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Analysis of applicability of Peleg model to the cooking-infusion of mackerel (*Scomber japonicus*) slices

Gerardo CHECMAREV^{1,2*}, María Rosa CASALES^{1,2}, María Isabel YEANNES^{1,2}

Abstract

Mass transfer kinetics in osmotic dehydration is usually modeled by Fick's law, empirical models and probabilistic models. The aim of this study was to determine the applicability of Peleg model to investigate the mass transfer during osmotic dehydration of mackerel (*Scomber japonicus*) slices at different temperatures. Osmotic dehydration was performed on mackerel slices by cooking-infusion in solutions with glycerol and salt ($a_w = 0.64$) at different temperatures: 50, 70, and 90 °C. Peleg rate constant (K_p) (h(g/gdm)^{-1}) varied with temperature variation from 0.761 to 0.396 for water loss, from 5.260 to 2.947 for salt gain, and from 0.854 to 0.566 for glycerol intake. In all cases, it followed the Arrhenius relationship ($R^2 > 0.86$). The E_a (kJ / mol) values obtained were 16.14; 14.21, and 10.12 for water, salt, and glycerol, respectively. The statistical parameters that qualify the goodness of fit ($R^2 > 0.91$ and $\text{RMSE} < 0.086$) indicate promising applicability of Peleg model.

Keywords: mackerel; osmotic dehydration; mass transfer; temperature effect; modeling.

1 Introduction

Osmotic dehydration (OD) is one of the commonly used methods for food preservation. It consists of water removal by soaking the food in a hypertonic solution with the aim of producing water flow from the product to the hypertonic solution. The driving force for mass transfer is the difference in osmotic pressure (OCHOA MARTINEZ; AYALA APONTE, 2005). Since the cell membrane acts as a semi-permeable film, two main fluxes occur simultaneously and in opposite direction: the diffusion of water out of the tissue into the osmotic solution and the uptake of solute from osmotic solution to the product (CORZO; BRACHO, 2009; URIBE et al., 2011). Other flow is the leaching out of the food tissue's own solutes (sugars, organic acids, minerals, and vitamins) into the solution. This last flow is unimportant due to the low solids loss, but it can modify some properties such as sensorial characteristics (CORZO; BRACHO, 2009). Different mathematical models have been applied for adjusting OD processes' experimental results in order to predict the behavior of food products. Models based on solution of Fick's second law have generally been used to describe OD process (CASALES; CAPACCIONI; YEANNES, 2009; CORZO; BRACHO, 2007; GERLA; RUBIOLO, 2003; GOU; COMAPOSADA; ARNAU, 2003; GRAIVER et al., 2006; RODGER et al., 1984; TELIS et al., 2003 among others). This model assumes that the solution concentration remained constant, the external resistance is negligible compared to the internal resistance, and the sample geometry is as simple as, for example, an infinite slab. Another alternative for modeling the osmotic dehydration process is the use of empirical models based on mathematical representations of the observed data, covering some of the Fick model inaccuracies. The use of the diffusive model depends on the estimation or experimental determination

of equilibrium values. The estimation of these values can be performed with empirical models, but its experimental determination needs long immersion times that can lead to food tissue changes (SCHMIDT; CARCIOFI; LAURINDO, 2009). Some of the empirical models were developed from polynomial adjustments, while others were developed from mass balances and relationships between process variables (OCHOA MARTINEZ; AYALA APONTE, 2005; CORZO; BRACHO, 2009). One of the most widely used empirical models to predict water loss/gain and salt gain in different foods is the equation proposed by Peleg (SCHMIDT; CARCIOFI; LAURINDO, 2009; CORZO; BRACHO, 2006; CZERNER; YEANNES, 2010; TURHAN; SAYAR; GUNASEKARAN, 2002). According to these authors, the Peleg model is able to represent satisfactorily the transfers of water and salt during osmotic treatments. Mass transfer kinetics in cherry tomato in different hypertonic NaCl solutions (with or without sucrose) was modeled according to Peleg, Fick, and Page equations (AZOUBEL; MURR, 2004). In addition, mathematical modeling of mass transfer during the osmotic dehydration of strawberries in a solution of sugar (40 °Brix) has been performed applying Newton, Henderson–Pabis, Page, and Weibull models (NUÑEZ-MANCILLA et al., 2011). The diffusive model, Azuara's model, Peleg's model, and an exponential (Weibull-type) model were used in the mathematical modeling of water gain/loss and salt gain by chicken breast cuts immersed in saline solutions (SCHMIDT; CARCIOFI; LAURINDO, 2009). In fish products, water loss, and acid and salt gain have been modeled using Fick, Peleg, Weibull, and Zugarramurdi & Lupín models (CORZO; BRACHO, 2009; CASALES; CAPACCIONI; YEANNES, 2009; CORZO; BRACHO, 2007; RODGER et al., 1984; TELIS et al.,

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2003; CORZO; BRACHO, 2006; CZERNER; YEANNES, 2010; CORZO; BRACHO, 2005; ZUGARRAMURDI; LUPÍN, 1977; ZUGARRAMURDI; LUPÍN, 1980).

Our research group has developed a new product with mackerel, with the a_w reduction as the principal hurdle to microbial growth. A ternary solution with glycerol and salt was used to reduce the a_w value. In the scientific literature, information available about the application of empirical models for the osmotic dehydration of different kinds of food in solutions with glycerol and salt is very scarce, and no information has yet been reported regarding fish products.

Therefore, the aim of this study was to determine the applicability of Peleg model to investigate the mass transfer during osmotic dehydration of mackerel (*Scomber japonicus*) slices at different temperatures in a hypertonic solution containing glycerol and salt.

2 Materials and methods

2.1 Raw materials

Mackerel (*Scomber japonicus*) caught in Mar del Plata, Argentina, in the months of October and November and stored at -18°C was used in this study. The skin, head, tail, and viscera were removed from frozen samples. The trunk was cut into slices of 0.72 ± 0.05 cm thick and 5.15 ± 0.15 cm diameter.

2.2 Infusion solution

The composition (w/w) of the infusion solution was as follows: 54% glycerol (Biopack, Zárate, Buenos Aires, Argentina, 99.5 g/100 g of purity), 38.3% water, 7% sodium chloride (Biopack, 99 g/100 g of purity), and 0.7% potassium sorbate (DQI, Medellín, Colombia, 99 g/100 g of purity). The a_w of cooking-infusion solution was 0.64. The ratio fish:solution was 1:10 (w/w) in order to minimize significant changes in the concentration of the osmotic solution as a result of water loss and solute uptake.

2.3 Cooking-infusion

The osmotic dehydration of mackerel slices was carried out in the aforementioned infusion solution at the following temperatures: 50 ± 1 , 70 ± 1 and $90 \pm 1^\circ\text{C}$ until equilibrium was reached (a maximum immersion time of 3 hours).

The slices were thawed under refrigeration until they reached 8°C and placed in the infusion solution at the fixed temperatures. At specified time intervals (5, 10, 15, 20, 25, 40, 60, 80, 120, 150, and 180 minutes), the samples were removed for physicochemical analysis. The slices were drained, superficially rinsed with distilled water, dried with absorbent paper, and weighed. Three slices were removed at each sampling time and each temperature tested.

Two runs were performed for the three temperatures tested.

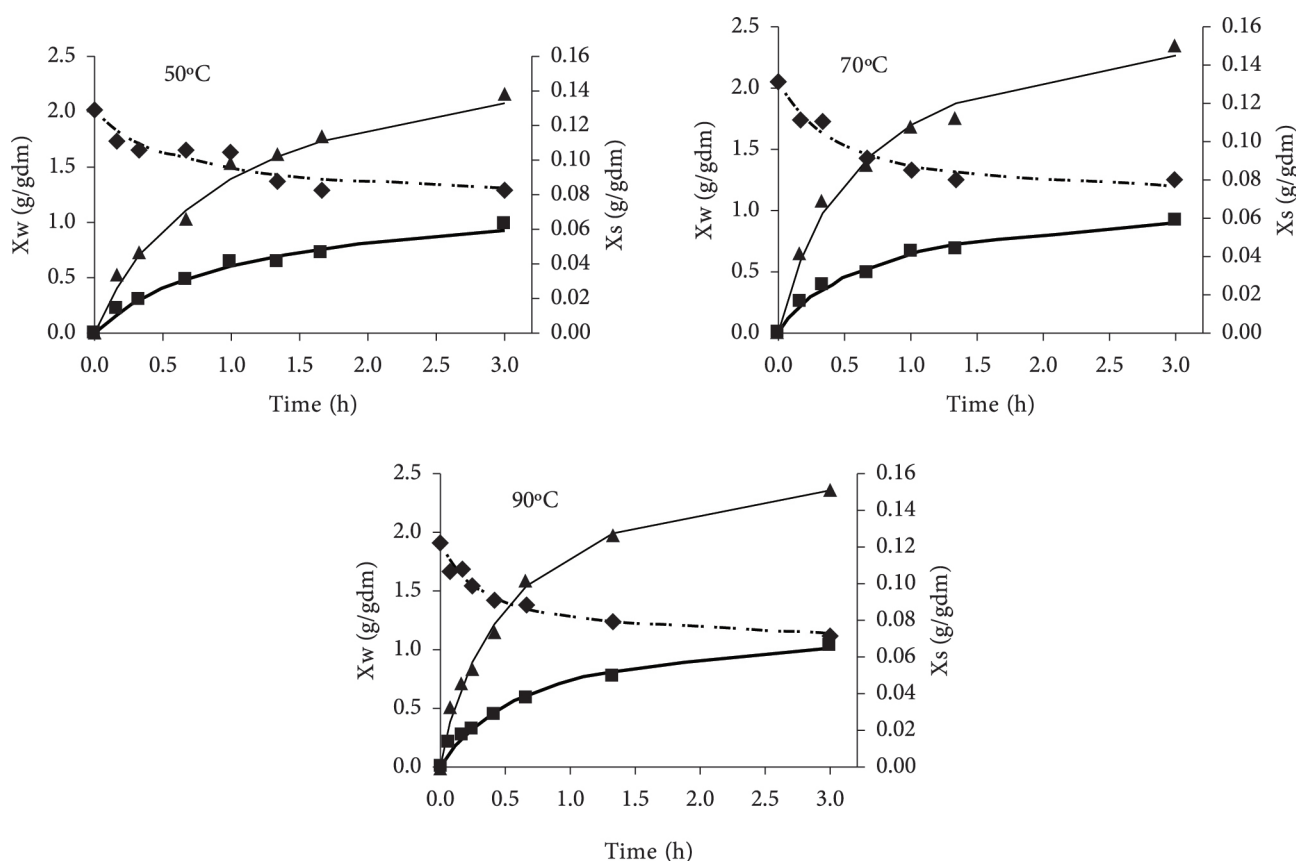


Figure 1. Fitting of the Peleg model to water loss and solute gain during OD of mackerel slices at different temperatures: water experimental (\diamond), water calculated ($-\cdot-\cdot-$), glycerol experimental (\blacksquare), glycerol calculated ($—$), salt experimental (\blacktriangle), salt calculated ($—$).

2.4 Physicochemical analysis

The water content was determined at 105 °C until constant weight (ASSOCIATION..., 1990) using a drying oven (Marne, 644, Córdoba, Argentina); sodium chloride content was determined using the Mohr method adapted to food (KIRK; SAWYER; EGAN, 1996); glycerol was determined using an enzymatic UV method (BoehringerMannheim/R-Biopharm, Darmstadt, Germany); and a_w was determined using an Aqualab hygrometer (Decagon, CX-2T, Pulman, WA, USA).

All analyses were performed in triplicate.

2.5 Peleg Model

Peleg (1988) proposed a two-parameter sorption equation:

$$X_t = X_0 \pm \frac{t}{K_1 + K_2 t} \quad (1)$$

where X_0 and X_t are content of water, salt, and glycerol (expressed as g on a non-salt and non-glycerol dry matter basis, g/gdm) at time 0 and time t , respectively. K_1 is the Peleg rate constant ($\text{h}(\text{g/gdm})^{-1}$), and K_2 is the Peleg capacity constant ($(\text{g/gdm})^{-1}$). In Equation 1 “ \pm ” becomes “+” for salt and glycerol gain and “-” for water loss. K_1 is related to the mass transfer rate at the beginning of the OD process (Equation 2). K_2 is related to water, salt, or glycerol contents at time $t \rightarrow \infty$ (Equation 3).

$$dX_t/dt = \pm 1/K_1 \quad (2)$$

$$X_{eq} = X_0 \pm 1/K_2 \quad (3)$$

where X_{eq} is water, salt or glycerol contents in the equilibrium ($t \rightarrow \infty$).

The major advantage of the Peleg model is to save time by predicting the kinetics sorption of osmotically dehydrated foods, including equilibrium values (Equation 3), using short-time experimental data (TURHAN; SAYAR; GUNASEKARAN, 2002; PELEG, 1988).

2.6 Statistical analysis

The fitting of the model to the experimental data was performed by nonlinear regression analysis using the

software Origin Pro 8.0 (OriginLab, Northampton, MA). The determination coefficient (R^2) and root mean square error (RMSE, Equation 4) were used to evaluate the goodness of fit of the model to the experimental data.

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (X_{ip} - X_i)^2} \quad (4)$$

where X_i and X_{ip} are the experimental data and the values predicted by the model, respectively, and n the number of data pairs.

3 Results and discussion

Peleg model parameters and equilibrium values for water, salt, and glycerol at the different temperatures tested are shown in Table 1.

Peleg rate constant (K_1) decreased from 0.761 to 0.396 $\text{h}(\text{g/gdm})^{-1}$ for water loss; from 5.526 to 2.947 $\text{h}(\text{g/gdm})^{-1}$ for salt gain; and from 0.944 to 0.566 $\text{h}(\text{g/gdm})^{-1}$ for glycerol gain, respectively, with increasing temperature from 50 to 90 °C. Since the inverse of K_1 (Peleg rate constant) (Equation 2) is related to mass transfer rate, both water loss and solute gain increased with temperature. Similar behavior for water loss and salt gain was found by Corzo and Bracho (2006) in sardine sheets and by Turhan, Sayar and Gunasekaran (2002) in chickpea. There is no information available on glycerol gain in the literature. The increase in temperature promoted faster water loss and faster solute gain probably due to swelling and plasticizing of the cell membranes. It also led to faster water diffusion within the product and improved water transfer characteristics on the product surface due to lower viscosity of the osmotic solution (TORTOE, 2010). In addition, the higher solid gains at higher temperatures may be due to the destruction of cell membrane structure (CORZO; BRACHO, 2006).

Peleg capacity constant (K_2) did not show a clear pattern with respect to the process temperature for salt and glycerol or water. Corzo and Bracho (2006) found similar results for OD of sardine sheets for water loss and salt gain.

The determination coefficient (R^2) ranged from 0.90 to 0.99 for water loss and glycerol and salt gain. RMSE values were <0.09 in all cases. According to the statistical parameters

Table 1. Peleg model parameters.

Solute	Temp. (°C)	K_1	K_2	R^2	RMSE	X_{eq} Peleg	X_{eq} Experim	Relative Error(E)*
Water	50	0.761	1.166	0.921	0.057	1.1545	1.2945	10.81
Salt		5.260	5.704	0.986	0.005	0.1753	0.1382	26.84
Glycerol		0.854	0.803	0.973	0.048	1.2453	0.9933	25.37
Water	70	0.428	1.022	0.968	0.052	1.0718	1.2506	14.34
Salt		3.436	5.775	0.990	0.004	0.1732	0.1500	15.33
Glycerol		0.639	0.909	0.982	0.037	1.1000	0.9255	18.85
Water	90	0.396	1.165	0.972	0.039	1.0562	1.1232	5.96
Salt		2.947	5.670	0.993	0.004	0.1764	0.1515	16.44
Glycerol		0.566	0.799	0.986	0.036	1.2516	1.0457	19.69

$$(*) E = \left| \frac{X_i - X_{ip}}{X_i} \right| 100 \quad \text{E: relative error, } X_i \text{ experimental value and } X_{ip} \text{ predicted value.}$$

that qualify the goodness of fit (RMSE and R^2), the Peleg model adequately described the kinetics of water loss and solute gain in the osmotic dehydration of mackerel slices.

The fitting of the model to the experimental data is shown in Figure 1 for water loss and glycerol and salt gain at 50, 70, and 90 °C.

The predicted and experimental data for water loss and salt and glycerol gain at the three temperatures tested are shown in Figure 2. It is observed that, for most of the conditions analyzed, the differences between the data and the values predicted by the model were small, which was verified by the statistical parameters R^2 and RMSE (Table 1).

The predicted equilibrium values obtained from Equation 3 are shown in Table 1. Peleg model underestimated the equilibrium water content and overestimated the equilibrium salt and glycerol content compared with the experimental equilibrium values.

The dependence of the Peleg rate constant on temperature is represented by the linearized Arrhenius equation (Equation 5):

$$\ln(K_1) = \ln(K_0) - E_a/RT \quad (5)$$

where K_1 is the Peleg rate constant ($\text{h}(\text{g/gdm})^{-1}$), K_0 is a constant ($\text{h}(\text{g/gdm})^{-1}$), E_a is the activation energy (kJ/mol), R the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K).

The plot of the logarithm of the Peleg rate constant vs. $1/T$ would result in a straight line with the negative of the slope equal E_a/R and intercept equal $\ln(K_0)$. The linearity of the data ($R^2 > 0.86$) indicated that the Peleg rate constants for water loss and salt and glycerol gain as a function of temperature represent an Arrhenius-type relationship (Table 2). Higher E_a value indicated greater temperature sensitivity of Peleg rate constant. The rate constant for water loss was found to be more temperature sensitive ($E_a = 16.14 \text{ kJ/mol}$) than the rate constant for salt ($E_a = 14.21 \text{ kJ/mol}$) and glycerol gain ($E_a = 10.12 \text{ kJ/mol}$). E_a value was similar to the values obtained by other authors for osmotic dehydration processes of fishery products (CORZO; BRACHO, 2006; FAVETTO; CHIRIFE; BARTHOLOMAI, 1981).

Table 2. Activation energy for Peleg rate constant during osmotic dehydration of mackerel slices.

Parameter	Water loss	Salt gain	Glycerol gain
E_a (kJ/mol)	16.14	14.21	10.12
K_0 ($\text{h}(\text{g/gdm})^{-1}$)	0.0017	0.025	0.019
R^2	0.862	0.948	0.961

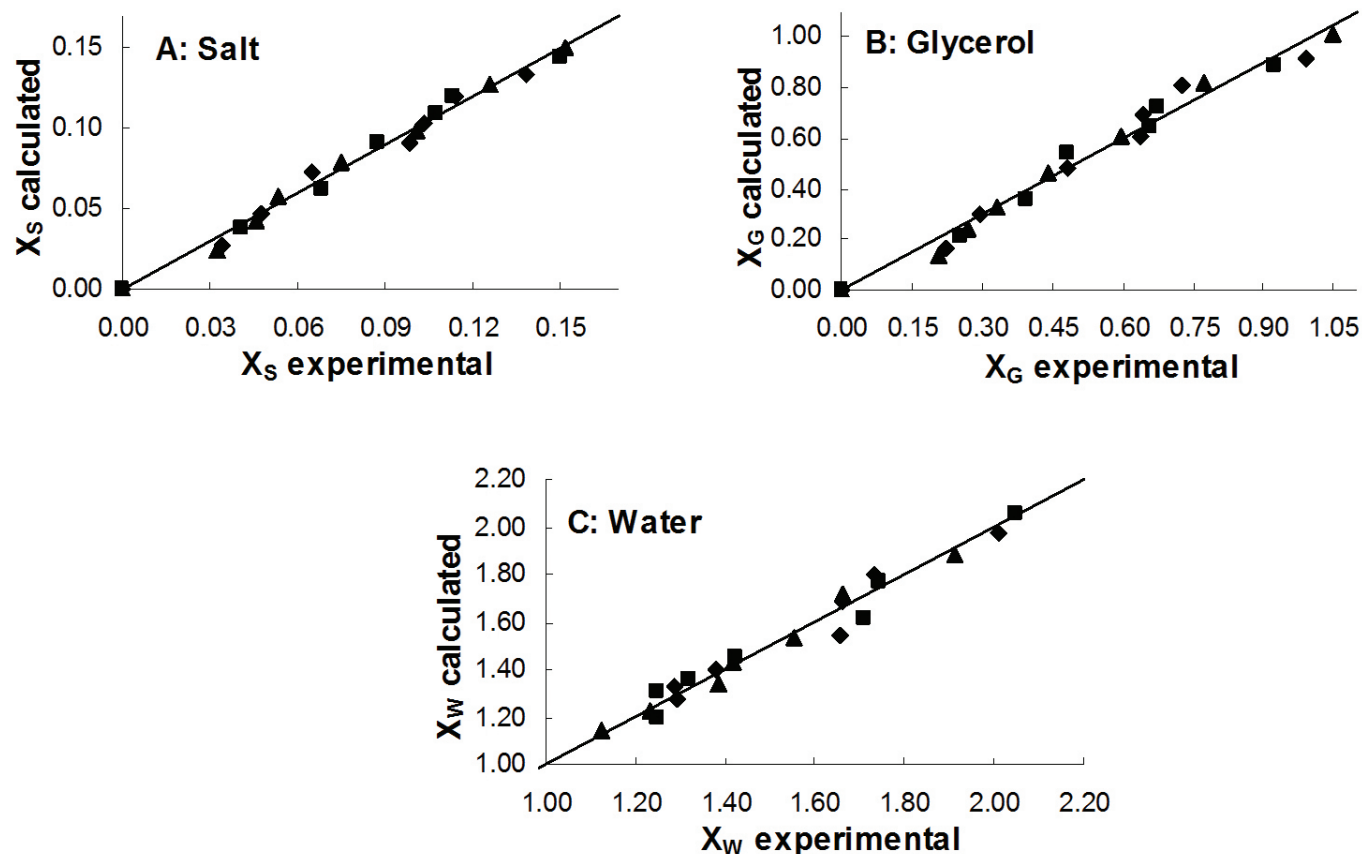


Figure 2. Comparison between experimental and Peleg-estimated data A: Salt, B: Glycerol and C: Water: 50 °C (◆), 70 °C (■), 90 °C (▲).

4 Conclusions

The Peleg model can be used to describe the OD process of mackerel slices in the range between 50 and 90 °C. It can be used for predicting equilibrium values. Temperature in the range between 50 and 90 °C influences the mass transfer phenomena during the OD process of mackerel slices immersed in a solution of glycerol (54% w/w) and salt (7% w/w).

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