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OSMOTIC DEHYDRATION OF MACKEREL (*SCOMBER JAPONICUS*) FILLETS BY MEANS OF BINARY AND TERNARY SOLUTIONS

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ABSTRACT

Osmotic dehydration of mackerel fillets was achieved by immersing them in binary and ternary solutions (NaCl/water or NaCl/sucrose/water). The kinetics of water loss and NaCl and sucrose gains were studied, as well as the accuracy of empirical models to explain these experimental behaviours. The results show how the presence of both solutes can enhance water loss and also interfere in each other's diffusion. Among the three empirical models analyzed, Peleg's equation proves to be the most suitable (R^2>0.836) to describe all the mass transfer process. A modified Peleg's model was also obtained with a high performance to describe the relationship between water content of mackerel fillets and sucrose and NaCl concentration in binary and ternary solutions.

Keywords: Osmotic dehydration, mackerel, sucrose, NaCl, empirical models.

INTRODUCTION

Osmotic dehydration (OD) is a valuable process that enables the partial loss of water by direct contact of a product with a hypertonic medium (Yao and Le Maguer, 1996). It implies two simultaneous crossed flows: a water outflow, from the food to the solution and a solute inflow from the solution into the food (Raoult-Wack et al; 1994; Collignan *et al.*, 2001). In particular, in fish species, the OD process produces a noticeable decrease of the water activity, a_w, and in consequence microbial growth is reduced or inhibited (Rastogi *et al.*, 2005) while the rates of other deteriorative processes in the fish tissues are changed, reaching a minimum at different levels of a_w (Collignan *et al.*, 2001). There has also been increasing interest in treatments of fish items in higher concentration solutions (60 to 70g solute $100g^{-1}$ solution) so as to obtain significant water removal with controlled solute incorporation (Collignan and Raoult-Wack, 1994). Then, this OD stage is often followed by a complementary air-drying (Sobukola and Olatunde, 2011) and/or smoking treatment (Deumier *et al.*, 2002). Sodium chloride (NaCl) is used as one of the principal components in the OD process as a dehydrating agent, on its own or in combination with other solutes (salts, sugars, acids, alcohols among others). Among these combinations, the mixture of NaCl and sucrose in a ternary solution has been reported as an advantageous method for food dehydration, leading to higher water loss without excessively over-sweetening or over-salting the product (Collignan and Raoult-Wack, 1994; Bohuon *et al.*, 1998; Medina-Vivanco *et al.*, 2002; Agustinelli *et al.*, 2014).

The modeling of the mass transfer process will be a helpful tool to design an OD process for commercial applications. In many cases, the OD process has been modeled assuming Fick's second law; this analytical approach considers regular geometries, neglecting changes in volume or in thickness (Medina-Vivanco *et al.*, 2002; Gallart-Jornet *et al.*, 2007a; Schmidt *et al.*, 2009). Besides, the use of high viscosity hypertonic solutions implies a considerable resistance to mass transfer from and towards the solution (Collignan *et al.* 2001; Ochoa-Martinez and Ayala-Aponte, 2005).

On the other hand, different empirical and semi-empirical approaches have been employed to study this process, allowing the modeling of mass transfer kinetics during osmotic dehydration.

In this context, Peleg (1988) published the basis of an empirical model, a simple two- parameter equation, which has been widely used to model sorption curves of different foods (Turhan *et al.*, 2002; Sopade *et al.*, 2007) and to determine dehydration rates of meat and fish treated with osmotic solutions (Schmidt *et al.*, 2009; Corzo and Bracho, 2006, 2007; Czerner and Yeannes, 2010). Likewise, empirical models based on a Weibull-type equation have been used to represent food drying processes (Cunha *et al.*, 1998; Corzo and Bracho, 2008; Deng and Zhao, 2008; Schmidt *et al.*, 2009).

Lastly, Zugarramurdi and Lupín (1980) proposed an empirical model to adequately explain water and NaCl kinetics behaviour in fish salting processes, where the external surface of the fish is exposed to very concentrated brines. Czerner and Yeannes (2010) applied this model to study OD of different cuts of salted anchovy; they obtained a more accurate prediction of water loss and equilibrium conditions with Z&L model than with Peleg's.

As for the product, mackerel is a pelagic fish that lives in the southwest Atlantic Ocean from latitude 22ºS in Brazilian waters to 39ºS in Argentine waters and has been classified within the underutilized species in this ocean. This condition encourages researchers to develop new products. OD process is presented as a viable alternative to produce intermediate or final fish products, giving also a potential barrier to implement the Hurdle Technology in the fish product development (Yeannes, 2006). For instance, dehydration is a critical step to guarantee high quality smoked products (Gallart-Jornet et.al., 2007b).

Therefore, aiming at the development of smoked mackerel, in this work we investigate the performance of binary and ternary hypertonic solutions (NaCl-water and NaCl-sucrose-water, respectively) on OD of mackerel fillets. Also, with this work we will generate more relevant scientific information about the OD dehydration process of mackerel fillets. This field of study was previously addressed in a research about the behaviour of moisture sorption in this product (Agustinelli *et al.*, 2014a). In order to achieve these objectives, the mass transfer kinetics of water, NaCl and sucrose in the fish tissue during the dehydration process was experimentally studied. Finally, the applicability of different empirical models to predict water loss and solutes gain was analyzed.

MATERIALS AND METHODS

The samples for this research were caught in September using lampara nets by a commercial fishing trawler around latitude 38ºS.

Captured fish were chilled with flake ice and were placed in plastic containers. The fish boxes were transported to the factory and the successive stages of washing, classifying, gutting and filleting were performed to get two fillets with skin from each specimen. The weight range for each individual fillet was 90–120 g and the average length was 22.1 ± 1.67 cm. The water and fat contents of the fresh mackerel were determined using AOAC (1990) method and Bligh and Dyer (1959) technique respectively. The values obtained, in wet basis, were 69.20 ± 0.45% for water content and 9.71 ± 0.56% for lipid content respectively.

The OD method was carried out using binary (NaCl-water) or ternary (NaCl-sucrose-water) solutions prepared according to the details presented in Table 1.

These solute concentrations were selected in order to ensure solutions with low a_w values and consequently sufficient driving force for the mass transport process (Corzo and Bracho, 2004; Medina-Vivanco *et al.*, 2006).

Fillets and solutions were previously conditioned in an incubator at 20 ºC. Afterwards, the fillets were placed in plastic containers with a fish:solution ratio of 1:4, which

Table 1- Hypertonic solutions used in the OD process

is an appropriate relation for the OD process (Medina-Vivanco *et al.*, 2006).Then the containers were placed in a termostatized incubator (20 ± 0.5 ºC). Two fillets were chosen randomly to determine water, NaCl and sucrose contents, at established sampling times among six hours of immersion. The fillets were gently blotted to remove surface moisture and then grounded and homogenized with an Omni-Mixer (Omni International Inc.) on an ice bath, to obtain a homogeneous paste. Each OD experiment was carried out in duplicate.

PHYSICOCHEMICAL DETERMINATIONS

Moisture content was determined in triplicate by drying 5 g of minced fish at 105 ± 1º C until constant weight (AOAC, 1990), ashes was measured by heating the sample in a muffle furnace at 500 ± 2º C until the ash had a white appearance (AOAC, 1990). The NaCl content was determined in triplicate as chloride using the Mohr method adapted to foods (Kirk *et al.*, 1996). The sucrose concentration was determined in duplicate by an enzymatic kit (Boheringer Mannheim/R-Biopharm, Germany) measuring the absorbance (λ=340 nm) of the solutions extracted from the samples. These samples were prepared according to the supplier instructions for products containing fat: first the samples were treated with hot water, and then they were cooled to allow the fat to be separated by filtration. Sucrose determination was done on three aliquots for each extract using the prepared reagents according to the manufacturer’s instructions. The content of sucrose was calculated and expressed as a percentage (%).

MATHEMATICAL MODELS

PELEG’S MODEL

Peleg’s model (1988) is given by the Eq. (1):

$$X_i = X_{i0} \pm \frac{t}{k_{i1} + k_{i2}t} \quad (1)$$

where X_i and X_{i0} are the water or solute (NaCl or sucrose) content (dry basis, g ⁄ g db) at a given time t (h) and at instant 0, respectively. In Eq. (1), ‘±’ becomes ‘+’ if it represents the solute gain and ‘-’ if it represents the water loss. The subscript *i* is equal to *w* to denote water fraction, to *s* to indicate soluble salt and to *suc* to indicate soluble sucrose.

According to this model, the reciprocal values of k_{i1} are the initial rates (t= 0) of water loss or solute gain respectively, (Eq. 2)

$$\left.\frac{dX_i}{dt}\right|_{t=0} = \pm\frac{1}{k_{i1}} \quad (2)$$

The capacity constant k_{i2} is related to the equilibrium condition. Therefore, as $t \rightarrow \infty$, Eq. 3 gives the content of each component at equilibrium in function of its initial concentration and k_{i2} parameter:

$$X_i\big|_{t_\infty} = X_i^{eq} = X_{i0} \pm \frac{1}{k_{i2}} \quad (3)$$

The Peleg’s model allows predicting the dehydration kinetics of food using short time experimental data (Turhan *et al.*, 2002; Czerner and Yeannes, 2010).

WEIBULL MODEL

The Weibull model is a probabilistic one and was developed to describe the behaviour of different processes that have some degree of variability such as the OD kinetics (Corzo and Bracho, 2008; Cunha et al, 1998). This exponential model includes three parameters to describe water loss and solid gain during osmotic dehydration (Cunha *et al.*, 1998):

$$n_i = \frac{X_i - X_i^{eq}}{X_{i0} - X_i^{eq}} = exp\left[-\left(\frac{t}{\beta_i}\right)^{\alpha_i}\right] \quad (4)$$

where n is the dimensionless concentration (fractional change in concentration between the initial concentration and that which would exist at equilibrium) and X_{i0}, X_i and X_i^{eq} are the same variables defined in the previously described models, i. e. moisture or solute content (expressed as g/g db) at t = 0, at a time t and at equilibrium, respectively. β is the Weibull's scale parameter related to the mass transfer rate (time required for n_i to change one log cycle), α is the Weibull's shape parameter (which quantifies the type of shape of the n_i versus time curve) , and t is the sampling time. The subscript *i* is equal to *w* to denote water fraction, to *s* to indicate soluble salt and to *suc* to indicate soluble sucrose.

ZUGARRAMURDI & LUPÍN'S MODEL (Z&L)

The following mathematical model was proposed by Zugarramurdi & Lupín (1980):

$$\frac{dX_i}{dt} = -K_i\left(X_i^{eq} - X_i\right), \quad (5)$$

Again, in this equation X_i and X_i^{eq} are the water or solute (NaCl or sucrose) content (dry basis, g / g db) at dehydration time t (h) and at equilibrium, respectively, and K_i ((g/g db) h)^2) the corresponding specific rate constant.
Integration of Eq (5) with the initial condition (*t*=0) results in:

$$X_i = X_{i0}(e^{-k_i t}) + X_i^{eq}(1 - e^{-k_i t}) \quad (6)$$

The subscript *i* is equal to *w* to denote water fraction, to *s* to indicate soluble salt and to *suc* to indicate soluble sucrose. This model was proposed to explain the observed behaviour on fish salting and applies to procedures where the external surface of fish is exposed to saturated or very concentrated brines. It was also used to predict the mass transfer kinetic that occurs during the OD of different food matrix immersed in hypertonic solutions (Rastogi and Raghavarao, 1994; Zúñiga and Pedreschi, 2012; Checmarev *et al.*, 2014; Agustinelli *et al.*, 2014a).

STATISTICAL ANALYSIS

Data analysis consisted of nonlinear regression analyses using the software OriginPro 7.5 (OriginLab Corporation, Northampton, MA, USA) to examine the data for good fit. To evaluate the performance of the models, the coefficient of determination (R^2), which should be close to 1 and the root mean square error (root- MSE, Eq 7) also expected to be very small,

$$root - MSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{Y_i - Y_{ip}}{Y_i}\right)^2} \quad (7)$$

where Y_i is the *i*th experimentally observed value, Y_{ip} is the *i*th predicted value and *N* is the number of observations.

The model parameters were also evaluated using the *p-value*, or significant level, to examine whether the fitting parameters are significantly different from zero.
Statistical analysis was performed on all data by an analysis of variance using the R statistical software (R Development Core Team version 2.10.1, 2010). Differences between means were analyzed using the Tukey's test. Significant differences were set at 95% confidence level.

RESULTS AND DISCUSSION

MASS TRANSFER DURING OSMOTIC DEHYDRATION

Figures 1, 2 and 3 show the contents of water (X_w), NaCl (X_s) and sucrose (X_{suc}) in mackerel muscle, during 6 h of immersion in binary and ternary solutions respectively.

An initial high rate of water removal and solute uptake followed by slower rates of both flows was observed. The curves show the typical exponential behaviour of mass transfer in OD (Collignan and Roult-Walk, 1994; Medina-Vivanco *et al.*, 2002; Czerner and Yeannes, 2010; Agustinelli *et al.*, 2014a). As it is shown in Fig. 1 A and B, the osmotic solution composition greatly affects the dehydration rate. The samples treated with the highest salt concentration in Fig. 1 (B) showed significantly lower ($p<0.05$) water content values than those obtained with less concentrated salt solutions (Fig. 1 (A)), throughout the entire OD process. These results are in accordance with the tendency observed in other fish species like sardine (Corzo and Bracho, 2006), cod (Thorarinsdóttir *et al.*, 2004) and Atlantic salmon (Gallart-Jornet *et al.*, 2007a, 2007b) treated with NaCl solutions. On the other hand, the sucrose concentration has a significant effect only in the early hours of treatment (<2 h). After 6 hours of OD, there were not significant differences in the water content of samples treated with solutions of identical NaCl concentration and different sucrose content (S1, S2 and S3 or S4, S5 and S6 respectively). These differences can be explained by the interaction between each solute (NaCl, sucrose) and the muscle matrix and also by the fillet's proximate composition (Collignan and Raoult-Walk, 1994; Gallart-Jornet *et al.*, 2007a; Medina-Vivanco *et al.*, 2002). The NaCl is involved in the osmotic process at the cellular level, while the sucrose remains in the food surface inducing water loss primarily by diffusion (Collignan and Raoult-Walk, 1994; Collignan *et al.*, 2001). Santchurn *et al.* (2007) studied meat OD using ternary solutions (NaCl-sucrose-water); they observed an initial stage characterized by a high rate of water and solute diffusion outside and inside the tissue respectively. Then, a concentrated solute layer is created over the meat surface, which depends primarily on the molecular weight and concentration of the second solute (the first being the salt). The presence of this thin layer on the surface encourages initially the diffusion of water from the centre of the product (high water content) to the interface (low water content), but limits this diffusion for large process times.

The mackerel fillet's proximate composition has a negative effect on the OD process, because of its high lipid content (> 10%). Gallart-Jornet *et al.* (2007a) studied the OD of lean and fatty fish species, and concluded that high lipid content limits the transport of solutes and water.

Regarding NaCl diffusion (Fig. 2 A and B), in samples treated in binary solutions (S1 and S4) a significant effect of the NaCl concentration was found: higher NaCl concentration in the OD solution implies higher NaCl gain.

In contrast, samples immersed in ternary solutions presented an interaction effect ($p<0.001$) between NaCl and sucrose content over NaCl diffusion into fish tissue. Salt gain decreases as sucrose concentration increases. Collignan and Raoult-Walk (1994) studied the solutes gain and water loss during osmotic dehydration of cod fillets treated with ternary solutions of sucrose and NaCl. According to their results, there is a competitive effect between solutes in relation with their molecular weight. The same interaction between NaCl and sucrose in solution was found in studies about processing of meat and fish in ternary hypertonic solutions, aiming to achieve dehydration, limiting the absorption of NaCl (Bohuon et al, 1998; Collignan and Raoult-Wack, 1994; Collignan et al, 2001; Deumier et al, 1996; Medina-Vivanco et al, 2002; Santchurn et al, 2007).

The sucrose gain kinetics (Fig. 3) was similar to the NaCl diffusion behaviour in samples treated with binary solutions. Thus, increasing the sucrose concentration in the solution raises the content of this solute in the tissue.

An analysis of variance and comparison of means was done to find the influence of time and solution composition on the sucrose content, being both factors significant ($p <0.001$) as well as their interaction ($p <0.001$). In the samples treated with more concentrated sucrose solutions, an increase in the solute gain was observed, regardless of the NaCl content in solution.

On the other hand, salt effect over sucrose content gain was only significant in samples treated with the higher sucrose content (S3 and S6). In these cases, when the salt content increased, the sucrose content in fish tissue decreased due to the interaction effect between solutes, results that are in accordance with the behaviour observed by Collingnan and Rault-Wack (1994) and Medina-Vivanco *et al.* (2002) in the OD of cod and tilapia respectively, using ternary solutions.

MATHEMATICAL MODELING OF OD OF MACKEREL FILLETS USING HYPERTONIC SOLUTIONS

Solute gain and water loss kinetics were fitted to the three empirical models detailed in Section 2.2, commonly used to model the OD process of fish and other foods (Agustinelli *et al.*, 2014a; Azoubel and Xidieh Murr, 2004; Checmarev *et al.*, 2013; Corzo and Bracho, 2006, 2007, 2008; Czerner and Yeannes, 2010; Schmidt *et al.*, 2009; Sopade *et al.*, 2007; Turhan *et al.*, 2002).

T

he fit goodness of these empirical models is shown in tables 2, 3 and 4 for water, NaCl and sucrose contents, respectively, by means of the coefficients of determination (R^2) and RMSE values.

According to the correlation coefficients (R^2> 0.783), the three models had a good performance and accurately described the kinetics of water loss and solute gain. However, in general Peleg's and Weibull's models showed higher R^2 values and lower RMSE than the Z&L approach, under the whole range of experimentally studied conditions.

Peleg's equation has been successfully applied to model mass transfer during OD of water and osmo-active solutes in several food commodities. The wide applicability of this model is confirmed by the good results obtained in different OD conditions. Schmidt *et al.* (2009) concluded that Peleg's model was able to accurately represent the rates of water gain/loss and salt gain during the osmotic treatment of chicken breast cuts in different saline solutions concentrations. Well fitting results were obtained with this model for different foods with a similar tissue matrix: Brazilian sardine sheets (*Sardinella aurita*) treated with salt solutions (Corzo and Bracho, 2006), catfish (*Clarias gariepinus*) fillets treated with salt solutions (Sobukola and Olatunde, 2010), common carp (*Cyprinus carpio*) fillets treated with salt and sucrose solutions (Agustinelli *et al.*, 2013), different cuts of anchovy (*Engraulis anchoita*) treated with salt solutions (Czerner and Yeannes, 2010) and mackerel loins (*Scomber japonicus*) treated with salt and glycerol solutions (Checmarev *et al.*, 2013).The Weibull's model provided good fit to explain the behaviour of water loss and salt gain of samples treated with binary solutions (S1 and S4) and with the less concentrated ternary solutions (S2 and S3). This probabilistic model has been used to model diverse engineering processes (Cunha *et al.*, 1998), since it is relatively simple. In this sense, Corzo and Bracho (2008) applied this approach to explain the experimental behaviour during the vacuum pulse osmotic dehydration of sardines. Similar results were reported by other authors to simulate the osmotic dehydration of chicken breast in salt solutions (Schmidt *et al.*, 2009) and squid (Uribe *et al.*, 2011).

In consequence, a deeper analysis of the performance of these two models was done; being the results detailed in table 5 and 6 detail for Peleg's and Weibull's models, respectively.

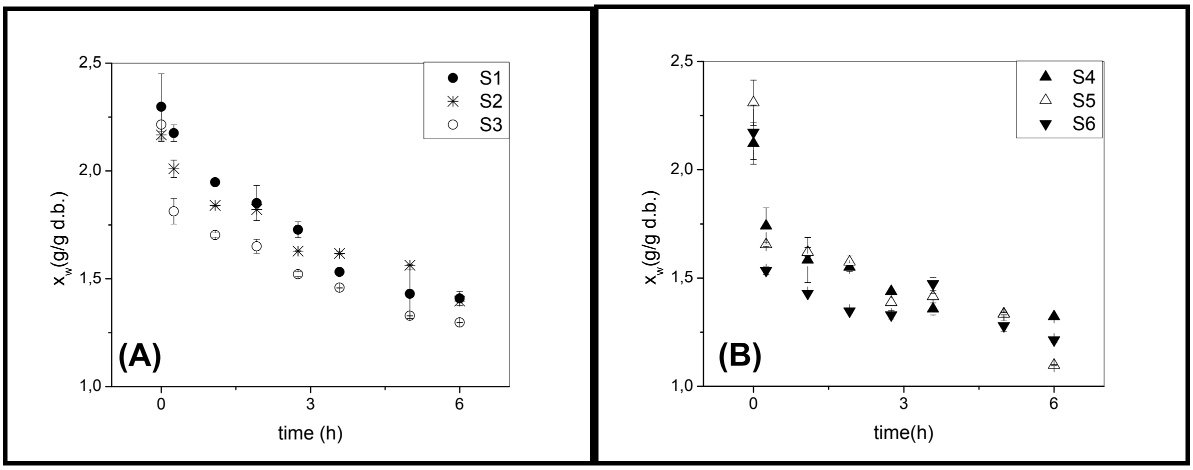

Fig. 1- Kinetics of mackerel moisture content, in fillets processed with binary and ternary OD solutions. (A) refers to treatments with solutions S1, S2 and S3. (B) refers to treatments with solutions S4, S5 and S6

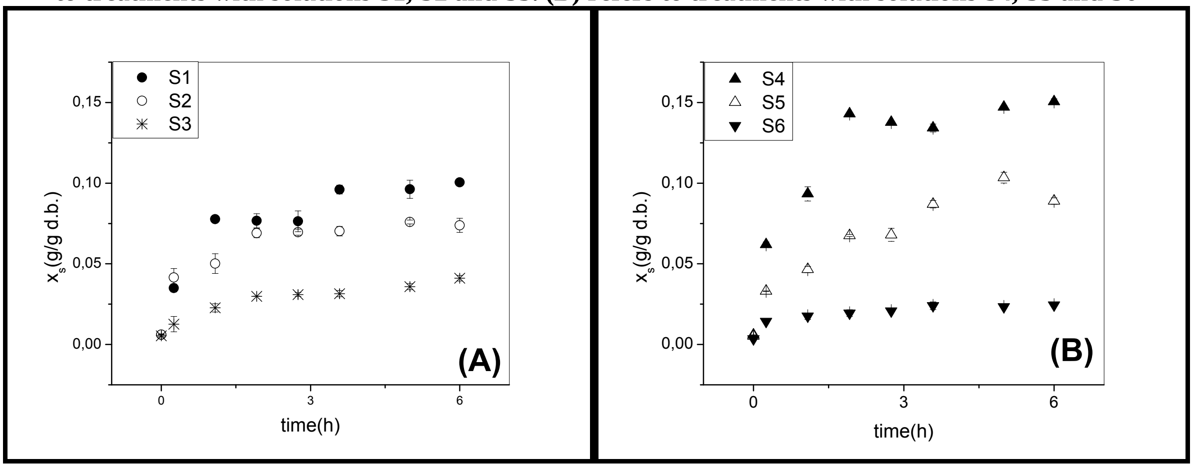

Fig. 2- Kinetics of NaCl content, in fillets processed with binary and ternary OD solutions. (A) refers to treatments with solutions S1, S2 and S3. (B) refers to treatments with solutions S4, S5 and S6

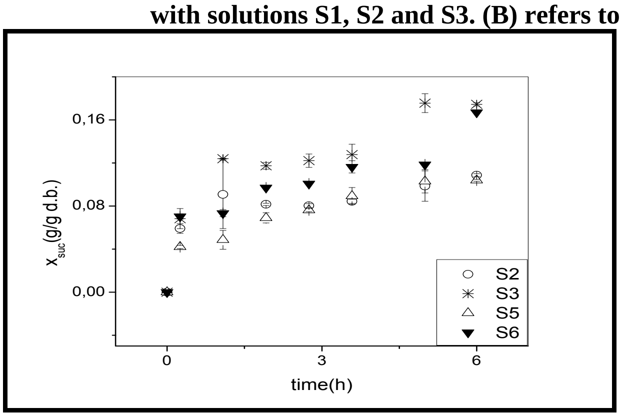

Fig. 3 - Kinetics of sucrose content, in fillets processed with ternary OD solutions

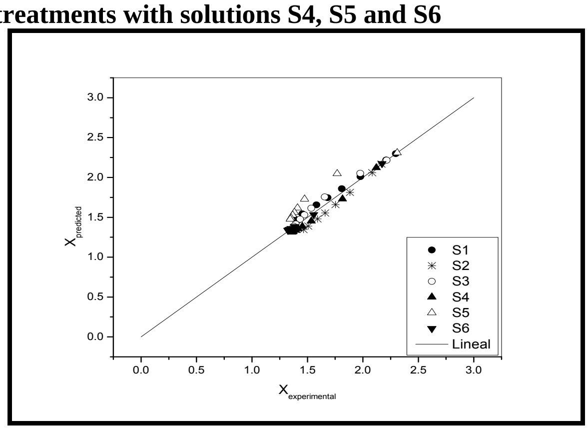

Fig. 4- Predicted mackerel water content with the generalized Peleg model, compared with experimental values

Table 2- root- MSE and coefficient of determination (R^2) of the predicted water loss values relative to the experimental data

Model	S1		S2		S3		S4		S5		S6	
	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE
Peleg	0.986	0.040	0.944	0.060	0.895	0.097	0.950	0.061	0.836	0.144	0.933	0.078
Weibull	0.986	0.040	0.986	0.040	0.945	0.070	0.955	0.057	0.824	0.149	0.944	0.071
Z&L	0.985	0.040	0.934	0.065	0.838	0.120	0.886	0.091	0.806	0.170	0.918	0.086

Table 3- root- MSE and coefficient of determination (R^2) of the predicted NaCl gain values relative to the experimental data

Model	S1		S2		S3		S4		S5		S6	
	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE
Peleg	0.962	0.007	0.998	1.187	0.973	0.002	0.962	0.010	0.928	0.009	0.946	0.002
Weibull	0.940	0.008	0.999	1.104	0.976	0.002	0.959	0.010	0.932	0.009	0.938	0.002
Z&L	0.936	0.008	0.910	0.007	0.957	0.003	0.948	0.012	0.919	0.009	0.884	0.002

Table 4- root- MSE and coefficient of determination (R^2) of the predicted sucrose gain values relative to the experimental data

Model	S2		S3		S5		S6	
	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE
Peleg	0.908	0.010	0.890	0.019	0.913	0.010	0.783	0.022
Weibull	0.927	0.009	0.846	0.022	0.932	0.009	0.829	0.020
Z&L	0.910	0.010	0.830	0.024	0.886	0.012	0.758	0.026

Peleg's equation was statistically significant (p-value<0.05) and suitable to describe the mass transfer kinetics over the whole range of concentrations of hypertonic solutions studied in this work. On the contrary, Weibull's model only showed accurate parameters in treatments with binary solutions, giving the poorest fitting results for the sucrose kinetics (p-value>0.05). Taking this into account, a particular analysis could be done over the fitting results of the mass transfer kinetics that occurs with the binary and ternary solutions treatments.

In regard to the dehydration rate of samples processed in binary solutions (S1 and S4), both models predict that the initial water loss rate increases as the solution concentration increases. This rate is assessed with the reciprocal of k_{w1} of Peleg's equation, i.e. smaller values of k_{w1} indicate higher initial rates of mass transfer. The same tendency was found by Corzo and Bracho (2006, 2008) studying the OD of anchovy fillets (*Sardinella aurita*) and Checmarev *et al.* (2013) in mackerel loins, although different NaCl concentrations were tested in their works. Also the β_w values of the exponential model refer to the dehydration rate, being lower as lower is the β_w parameter. Concerning this, a higher dehydration rate was predicted for the samples immersed in S4.

About the values of water loss for large immersion times, the results predicted by the exponential model (X_w^{eq}) were always lower than the values estimated by the Peleg's model ($X_{w0} - 1/k_{w2}$). Attending to the fitting results (p-value), the Peleg model is more reliable. The Weibull's model tends to overestimate samples content of water at the equilibrium state.

For the NaCl gain kinetics, the model's parameters shown in Table 5 indicate that it depends on the solution concentrations. The reciprocal of k_{s1} of the Peleg's model, representative of the initial salt transfer rate, increases with the increase of NaCl concentration (S4 vs. S1). These results are directly related to the NaCl gradient between osmotic and intercellular solutions. The same tendency was observed in the β_s values of the Weibull's model. Both k_{s1} and β_s values indicate that salt gain is slower than the dehydration process.

As for the NaCl gain verified at large immersion periods (X_s^{eq}), both models predicted that it increases as the NaCl solution concentration increases, being the predicted values in the order of the ones obtained by Corzo and Bracho (2006) and Sobukola and Olatunde (2011) for fish fillets osmodehydrated in similar conditions.

As for the samples treated with ternary solutions, the Peleg's fitting values clearly represent the effect of the solution concentration over the OD process. About the water loss kinetics, the initial mass transfer rate represented as $1/k_{w1}$ shows an increase trend when the concentration of both solutes in solution increases. Thus, samples treated with S2 presented the lowest initial water loss rate and those treated with S6 the highest one. Moreover, with the exception of the sample immersed in S2, the dehydration rate is significantly higher in samples treated with ternary solutions. Similar trends were obtained by Agustinelli *et al.*, 2014a) using Peleg's and Z&L models to describe the OD of common carp (*Cyprinus carpio*) fillets treated with binary and ternary solutions, and Corzo and Bracho (2005) and Corzo *et al.* (2007) using the same models for the modeling of OD of *Sardinela aurita* fillets, comparing the brine solute increment.

About NaCl diffusion kinetics in samples treated with ternary solutions, the initial mass transfer rate ($1/k_{1s}$) presents a significant dependence (p<0.05) on the sucrose concentration higher sucrose-concentrated solutions resulted in lower initial rate of salt gain (S2 vs. S3, S5 vs. S6). These results are in accordance with the previously analysis of experimental data, related to the sucrose barrier effect which prevents salt gain in mackerel muscle. In this sense, in relation to the salt equilibrium content, the Peleg's capacity contants (k_{s2}) of samples treated with ternary solutions were always higher than the ones obtained for binary solutions, confirming the barrier effect of sucrose. There are few experimental works related to OD of fish muscle using ternary solutions, none of them modelled the mass transfer (Medina-Vivanco *et al.*, 2002; Medina-

Table 5- Peleg's parameters for mass transfer kinetics during mackerel OD process

	Water				NaCl				Sucrose			
Solution	**k_{w1} h(g/g db)$^{-1}$**	**p-value**	**k_{w2} (g/g db)$^{-1}$**	**p-value**	**k_{s1} h(g/g db)$^{-1}$**	**p-value**	**k_{s2} (g/g db)$^{-1}$**	**p-value**	**k_{suc1} h(g/g db)$^{-1}$**	**p-value**	**k_{suc2} (g/g db)$^{-1}$**	**p-value**
S1	2.69	1.22E-04	0.65	1.48E-04	5.98	6.15E-03	10.05	3.34E-06	-	-	-	-
S2	2.78	4.83E-03	0.96	1.34E-03	5.45	1.08E-02	13.42	1.10E-07	1.70	1.23E-02	10.35	3.94E-04
S3	0.79	3.84E-02	1.06	9.55E-05	34.24	1.33E-03	24.60	1.45E-05	2.86	5.61E-02	5.98	4.18E-05
S4	0.51	1.19E-02	1.23	2.47E-06	3.49	5.99E-03	6.41	2.38E-06	-	-	-	-
S5	0.21	1.41E-02	1.00	2.68E-05	14.05	1.21E-02	8.73	3.67E-04	10.47	1.89E-02	8.21	2.62E-04
S6	0.12	8.26E-02	1.16	7.48E-07	16.97	1.62E-02	49.38	2.13E-06	4.95	1.27E-02	6.82	8.03E-04

Table 6- Weibull's parameters for mass transfer kinetics during mackerel OD process

	Water						NaCl						Sucrose					
Solution	**α_w**	**p-value**	**β_w (h)**	**p-value**	**X_w^{eq} (g/g db)**	**p-value**	**α_s**	**p-value**	**β_s (h)**	**p-value**	**X_s^{eq} (g/g db)**	**p-value**	**α_{suc}**	**p-value**	**β_{suc} (h)**	**p-value**	**X_{suc}^{eq} (g/g db)**	**p-value**
S1	3.18	8.90E-07	0.96	2.56E-05	1.18	7.13E-03	0.59	9.24E-03	1.16	5.80E-03	0.11	1.80E-02	-	-	-	-	-	-
S2	2.77	9.08E-05	0.80	1.02E-03	1.35	1.16E+00	0.46	4.20E-02	1.38	4.52E-01	0.09	1.02E-02	0.16	0.80	1.72	1.00	2.06	1.00
S3	1.43	1.47E-03	0.52	1.86E-03	1.26	1.22E-03	0.58	2.23E-02	4.57	5.62E-01	0.05	9.66E-02	0.66	0.09	0.46	0.10	0.14	0.96
S4	0.57	6.63E-03	0.58	3.47E-03	1.38	3.04E-02	0.67	5.05E-03	0.86	3.11E-03	0.01	1.17E-04	-	-	-	-	-	-
S5	0.21	3.79E-01	0.45	2.05E-01	1.41	3.41E-01	0.49	1.70E-01	14.16	8.90E-01	0.20	6.71E-01	0.64	0.00	1.35	0.00	0.10	0.96
S6	0.17	2.64E-01	0.28	2.96E-02	1.24	1.34E+00	0.58	1.68E-02	0.42	2.81E-02	0.02	8.56E-02	0.51	0.04	0.97	0.05	0.14	0.86

Vivanco *et al.*, 2004 Ooizumi *et al.*, 2003). Results obtained indicate that at $t \rightarrow \infty$ the salt content in samples treated with ternary solutions would be lower than the concentration in the samples treated with binary solution.

Finally, the initial sucrose diffusion rate through mackerel tissue presents a clear dependence ($p<0.05$) with NaCl solution concentration. The samples treated with lower salt content presents higher sucrose diffusion rate ($1/k_{suc1}$) showing the interaction between both solutes. At large immersion times the equilibrium sucrose content only depends on sucrose solution concentration.

GENERALIZED PELEG's MODEL TO REPRESENT THE WATER CONTENT KINETIC IN MACKEREL FILLETS AND ITS VALIDATION

According to the previous analysis, Peleg's model showed the best performance to predict mass transfer rates during OD of mackerel fillets. Therefore, to complete the modelling of dehydration kinetics considering both binary and ternary OD solutions, a generalized equation was proposed. It follows Eq. (1), the generalized Peleg's parameters K_{w1} and K_{w2} depend on NaCl and sucrose solution concentration.

$$K_{w1} = 8.171 - 43.477 \cdot Conc_{NaCl} - 10.487 \cdot Conc_{Suc}$$

$$K_{w2} = 6.775 \cdot Conc_{NaCl} + 1.633 \cdot Conc_{Suc}$$

, were the reciprocal values of K_{w1} are the initial rates (t= 0) of water loss and K_{w2} is the capacity constant related to the equilibrium condition.

Then, the complete generalized Peleg's model can be rewritten as:

$$X_w = X_{w0} - \left(\frac{t}{\left(\left(8.171 - 43.477 \cdot Conc_{ClNa} - 10.487 \cdot Conc_{Sac}\right) + \left(6.775 \cdot Conc_{ClNa} + 1.633 \cdot Conc_{Sac}\right) \cdot t\right)} \right)$$

where X_{w0} refers to the initial water content in dry basis while $Conc_{NaCl}$ *and* $Conc_{Sac}$ to the NaCl and sucrose solution concentration (g/g d.b.), respectively and *t* is the immersion time (h).

To validate this model, experimental and predicted values of water content of mackerel fillets during OD in the different solutions used in this work are compared in Fig 4. A narrow scatter around a 45º line indicates a good fit of the new modified Peleg model. In this sense, the proposed model allows to predict the behaviour of mackerel osmotic dehydration under immersion in the studied conditions, as a function of processing time and sucrose and NaCl concentration in the hypertonic solutions.

CONCLUSIONS

The mackerel fillet OD with ternary solutions showed that the solute concentration presented a significant influence over the initial water and sucrose kinetics. The presence of sucrose as a high molecular weight solute in solution allowed controlling the NaCl diffusion. Peleg model described accurately the OD behaviour at all the treatments studied. A modified Peleg model was also obtained with a very good performance to describe the relationship between water content of mackerel fillets and sucrose and NaCl concentration in binary and ternary solutions.

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