008[f]

Different lowercase letters indicate significant differences ($p < 0.05$) in the same row converges to an exponential tail, which confirms the anomalous nature of the diffusion phenomena.

The anomalous diffusion parameters and fractional order vary with the applied electric field. The change in these values can be associated with the substrate structure, whereas the electric field increases electroporation and changes the nature of diffusion. The fractional order values, which vary between 0.737 and 0.987, are associated with the diffusion path of the salt in the tissue and the role of the cell membrane in the diffusion process (Simpson et al., 2015).

Traditionally, the mean squared displacement is taken as proportional to time, $\langle x^2 \rangle\ t$, in a diffusion process, which is what the Fick's law of diffusion describes. However, in complex systems, as in biological materials, this is not the case, and the dependence of the mean square displacement is proportional to a power law with time, $\langle x^2 \rangle\ t^{\alpha}$. Here, $\alpha < 1$ corresponds to subdiffusion, $\alpha > 1$corresponds to superdiffusion, and $\alpha = 1$ is Fickian diffusion. The subdiffusion/superdiffusion nature does not indicate the speed of the process. Rather, this nature associated with the stochastic processes on a micro scale, where subdiffusion suggests a more dispersive pattern of diffusion and superdiffusion a more channeled pattern of diffusion (Klafter and Sokolov, 2005).

The results of the regression for the Fickian and anomalous diffusion models, are shown in Table 2**.** In both cases, fitting was satisfactory, with R^2 values varying between 0.9233 and 0.9967 in the case of Fick's second law model and R^2 between 0.9902 and 0.9962 in the case of the anomalous diffusion model. These results show the clear superiority of the anomalous diffusion model.

With respect to the values of the effective diffusion coefficients obtained for the Fickian (De) and anomalous models (De*), in general, the results showed that De and De* were dependent on the voltage applied and the salt content.

For instance, for the samples brined at 6 and 24% without MEF, when De was determined by the Fick's second law model, the results showed that the De values obtained for both concentrations were not significantly different. When MEF was applied, the results showed a significant increase in the De values beyond the brining concentration and electric field applied. For example, at 6%, the results for MEFs of 1 V/cm and 2 V/cm were not significantly different, with values close to 7 $x10^{-10}$ m/s^2. However, at 24%, a significant increase was observed only when 1.2 V/cm was applied, attaining a De of 8.02×10^{-10} m/s^2.

When the concentration data were analyzed with the anomalous model, the results showed that for non-MEF samples, the De* attained at 6% (6.11×10^{-10} $m/s^{0.987}$) was significantly lower than that attained at 24% (9.70×10^{-10} $m/s^{0.918}$). However, when the MEF was applied, the De* values calculated for 6% were significantly higher than those calculated for 24%. The results presented in Table 2 depict a fractional order of < 1 ($\alpha < 1$, subdiffusive) for diffusion for the whole range of analyzed conditions with a range of α values of 0.737 for 6-MEF 1 V/cm to 0.9873 for 6-BS.

In the case of the lowest salt concentrations and without an MEF, the diffusion phenomenon tended to be Fickian with $\alpha = 0.987$. However, as the MEF increased, the results tended to be more subdiffusive, with α equaling approximately 0.74, which represents a

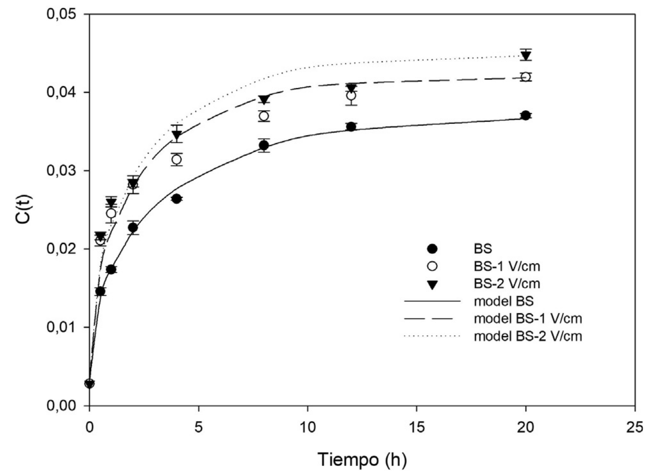

Fig. 4. Experimental data and Fick's model for brine salting at 6% with or without application of an MEF (• BS, ° BS-1 V/cm, ▾ BS-2 V/cm, —— model BS, - - - model BS-1 V/cm, and ········ model BS-2 V/cm).

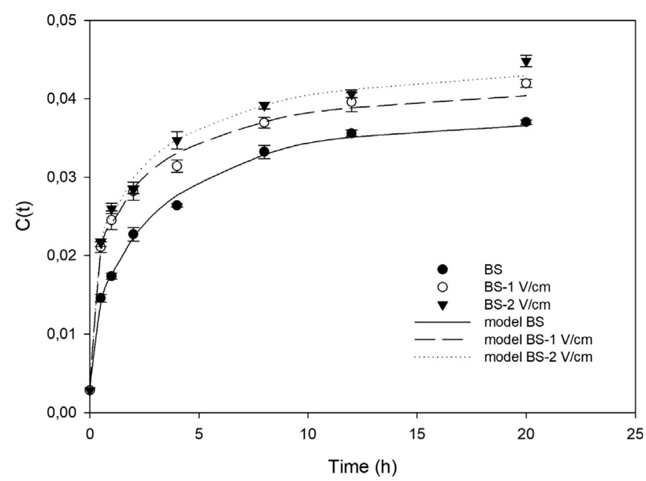

Fig. 5. Experimental data and anomalous model for brine salting at 6% with or without application of an MEF (• BS, ° BS-1 V/cm, ▾ BS-2 V/cm, —— model BS, - - - model BS-1 V/cm, and ········ model BS-2 V/cm).

deviation from Fick's second law. For the case of 24%, the results showed that the control presented an α value of 0.918, and when the electric field was applied, the α values were not significantly different. Clearly, the α value represents a structural change but also includes the environmental conditions. This finding could be explained by the high salt concentration, which causes protein denaturation, and loss of cell structuring. Then diffusant movement through meat tissue is less tortuous, which would lead to Fickian behavior.

To compare the Fickian and anomalous cases, it is convenient to define a penetration thickness (Eq. (12)); in this way, we consider the

Table 2
Effective diffusion coefficient for brine salting (BS) and brine salting coupled with a moderate electric field (BS-MEF) at 6 °C for 20 h.

Concentration (%)	C_e	Fickian			Anomalous			
		D_e (m^2/s) ($\times 10^{10}$)	SSE	R^2	D_e* (m^2/s^{α}) ($\times 10^{10}$)	α	SSE	R^2
6-BS	0.0370 ± 0.0003 ^{a}	5.43 ± 0.52 $^{a,\ b,\ d}$	0.0027	0.9967	6.11 ± 0.62 ^{a}	0.987 ± 0.011 ^{a}	0.0027	0.9962
6-MEF 1 V/cm	0.0419 ± 0.0005^{b}	7.82 ± 2.46 $^{a,\ c}$	0.0245	0.9963	84.8 ± 10.7^{b}	0.737 ± 0.014^{b}	0.0047	0.9925
6-MEF 2 V/Cm	0.0448 ± 0.0007^{c}	7.35 ± 2.26 $^{a,\ c}$	0.0238	0.9669	78.3 ± 9.31^{b}	0.740 ± 0.013^{b}	0.0042	0.9932
24-BS	0.1183 ± 0.001 ^{d}	4.38 ± 0.67$^{b,\ d}$	0.0065	0.9914	9.70 ± 1.19^{c}	0.918 ± 0.013^{c}	0.0045	0.9932
24-MEF 0.8 V/cm	0.1361 ± 0.0023 ^{e}	6.04 ± 1.07 $^{a,\ b,\ c}$	0.0082	0.9900	11.8 ± 1.87^{c}	0.928 ± 0.016^{c}	0.0068	0.9902
24-MEF 1.2 V/cm	0.1408 ± 0.0008^{f}	8.02 ± 1.12^{c}	0.0048	0.9943	16.3 ± 1.89 ^{d}	0.921 ± 0.013^{c}	0.0034	0.9952

Different lowercase letters indicate significant differences ($p < 0.05$) in the same row.

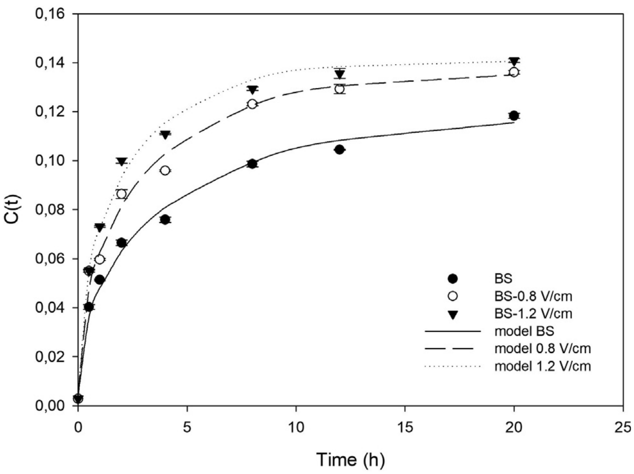

Fig. 6. Experimental data and Fick's model for brine salting at 24% either with or without the application of an MEF (• BS, ° BS-0.8 V/cm, ▾ BS-1.2 V/cm, —— model BS, - - - model 0.8 V/cm, ········ model 1.2 V/cm).

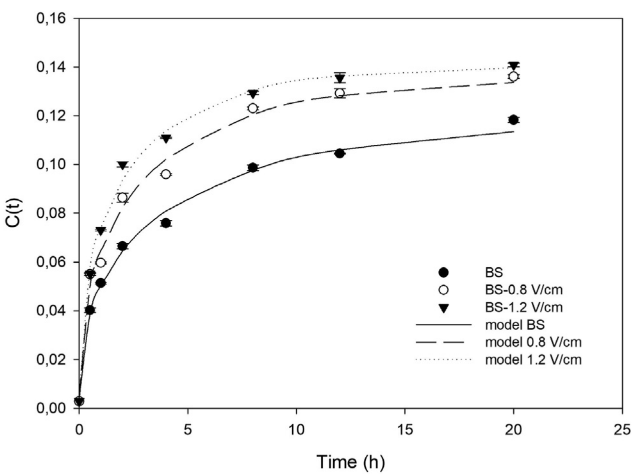

Fig. 7. Experimental data and anomalous model for brine salting at 24% either with or without the application of an MEF (• BS, ° BS-0.8 V/cm, ▾ BS-1.2 V/cm, —— model BS, - - - model 0.8 V/cm, ········ model 1.2 V/cm).

fractional order and the influence of the mass transfer rate of the salt. For example, for an experiment time of 10 h, the diffusion thickness values obtained for the 6% treatments were 0.0044 (1 V/cm) and 0.0043 (2 V/cm), and for the 24% concentration, these values were 0.0047 (0.8 V/cm) and 0.0051 (1.2 V/cm), coinciding with the order of the effective diffusion observed in the experiment, which increased with the concentration of salt and with the electric field.

$$\delta = \sqrt{D_e * t^{\alpha}} \tag{12}$$

With respect to the equilibrium concentration of NaCl (Ce), the results showed that at 6%, the Ce was dependent on the electric field applied, increasing from 0.037 for 0 V/cm to 0.0448 when 2 V/cm was applied. In the case of 24%, Ce also increased as the electric field increased, from 0.118 at 0 V/cm to 0.1361 at 0.8 V/cm and 0.1408 at 1.2 V/cm.

The results obtained for both Ce and De show the effect of the MEF on the diffusion path and how salt migrates into and remains within the cells.

However, a strong difference was observed when the fits of the tails (end portions of the curves) of the diffusion process were compared (Fig. 9). This difference is noticeable when a logarithmic scale is used (Fig. 9). A Fickian diffusion approach is unable to satisfactorily represent the process, as the concentration tends towards the equilibrium salt concentration, which has been reported as a limitation of Fickian diffusion (Simpson et al., 2015). The anomalous diffusion approach successfully represents the findings since it can be adjusted to accommodate the whole process, including the "heavy-tailed" kinetics. These findings mean that cases in which the kinetic decay is slow cannot be represented by the exponential kinetics of the Fickian model.

This can be explained by the electroporation effect. This produces a more open structure, which eases the diffusant movement across the salmon muscle tissue. The diffusion coefficient, D_e^*, and fractional order α are characteristics of the specific material (i.e., food material microstructure) and diffusant. Eq. (7) should be evaluated considering the initial salt concentration in the salmon (C_O) and the equilibrium salt concentration (C_e). The initial concentration is not expected to vary, whereas the equilibrium salt concentration depends on the temperature and applied voltage. The experimental data show that the process is completed during the test run and that each sample has the expected equilibrium value. A comparison of the data for both salt concentrations indicates that, for the same salt solution, the equilibrium salt concentration marginally depends on the applied voltage (Figs. 4-7). The different curves correspond to the different MEFs applied. It can be observed (Figs. 4-7) that the fractional approach represents the process better than the Fickian approach, especially in the region with a more pronounced curvature. For further analysis, the normalized concentration is used (Fig. 9). This allows us to consider only the kinetic effect (diffusion) and not the equilibrium concentration. When comparing the salting rate equilibrium salt concentration of each brine solution in the presence or absence of an applied voltage, it is apparent that the voltage has a strong effect on the brining process (Fig. 8),

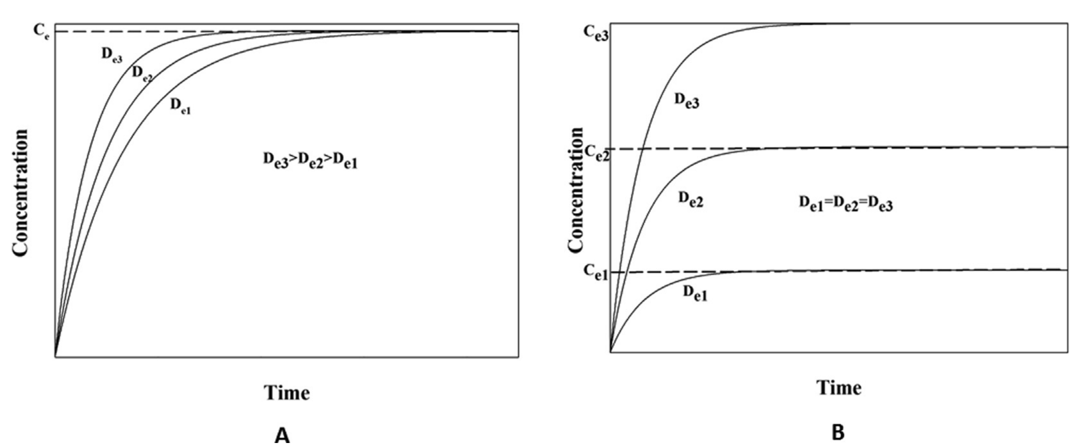

Fig. 8. Influence of the model parameters (C_e and D_e) on the salting process. A: Influence of an increased equilibrium concentration and B: influence of an increased diffusion coefficient.

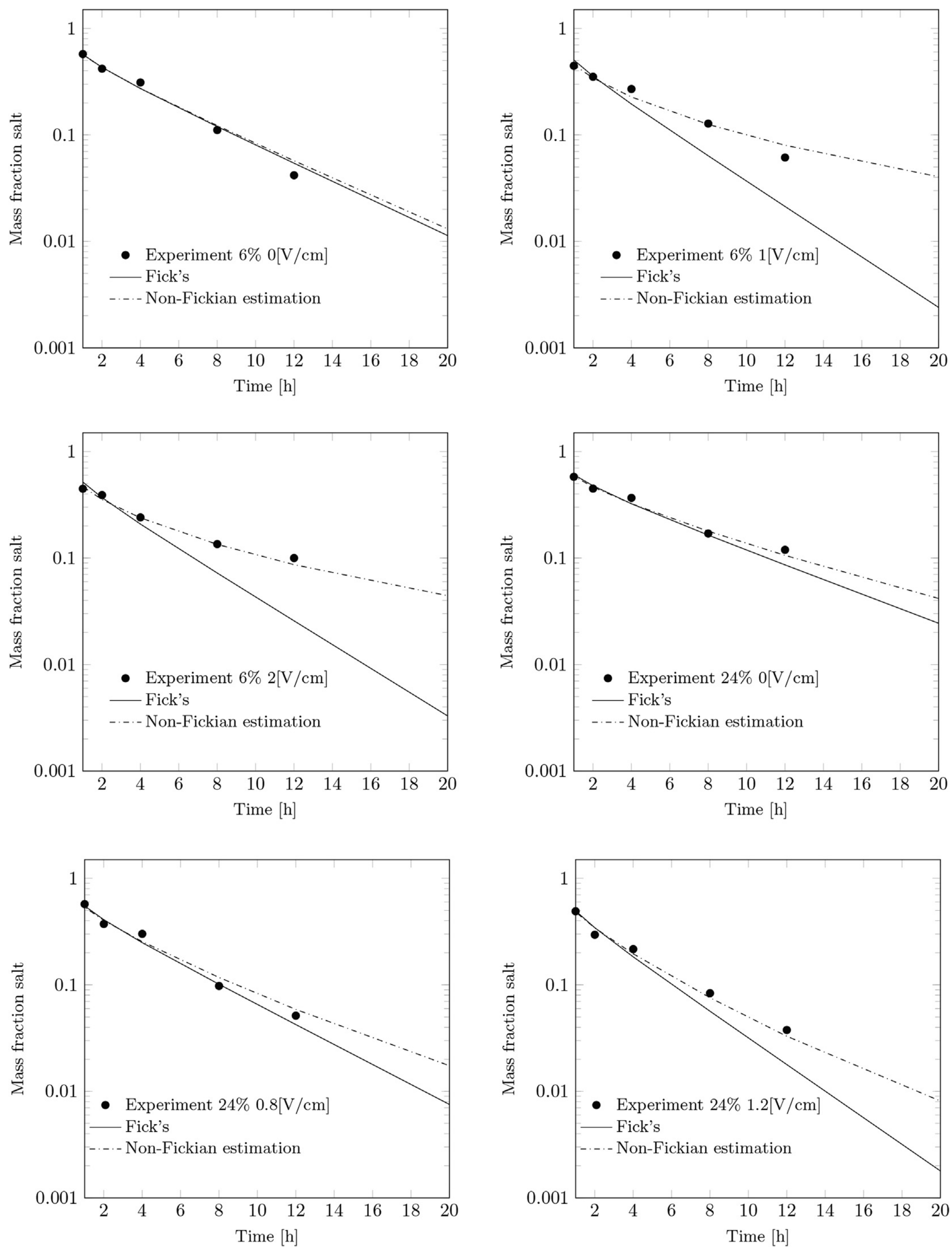

Fig. 9. Salt content vs time for the different configurations analyzed. The semilog plot allows us to compare the fitting using the Fickian approach and the fractional approach for diffusion.

which may be due to a physical effect of the electric field applied to the salmon tissue during electroporation. Electroporation allows the salmon tissue to "hold" additional solute, thus increasing the salt loading and homogeneity of the sample.

The Fickian diffusion model does not represent this phenomenon, and thus, a different approach to a phenomenological explanation is justified. The results presented in Fig. 9 justify the use of an anomalous diffusion model solved using a fractional calculus approach for the diffusion process in salmon salting.

4. Conclusions

Application of an electric field during the brining process leads to increased salting of salmon. This effect is predominantly due to an increase in the equilibrium salt concentration in salmon tissue. This increase is also affected by the concentration of the salt solution used. The use of an electric field allows for a higher salt concentration to be achieved with shorter processing time at a given temperature.

The diffusion process is shown to be anomalous (non-Fickian). The anomalous diffusion model adequately represents the salt intake during the experiment. The fractional order of the anomalous diffusion varies with the strength of the electric field and with the salt concentration.

These results can be used to determine the optimum process conditions.

CRediT authorship contribution statement

H. Núñez: Conceptualization, Methodology, Software, Writing - original draft, Writing - review & editing, Formal analysis. **G. Cavada:** Investigation, Validation. **C. Ramírez:** Writing - original draft, Writing - review & editing, Visualization, Formal analysis. **J. Moreno:** Formal analysis. **G. Cornejo:** Software, Formal analysis. **A. Jaques:** Methodology, Software, Formal analysis. **M. Pinto:** Resources, Supervision. **O. Vega:** Visualization. **R. Simpson:** Methodology, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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