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Mathematical modeling and simulation of soluble protein extraction during leaching process in surimi elaboration

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ABSTRACT

This work presents a mathematical model to simulate the extraction process of soluble protein from *sábalo* (*Prochilodus platensis*) during the surimi elaboration. The mathematical model consists of both partial differential and algebraic equations. Central finite difference method and the explicit scheme were applied to discretize the partial differential equation. The resulting model was implemented into the optimization environment General Algebraic Modeling System (GAMS). Experimental data obtained from laboratory scale using *sábalo* as raw material, was used to verify the output results of the proposed model. A good agreement between experimental and simulated extraction yields was obtained ($R^2 = 0.9552$). Once validated, the model was used to investigate the influence of several parameters such as, particle's diameter, volume fraction of the solvent, residence time and agitation velocity on the extraction efficiency. The results are presented and discussed through different case studies.

1. Introduction

The possibility of using Argentinian freshwater species of fishes as raw materials in the elaboration of surimi has been previously addressed (Medina, 2000; Medina and Garrote, 2002; Medina et al., 2010). More precisely, *surubí* (*Pseudoplatystoma coruscans*) and *sábalo* (*Prochilodus platensis*) fish species have been studied.

Specifically, *sábalo* is the most abundant fishery resource in the Argentine lower Río de la Plata basin. Surimi technology presents advisable advantages for the marketing and operation of food products based on proteins from *sábalo*, which is a fish resource only exploited for freshly consume.

Most advances related to surimi technology deal with marine or low fat content fish species of lesser commercial value (Suzuki, 1981; Mireles De Witt and Morrisey, 2002; Karthikeyan et al., 2004; Ohkuma et al., 2008; Sánchez-González et al., 2008). Hence, processing fatty fish species for surimi manufacture faces many challenges, for example: high oil content, intense odor, darker flesh and faster deterioration rate. Anyway, researchers as (Tokunaga and Nishioka, 1988; Nishioka and Tokunaga, 1990) have achieved important improvements in processing technology of fatty species, attaining surimi with excellent functional properties, which is a good prospect for this research area.

Myofibrillar proteins have functional properties, such as emulsifying properties, gel-forming ability and water holding capacity (Ohkuma et al., 2008). Generally, fish myofibrillar protein is thermally and chemically less stable than chicken or mammal proteins (Lanier, 1986). The gelling process involves the association of myofibrillar protein chains which produces a continuous three-dimensional network in which water and other components are ensnared (Sánchez-González et al., 2008). Sarcoplasmic proteins have an adverse effect on the gel formation by interference in myosin cross-linking during gel matrix formation (Suzuki, 1981). Hence, the washing process is a fundamental step to remove sarcoplasmic protein fractions which have the characteristic of being soluble in water or soluble in low ionic strength solutions (Wahyuni et al., 1998). Also, this stage is more critical when fatty fish species are processed, either marine or freshwater, which entails a thorough wash treatment.

The surimi process starts from holding fish, sorting by size and cleaning. After that, process stages for meat separating are achieved, which are heading and gutting by mechanical fish meat separators, a preliminary washing to remove the blood and adherent particles and then, deboning and mincing.

The cyclic washing and rinsing processes of the minced fish, which is also called leaching process are the central stage. The objective of this process stage is to remove soluble compounds

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Nomenclature

a	specific surface for mass transfer (m^2/m^3)
c	protein concentration (mg/ml)
C_D	friction coefficient
D_p	particle's diameter (m)
$D_{\beta\gamma}$	mass diffusivity (m^2/s)
i	spatial node index
j	temporal node index
J_D	Chilton and Colburn factor
k_c	global mass transfer coefficient (m/s)
K	distribution constant
M_w	molecular weight (kDa)
M	number of radial discretization points
N	number of temporal discretization points
R	sample radius (m)
r	variable radius (m)
T	temperature (°C)
t	time (s)
Δt	temporal grid with (s)
v	agitation velocity (m/s)
V_γ	volume of the solvent phase (m^3)
V_β	volume of the minced fish (m^3)
Y	percentage of extraction (%)

Dimensionless groups

Re	Reynolds's number
Sc	Schmidt's number

Greek symbols

ε	volume fraction of solvent
δ	spatial grid with (m)
ρ	density (kg/m^3)
μ	viscosity ($N\,s/m^2$)
θ	residence time (s)

Subscripts

0	at initial
c	cycle
i	at interface
β	minced fish
γ	solvent phase
EP	from the removable proteins
f	at final time
p	particle
T	from total proteins

resulting in concentrated myofibrillar proteins, which mainly contribute to gel formation (Suzuki, 1981; Benjakul et al., 2003).

The leaching process is achieved in three stages. Each stage is formed by a leaching tank, *LTK*, and rotary sieve, *RS*, at the industrial scale (Fig. 1). In this work, the same leaching tank is sequentially used at the laboratory scale to validate the model. In the first two of these cycles distilled water is used as washing stream, and in the last cycle NaCl solution at 0.2% is used.

In this work, a mathematical model is proposed in order to investigate the influence of several operating variables on the washing efficiency, during the elaboration of surimi made from *sábalo*. The following are the main operating variables to be studied: water: mince ratio, temperature, time, number of cycles, and agitation velocity. Also, based on experimental data obtained from laboratory scale, mass transfer coefficients and the distribution constant will be studied.

2. Process modeling

In this section the study of the washing stage in three leaching cycles, which is sketched in Fig. 1, will be presented.

In the proposed mathematical model, the contents of soluble and crude protein in the minced fish and the washing solutions in each cycle, respectively, are defined as parameters in order to follow the evolution of the unit operation. The mass transfer process will be studied at micro (minced particles) and macro (washing equipment) levels to determine protein concentration profiles and mass transfer coefficients of the leaching process.

Each cycle, c, in the washing stage is modeled as solid–liquid extraction of sarcoplasmic proteins within fish meat spheres of known diameter, D_p, coming from the mincing process stage. Soluble proteins are transferred from the solid matrix of each sphere to the bulk phase of the washing solution.

The phenomenon involved by the extraction process is quite complex and several possible mechanisms of mass transfer for food materials have been proposed in the literature in order to model the extraction process (Aguilera and Stanley, 1999). Basically, the following phenomenological steps are considered:

- Entrance of the solvent into the solid matrix.
- Solvent penetration and diffusion inside the solid matrix.
- Solubilization of the soluble compound.
- Transport of the solute to the exterior of the solid matrix by diffusion.
- Migration of the extracted solute from the external surface of the solid into the bulk solution.

The following assumptions are used to derive the mathematical model:

- Soluble proteins diffuse to the surface of each sphere according to Fick's second law
- Model 1-D. Temporal variations of the concentration in the radial direction are contemplated.
- Spherical particles do not change of size and shape during the leaching process.
- The external surface of each sphere is supposed to be surrounded by the extracting solvent.
- Perfect mixture.
- Only the soluble proteins diffuse from the minced fish to the surface. Then, sarcoplasmic proteins are transferred by convection in the interface spheres-solvent.
- Soluble proteins' concentration is homogeneous at the solvent phase.

Based on the above assumptions, the following mathematical model is developed:

$$\frac{(1-\varepsilon_c)}{D_{\beta\gamma}}\frac{\partial c_{\beta,c}(r,t)}{\partial t} = (1-\varepsilon_c)\cdot\frac{\partial^2 c_{\beta,c}(r,t)}{\partial r^2} + \frac{2\cdot(1-\varepsilon_c)}{r}\frac{\partial c_{\beta,c}(r,t)}{\partial r}, \quad 0 < r < R \tag{1}$$

$$c_{\beta,c}(r,t) = \langle c_{\beta 0}\rangle_c, \quad t = 0, \quad \forall\, 0 \leqslant r \leqslant R \tag{2}$$

$$\frac{\partial c_{\beta,c}(r,t)}{\partial r} = 0 \quad r = 0, \quad \forall t > 0 \tag{3}$$

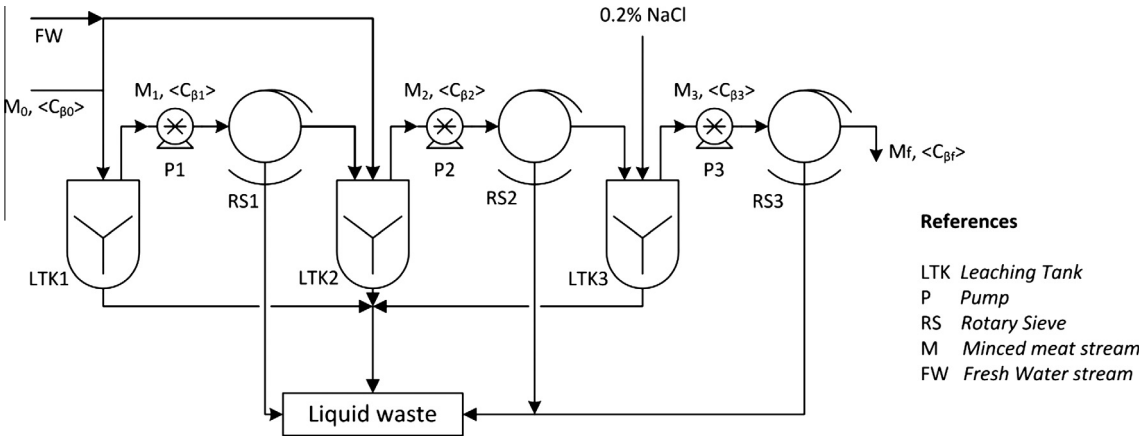

Fig. 1. Flow sheet of continuous leaching stage using three cycles of washing.

$$-D_{\beta\gamma}\frac{\partial c_{\beta,c}(r,t)}{\partial r} = k_{c\gamma}(c_{\gamma i,c} - c_{\gamma,c}), \quad r = R, \quad \forall t > 0 \tag{4}$$

$$\varepsilon_c \frac{dc_{\gamma,c}(t)}{dt} = k_{c\gamma}(1-\varepsilon_c)a(c_{\gamma i,c} - c_{\gamma,c}) \tag{5}$$

Eq. (1) represents the unidirectional diffusion of soluble proteins in the spheres of minced fish (β), being $D_{\beta\gamma}$ the diffusivity coefficient of soluble proteins (β). The multiphase flow with disperse phase consisting of solid particles can be modeled assuming the continuum media theory (Anderson and Jackson's, 1967; Wachem et al., 2001). In fact, the multi-fluid continuum model assumes that different phases behave as interpenetrating continua and the instantaneous variables are averaged over a region that is large compared with the particle spacing but much smaller than the flow domain. New field variables, phasic volume fractions, are introduced to track the fraction of the averaging volume occupied by various phases. This theory was applied successfully in different applications (Fan, 2006; Lu et al., 2003; Renade, 2002). Using this theory, Eq. (1) is derived from the continuity equation for the solid phase.

Eq. (2) assumes homogeneous initial concentration of proteins in the minced fish. Eq. (3) corresponds to the boundary condition at the center of each sphere and states that there is no mass transfer in the center of the meat sphere. Eq. (4) represents the interfacial soluble proteins flux, where $k_{c\gamma}$ is the global mass transfer coefficient in the solvent phase and $c_{\gamma i}$ is the concentration of soluble proteins at the interphase solid-solvent. Finally, Eq. (5) describes the macroscopic mass transfer in solvent phase, where ε_c is the volume fraction of solvent, estimated as:

$$\varepsilon_c = \frac{V_\alpha}{V_\alpha + V_\beta} \tag{6}$$

and a is the specific surface for mass transfer of spherical particles, defined as:

$$a = \frac{6}{Dp} \tag{7}$$

The equilibrium of soluble proteins concentration under diluted assumption is expressed as (Espinoza-Pérez et al., 2007):

$$c_{\gamma i} = K \cdot c_{\beta i} \tag{8}$$

The estimation of the average concentration at the end of each cycle ($t = \theta_c$) of the total crude protein in the meat spheres is obtained by integrating the local concentration over each volume. Specifically, the average concentration of the total crude protein in phase β is expressed as stated below:

$$\langle c_{\beta f}\rangle_c = \frac{\int_0^V c_\beta(r,t)dV}{\int_0^V dV}, \quad t = \theta_c \tag{9}$$

As can be observed in Fig. 1, the following hypothesis is assumed in the model: the initial average concentration of protein in the washed minced is equal to the final average protein concentration of the previous cycle, that is:

$$\langle c_{\beta f}\rangle_c = \langle c_{\beta 0}\rangle_{c+1}, \quad c = 1,2 \tag{10}$$

The percentage of extraction from the total proteins (%) is calculated as the ratio of the amount of proteins extracted after washing and the amount of proteins of the unwashed minced flesh:

$$Y_T\% = \frac{\langle c_{\beta 0}\rangle_1 - \langle c_{\beta f}\rangle_3}{\langle c_{\beta 0}\rangle_1}\% \tag{11}$$

Sarcoplasmic proteins are 25% of the total protein present in the muscle; this percentage corresponds to the maximum of removable protein (Medina and Garrote, 2002; Medina et al., 2012). Then, the maximum percentage of extraction [Y_{EP}] is defined as the ratio of the amount of proteins extracted after washing and the maximum amount of proteins that can be extracted, according to the following constraints:

$$Y_{EP}\% = \frac{\langle c_{\beta 0}\rangle_{EP,1} - \langle c_{\beta f}\rangle_{EP,3}}{\langle c_{\beta 0}\rangle_{EP,1}}\% \tag{12}$$

where

$$\langle c_{\beta 0}\rangle_{EP,1} = 0.25 \cdot \langle c_{\beta 0}\rangle_1 \tag{13}$$

3. Materials and methods

3.1. Materials

Fresh *sábalos* (*Prochilodus platensis*) were purchased from a local market and processed within 24 h of capture. *Sábalo* samples were covered with crushed ice in order to avoid increasing temperatures during transportation, and directly brought to the laboratory for further processing. Manually, skinless and deboned fillets were obtained and minced in a meat grinder adapted with a hole mincing plate, which made it possible to obtain spherical particles of 5 mm of diameter.

3.2. Preparation of frozen surimi mixture

Surimi was prepared at laboratory scale. Every stage (heading, gutting, washing, deboning and mincing) was carried out at an average ambient temperature of 10 °C to minimize degradation of the fish muscle.

The following washing conditions were tested: Temperature (2–10–18 °C), volume fraction of the solvent phase (0.666–0.777–0.833) and residence time (60–277 and 420 s).

In a previous work, Medina and Garrote (2002) found that the washing conditions to produce a surimi of acceptable functional quality were: 3 washing cycles of 4.6 min/cycle, using a washing media:mince ratio of 3.5:1 at a process temperature of 18 °C. These washing conditions were obtained for the laboratory scale production of surimi made from *surubí* and applied with satisfactory quality results to the elaboration of surimi made from *sábalo* using conventional washing method (Medina et al., 2010).

3.3. Protein determination

In order to characterize chemically the meat and surimi, crude protein (N × 6.25) content the Kjeldahl method according to standard AOAC methods (1995) was used. Also, protein concentration at the solvent phase was determined by spectrophotometric determination according the method of Whitaker (2001). Results are presented as mean values ± standard deviation of three measurements.

3.4. SDS–PAGE electrophoresis

In order to determine protein's molecular weight in the washing solutions after each cycle, protein patterns were analyzed by SDS–PAGE according to the method of Lammeli (1970). Protein samples were solubilized in 0.125 M Tris–HCl buffer (pH 6.8), containing 2% SDS, 2% 2-mercaptoethanol, 10% glycerol and 0.025% bromophenol blue. The homogenate was incubated at 85 °C for 60 min, followed by centrifugation at 8000 g for 5 min at room temperature. The samples (5 μg protein were loaded into the polyacrylamide gel. The electrophoretic pattern of proteins was determined using polyacrylamide 10% gel slabs with a constant current of 20 mA per gel.

3.5. Protein extraction

To validate model, output results obtained by the proposed mathematical model were compared with experimental data obtained from the laboratory scale washing equipment. Experimental data were obtained using a cylindrical tank made of stainless steel with 50 cm of length and 6 cm of diameter, containing a cylindrical basket for the minced fish of 30 mesh-holes. The washing system is provided by a thermostatic bath in order to maintain the system temperature constant and a reducing motor with a power selector in order to regulate the agitation. In the experiments, the washing system was filled with 300 g of *sábalo* minced flesh. Distilled water was used as solvent in the first two cycles and 0.2% NaCl solution in the last leaching cycle. After the third cycle, the drained washed minced fish was mixed with cryoprotectants at a 1:1 ratio of sucrose to sorbitol at a level of 8% at the final block basis, and kneaded for about 4–5 min. After that, the mixture was chopped into blocks and finally frozen and stored at −25 °C.

During the experiments, solvent samples using a siphon arm were taken with 1 min of frequency in order to determine protein concentration at the solvent phase (γ). Due to the washing equipment's design, washed minced samples could not be taken during the leaching process; therefore, protein concentration in the washed minced (β) was measured at the beginning and end of each washing cycle.

3.6. Model solution strategy

Eqs. 1, 3, 4, and 5 were discretized using the central finite difference method (CFDM) and the explicit second-order accurate method in both space and time, defining:

$$\delta = \frac{R}{M}; \quad \Delta t_c = \frac{\theta_c}{N} \tag{14}$$

for the radial and temporal variations, respectively, with $M = 20$ and $N = 50$. The chosen values of δ and Δt_c fulfill the stability criterion of the discretization method, as result, non-divergent or non-oscillatory protein concentration profiles are expected.

The second-order accurate in time and in space ($0[(\Delta t)^2, (\Delta r)^2]$) is the chosen method and is applied as follows:

3.6.1. First derivatives

The two-point formulae was used for internal nodes, that means $i \neq 0, 20$ and/or $j \neq 0, 50$. The three-point formulae was applied for boundary nodes, i or $j = 0$ or 10. Three or four-point formulae were useful to compute the first derivative at a node on the boundary by using more than two grid points on one side of the boundary in order to improve the accuracy of approximation (Ozisik, 1994).

3.6.2. Second derivatives

The *central* finite difference approximation is used at internal nodes ($i \neq 0, 20$ and/or $j \neq 0, 50$), and the *forward* finite difference approximation is applied at the origin node, $i = 0$, at the boundary condition in the center of the sphere.

Thus, the following constraint computes the approximation of Eq. (1) for internal nodes:

$$\begin{aligned}(1-\varepsilon_c)\cdot\frac{1}{D_{\beta\gamma}}\frac{(c_{\beta,c}(i,j+1)-c_{\beta,c}(i,j-1))}{2\Delta t_c} \\ = (1-\varepsilon_c)\cdot\left[\frac{c_{\beta,c}(i-1,j)-2\cdot c_{\beta,c}(i,j)+c_{\beta,c}(i+1,j)}{\delta^2}+\frac{2}{(i-1)\delta}\right. \\ \left.\left[\frac{c_{\beta,c}(i+1,j)-c_{\beta,c}(i-1,j)}{2\cdot\delta}\right]\right], \qquad i:1,2,\ldots,19;\ j:1,2,\ldots,49\end{aligned} \tag{15}$$

The following constraint computes the temperature variation of the internal nodes at final time:

$$\begin{aligned}(1-\varepsilon_c)\cdot\frac{1}{D_{\beta\gamma}}\frac{(c_{\beta,c}(i,j-2)-4\cdot c_{\beta,c}(i,j-1)+3\cdot c_{\beta,c}(i,j))}{2\Delta t_c} \\ = (1-\varepsilon_c)\cdot\left[\frac{c_{\beta,c}(i-1,j)-2\cdot c_{\beta,c}(i,j)+c_{\beta,c}(i+1,j)}{\delta^2}+\frac{2}{(i-1)\delta}\right. \\ \left.\left[\frac{c_{\beta,c}(i+1,j)-c_{\beta,c}(i-1,j)}{2\cdot\delta}\right]\right], \qquad i:1,2,\ldots,19;\ j:50\end{aligned} \tag{16}$$

The following are the constraints related to the discretizations of Eqs. (3) and (4), which are the boundary conditions at the center and surface, respectively:

$$\frac{-3\cdot c_{\beta,c}(i,j)+4\cdot c_{\beta,c}(i+1,j)-c_{\beta,c}(i+2,j)}{2\cdot\delta}=0, \quad i:0;\ j:1,2,\ldots,50 \tag{17}$$

$$\begin{aligned}-D_{\beta\gamma}\frac{c_{\beta,c}(i-2,j)-4\cdot c_{\beta,c}(i-1,j)+3\cdot c_{\beta,c}(i,j)}{2\cdot\delta} \\ = k_{c\gamma}(c_{\gamma i,c}(j)-c_{\gamma,c}(j)), \quad i:20;\ j:1,2,\ldots,50\end{aligned} \tag{18}$$

Eqs. (19) and (20) compute the approximation of Eq. (5) for internal nodes and final time, respectively.

$$\varepsilon_c \cdot \frac{(c_{\gamma,c}(i,j+1) - c_{\gamma,c}(i,j-1))}{2\Delta t_c} = k_{c\gamma} \cdot a \cdot (c_{\gamma i}(j) - c_\gamma(j)), \quad i:1,2,\ldots,19;\ j:1,2,\ldots,49 \tag{19}$$

$$\varepsilon_c \cdot \frac{(c_{\gamma,c}(i,j-2) - 4 \cdot c_{\gamma,c}(i,j-1) + 3 \cdot c_{\gamma,c}(i,j))}{2\Delta t_c} = k_{c\gamma} \cdot a \cdot (c_{\gamma i}(j) - c_\gamma(j)), \quad i:1,2,\ldots,19;\ j:50 \tag{20}$$

Average concentration of phase β was obtained by integrating the node concentrations ($c_\beta(r,t)$) over volume (Eq. (9)) by trapezoidal rule.

Thus, Eqs. (6)–(20) are basically the model constraints that approximate the leaching process in three cycles during surimi manufacture. This work is the first step of a challenging project, which consists of the model-based optimization of a full-scale facility to manufacture surimi. Therefore, this mathematical model will be the basis of the optimization model. In this work, the model is implemented in GAMS (Brooke et al., 1992) but it is only used to simulate the leaching stage. To that end, a dumb variable is optimized subject to the equation system of the simulation mathematical model. Due to the fact that the model is formed by partial differential equations, a discretization method must be used to implement the model in GAMS. Then, a set of nonlinear equations is achieved because of the appearance of bilinearities in the estimation of the model parameters (for example, mass diffusivity and mass transfer coefficient). An NLP local solver based on the generalized reduced gradient algorithm CONOPT 2.041 was used to solve the model (Drud, 1992).

Intel Core i7 2670QM 2.20 GHz processor and 8 GB RAM has been used to perform the simulations.

3.7. Parameter estimation

3.7.1. Distribution constant

The distribution constant (K, Eq. (8)) was calculated by linear regression of protein at equilibrium. Fig. 2 plots the equilibrium protein concentration at different solvent:mince ratio and cycles. From this figure it was obtained that the distribution constant (K) is approximately equal to 0.006 (R^2 = 0.921). That is, under protein saturation concentration in solvent:

$$c_{\gamma i} = 0.006 \cdot c_{\beta i} \tag{21}$$

The resulting value of K is small, which indicates a low degree of extraction. Therefore, it is important to highlight the significance of several cycles of extraction during the leaching process to extract soluble proteins.

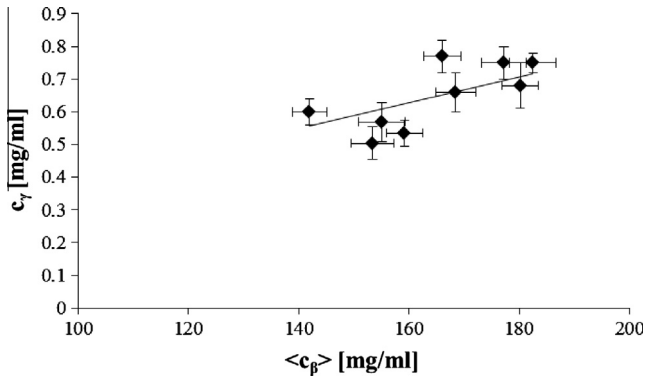

Fig. 2. Equilibrium protein concentration obtained at different extraction cycles and solvent volume fraction.

3.7.2. Diffusion coefficient

The semi-empirical equation of Polson (1950) was used to estimate the protein diffusion coefficient, D_β, which is recommended for biological solutes:

$$D_{\beta\gamma} = \frac{9.40e-15 \cdot T}{\mu \cdot (Mw_\beta)^{1/3}} \tag{22}$$

Fig. 3 shows SDS–PAGE patterns of water–soluble proteins in the surimi wash-water subjected to different washing cycles. Soluble proteins correspond to multiple bands in the range of 28–97 kDa. However, majority bands of protein fractions in the order of 45 kDa can be observed, therefore a major value of 50 kDa is used as average molecular weight for the estimation of the diffusivity coefficient with Eq. (22).

Comparing with other fish species, Karthikeyan et al. (2004) obtained by SDS–PAGE patterns of soluble proteins for Sardine (*Sardinella longiceps*) different bands in the range of 29–97 kDa. Mendes and Nunes (1992) and Kawai and Shinano (1991) reported predominance of bands of 94 and 56 kDa of soluble proteins during the manufacture of surimi made from sardine, *Sardina pilchardus* and *Sardinops melanostictus*, respectively.

3.7.3. Global mass transfer coefficient

Suspension of solid particles during leaching in an agitated system can be assumed as a fluidized bed (Geankoplis, 1993). The overall mass transfer coefficient was calculated using the correlation proposed by Geankoplis (1993) for fixed beds and also valid for fluidized beds of spheres in the Reynolds number range of 10–4000:

$$J_D = \frac{0.4548}{\varepsilon_c} \cdot \mathrm{Re}^{-0.4069} \tag{23}$$

$$kc_\gamma = \frac{J_D \cdot v}{Sc^{2/3}} \tag{24}$$

where

$$Re = \frac{Dp \cdot \rho_\gamma \cdot v}{\mu_\gamma} \tag{25}$$

and

$$Sc = \frac{\mu_\gamma}{D_\beta \cdot \rho_\gamma} \tag{26}$$

The velocity of solvent around the particles, v, for every cycle, was estimated considering an agitation speed of 60 rpm, and also an average agitation distance, obtaining a value of 0.15 m/s.

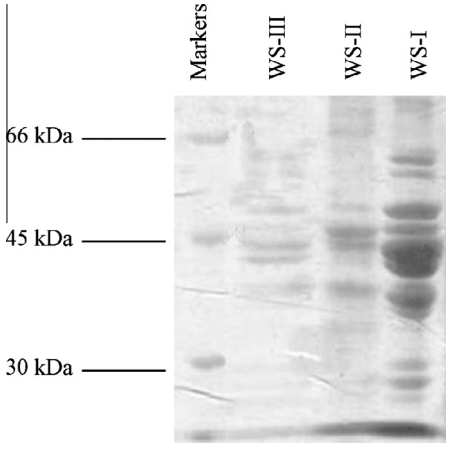

Fig. 3. SDS–PAGE patterns of water–soluble proteins in surimi wash-water at different wash stages.

Table 1
Operating conditions used for model validation.

Experimental run	Temperature T (°C)	Volume fraction of solvent ε_c	Residence time Θ_c (s)	Agitation velocity v (m/s)	Particle diameter D_p (m)
1	18	0.777	277	0.15	0.005
2	10	0.777	277	0.15	0.005
3	2	0.777	277	0.15	0.005
4	18	0.666	277	0.15	0.005
5	18	0.833	277	0.15	0.005
6	18	0.777	60	0.15	0.005
7	18	0.777	420	0.15	0.005

Eq. (24) takes into account the hydrodynamic effects of the model and it is validated for the regime used in the experiments.

4. Results

4.1. Model validation

To validate the model different experimental operating conditions were tested and the protein extraction yields are compared. Variations of the temperature, volume fraction of solvent and residence time were taken into account to verify the model. Table 1 resumes the operating conditions used for model validation.

For the experimental run 1, Fig. 4 shows simulated average protein concentration profiles and experimental data in the washed minced fish during the three cycles of extraction and Fig. 5 presents simulated and experimental protein evolution in solvent during the extraction. For these experiment's conditions, the diffusion and global mass transfer coefficients are 4.366e − 11 m^2/s and 7.54e − 6 m/s, respectively.

Diffusion coefficient for fish proteins are in the order of 10e − 11 m^2/s according to the values reported by Barrow (1986) and Canpolar Inc. (1988), which is in agreement with the diffusion coefficient obtained.

In addition, Fig. 6 compares the experimental and simulated percentages of extracted proteins for the experimental runs presented in Table 1.

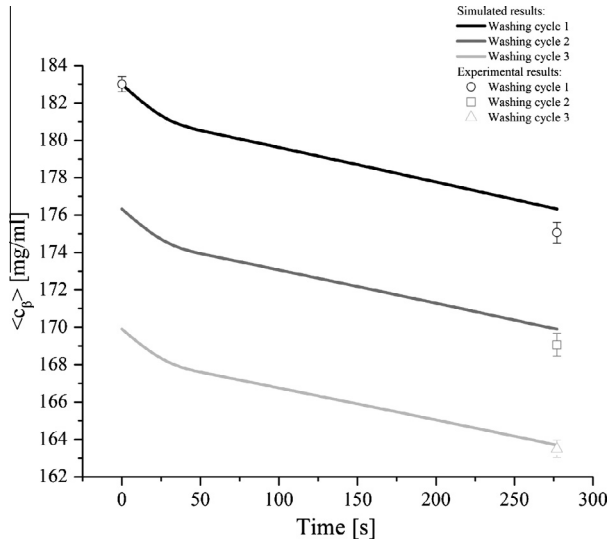

Fig. 4. Experimental and simulated results of protein content in the washed mince during the washing process (T = 18 °C, Θ_c = 277 s, ε_c = 0.777, D_p = 0.005 m and v = 0.15 m/s).

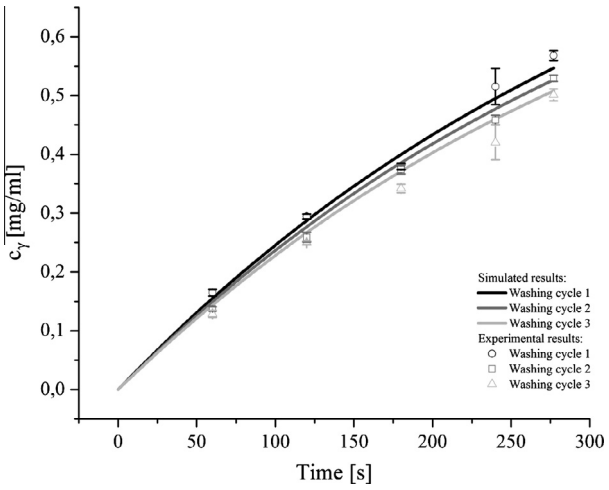

Fig. 5. Experimental and simulated results of protein content in the solvent phase during the washing process (T = 18 °C, Θ_c = 277 s, ε_c = 0.777, D_p = 0.005 m and v = 0.15 m/s).

The results indicate a good agreement among experimental and simulated extraction yields (R^2 = 0.9552). Different operating conditions were tested in an adequate range to this process stage and the model responded with acceptable results.

4.2. Process analysis

After model validation, simulations to study the effects of particle diameter, mince-solvent ratio, and residence time and agitation velocity is presented in this section in order to compare each case study with the experimental conditions reported for the experimental run 1 in the model validation section. The input data used at the different case studies [CS] is presented in Table 2.

4.2.1. Case study I: Influence of particle diameter

In this section, simulations of the leaching process changing the particle diameter will be carried out. If in the previous stage of mincing, a 7 mm diameter hole plates is used, 2 mm more than the used for the experimental part, the percentage of extracted proteins decreases from Y_T = 10.546% (Y_{EP} = 42.183%) to Y_T = 8.28% (Y_{EP} = 33.12%) for the same residence time compared to the time informed for the experimental run 1.

Analyzing the residence time, if the percentage of extracted proteins is expected to be the same that for 5 mm diameter hole plates, the residence time per cycle needs to be 402 s. Therefore,

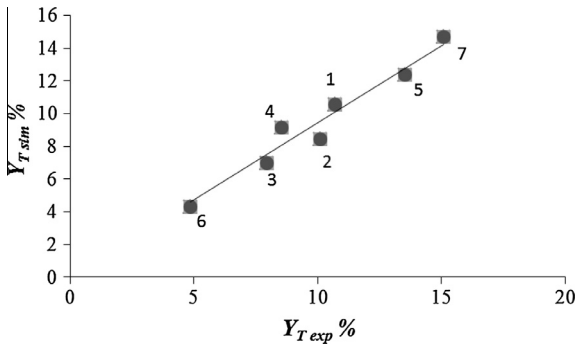

Fig. 6. Experimental vs. simulated total protein extraction percentages.

Table 2
Input data for case studies [CS].

Parameter	CS I	CS II	CS III
Particle diameter, D_p (m)	0.007	0.005	0.005
Distribution constant, K (dimensionless)	0.006	0.006	0.006
Volume fraction of solvent, ε (dimensionless)	0.777	0.667	0.777
Specific surface for mass transfer, a (m^2/m^3)	190.47	400	266.67
Water temperature, T (°C)	18	18	18
Residence time, Θ_c (s)	277	N/A	277
Protein's diffusion coefficient, $D_{\beta\gamma}$ (m^2/s)	4.366e−11	4.366e−11	4.366e−11
Density of the solvent phase, ρ_γ (kg/m^3)	998.104	998.104	998.104
Viscosity of the solvent phase μ_γ (Pa s)	1.052e−3	1.052e−3	1.052e−3
Global mass transfer coefficient, kc_γ (m/s)	6.79e−6	8.79e−6	N/A
Agitation velocity, v (m/s)	0.15	0.15	N/A
Percentage of extraction Y_T (%)	N/A	10.546%	N/A

an increment of 125 s. per cycle is required respect to the experimental run 1.

Not only an increment of operating cost is evident for particle diameter of 7 mm; also meat particles larger than 5 mm make more difficult to remove the sarcoplasmic proteins and other impurities during the subsequent washing process (Lee, 1984; Park and Lin, 2005).

4.2.2. Case study II: Influence of residence time and water:mince ratio

An important aspect in surimi technology is the minimization of water usage for leaching. Lin and Park (1997) investigated minimizing water consumption by reducing the solvent:mince ratio and increasing the washing time and cycles.

An approach to achieve the same washing effect than the experimental conditions with less water, but maintaining three washing cycles, would be to increase the washing time with a lower solvent:mince ratio. Thus, for a water:mince ratio equal to 2:1 ($\varepsilon_c = 0.666$), the required residence time per cycle to extract 10.546% of the total proteins is 342 s, which means an increment of 65 s (23.46%) per cycle compared to experimental run 1 ($\varepsilon_c = 0.777$).

Consequently, an evident trade-off between operating costs (amount of washing solvent and electricity consume) and extraction yields exists. Therefore, further studies of optimization are required to analyze it.

4.2.3. Case study III: Influence of agitation velocity

Blakerbrough (1967) states that for a liquid–solid dispersion, increased agitation over and above that necessary to suspend small particles has very little effect on the mass transfer coefficient to the particle. To analyze this phenomenon, the sedimentation velocity has been calculated, and different simulation runs has been done increasing the agitation velocity above this value in order to study the percentage of protein extraction. The results are presented in Fig. 7.

For the suspension of minced fish during leaching, considering a particle diameter of 5 mm, the sedimentation velocity is 0.07 m/s (friction coefficient for transient flow regime (Camp, 1946), $C_D = 18.5/Re^{0.6} = 0.566$ and Reynolds number, $Re = 334.36$). It can be noticed that with Reynolds numbers greater than 500 the flow regime is turbulent (Fueyo and Dopazo, 1995).

For an agitation velocity, $v = 0.6$ m/s and residence time, $\theta_c = 277$ s/cycle, the total of the removable proteins are extracted,

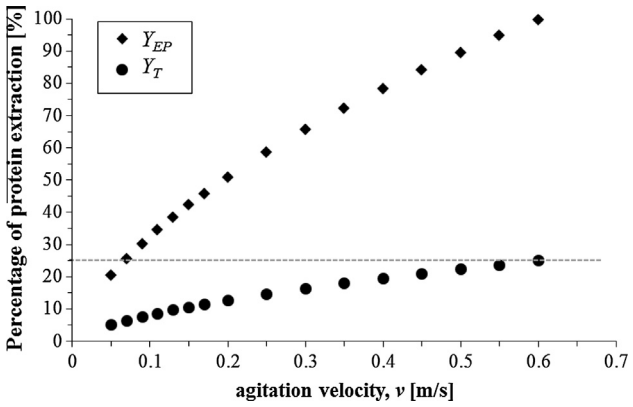

Fig. 7. Relationship between agitation velocity and percentage of extraction for three extraction cycles of $\Theta_{1,2,3} = 277$ s/cycle.

as can be observed in Fig. 7. However, from the point of view of product quality, with the experimental conditions ($v = 0.15$ m/s, $Re = 711.57$), surimi's gels of adequate quality have been obtained (Medina et al., 2010; Medina et al., 2012). Therefore, a trade-off between percentage of extraction and quality aspects is evidenced, being not necessary to extract all the removable proteins in order to obtain adequate quality (Green and Lanier, 1999).

5. Conclusions

A mathematical model to study the soluble protein leaching process during the elaboration of surimi made with *sábalo* (*Prochilodus platensis*) was developed. The model was successfully verified using experimental data. Also, experimental data were used to estimate the distribution constant. As described in the manuscript, the diffusion coefficient and the mass transfer coefficient were estimated with semi-empirical equations. For modeling purpose, it was assumed that spherical particles of fish meat are obtained in the mincing stage and are then subjected to the leaching process. The influence of the particle diameter, agitation velocity residence time and water:mince ratio on the extraction efficiency was investigated. The results reveal that, for a same residence time (277 s), the percentage of extracted proteins decreases almost 21.48% (from 10.546% to 8.28%) when the particle diameter increases from 5 to 7 mm.

Also, it was investigated the trade-offs between washing performance, amount of washing water and washing residence time. It was concluded that for a water:mince ratio equal to 2:1 ($\varepsilon_c = 0.666$), the required residence time per cycle to extract 10.546% of the total proteins is 342 s, which means an increment of 65 s (23.46%) per cycle compared to a water:mince ratio equal to 3.5:1 ($\varepsilon_c = 0.777$). Thus, an evident trade-off between the amount of washing water (which is strongly related to the operating cost) and extraction yields exists.

As future work, the simultaneous optimization of the whole production process of surimi will be addressed. According to this, the simulation model here presented will be used as base model and will be adequately expanded to optimize the design of the entire production process from a cost point of view. In addition, the inclusion of investment (sizes of extraction units) and operating costs (amount of washing water, pumping and electricity costs, such as others) will be also considered.

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