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Optimal Design of the Leaching Stage in the Manufacturing Process of Surimi Gel

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ABSTRACT: The leaching stage in the manufacturing process of surimi gel requires a large amount of wash water contributing to a high operating cost. Therefore, the minimization of the wash water demand is essential for a low cost operation. In this paper, a complete mathematical model for the simultaneous optimization of the process configuration and the operating conditions of the continuous leaching process is presented. A superstructure formulation that embeds not only known process arrangements for the leaching process but also hybrid configurations is proposed. It is modeled as a nonlinear programming mathematical model. Given the design goal (extraction rate), the aim is to obtain the best process arrangement and operating conditions at minimum wash water demand. An interesting result obtained from the superstructure optimization is that, for a given extraction yield of soluble protein and total volume of leaching tank, the same minimum fresh water requirement is obtained with different leaching arrangements and with different distributions of flow rates. In addition, a sensitivity analysis was conducted in order to study the influence of the total volume of leaching tanks, number of leaching cycles, and extraction yield of soluble protein on the minimum fresh water consumption (countercurrent arrangement). As expected, for a given percentage of extraction from soluble proteins, the fresh water consumption significantly decreases, following an exponential decay law, as the total volume increases. A sensitivity analysis reveals that the minimum theoretical water consumption is obtained for four or higher number of washing cycles.

■ INTRODUCTION

The manufacturing stage of surimi gel is an old traditional-food preparation technique. Design procedures based on statistical methods or on trial-and-error techniques have been traditionally used. Using these techniques, it may be difficult to analyze and therefore to improve the manufacturing process if the number of variables to be analyzed is too large. Currently, one of the major challenges in the design of food engineering processes is to make decisions based on physics-based mathematical models. Certainly, they allow the understanding of the involved mechanisms and the identification of the process variables that have an important impact on the product quality and on the investment and operating costs.

Figure 1 shows the basic steps in the manufacturing process of frozen surimi. It starts from holding fish, sorting by size, and cleaning. After that, several process stages are needed for fish meat separation, (heading, gutting, preliminary washing, deboning, and mincing). The preliminary washing is needed to remove the blood and adherent particles. Next, in the leaching process, the minced meat acquires gel-forming capability. Finally, the leached mince is then refined, dewatered, and mixed with cryoprotectants (sugar, sorbitol, polyphosphate) for long-term frozen storage.[1,2]

On the basis of round fish weight, the yields from processing different fish species into surimi varies from 22 to 32%.[3] For this study, a production yield of 47% of minced flesh before the leaching process is estimated, resulting in a surimi yield of 24% from the weight of the raw fish input. The total requirement of fresh water for the manufacturing process is one of the most important aspects to be considered. More than 65% of the total amount of fresh water required by the entire process is used in the leaching process resulting in high operating cost.[4] Therefore, the leaching process is one of the most critical stages listed in Figure 1, and its optimization is the most important key to obtain cost-effective designs. It involves several washing cycles of minced meat with aqueous solution to remove fat, pigments, and other water-soluble substances and to produce a crude myosin extract.[5] Excessive washing not only increases the cost of water usage and wastewater treatment but also results in a loss of myofibrillar proteins.[3]

In this work, the leaching process is performed by three continuous cycles of washing, each with a separate set of leaching tank and rotary sieve.[6]

Figure 2 illustrates the two most used leaching configurations. As shown, the conventional leaching process entails copious amounts of fresh water in a lateral flow direction with minced fish.[7] Fresh water is added at each one of the three leaching tanks, and the wastewater is subsequently removed from the meat by a rotary sieve before the next washing stage.[4] This configuration will be hereafter referred as conventional arrangement. On the other hand, in the other configuration, the fresh water is only

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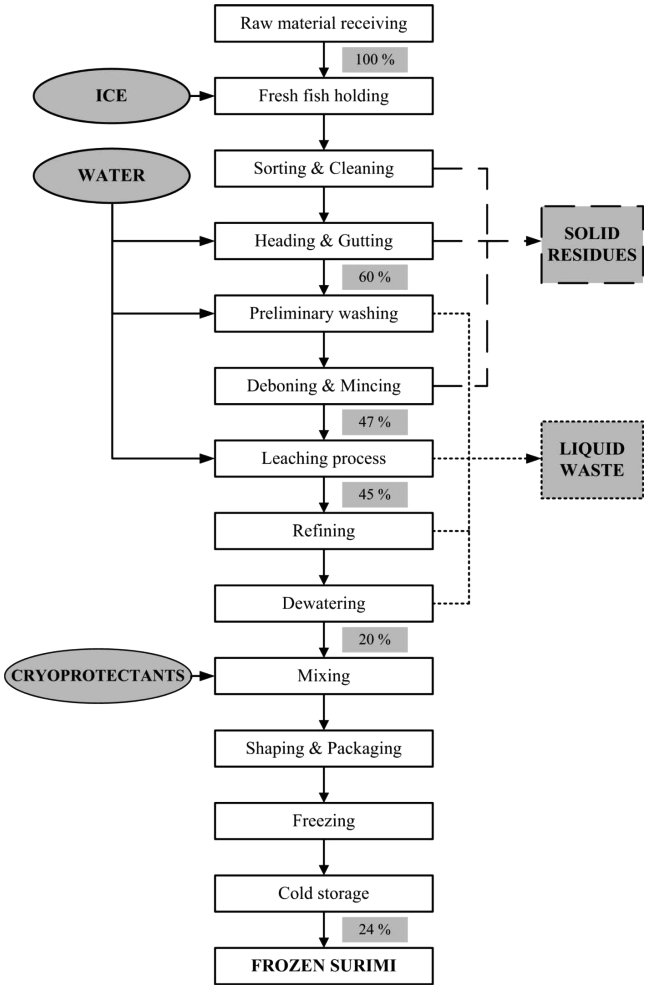

Figure 1. Flowchart for the manufacturing process of surimi gel.

supplied into the third cycle. Then, the wash water coming from the second and third cycles is recycled to the previous cycle (first and second cycles, respectively) as indicated in Figure 2, while the wash water leaving the first stage is discharged due to the high levels of undesirable impurities.[2,8] As shown, the direction of the flow of the wash water is opposite to the direction to the flow of the stream to be treated. This configuration will be hereafter referred to as countercurrent arrangement. It has been widely used in the extraction of food components,[9−11] and it may be successfully applied in the manufacturing process of surimi gel in order to achieve a more efficient use of the wash water.

Carawan and co-workers[4] as well as Green and Lanier[8] compared the conventional and countercurrent configurations for the leaching process of minced fish muscle in the manufacturing process of surimi gel in terms of the effects of water-soluble nitrogen components. They concluded that the countercurrent configuration removes an equal or higher amount of soluble proteins than that removed by the conventional arrangement, and also requires approximately one-third of the amount of fresh water in comparison to the conventional arrangement. Kanda and co-workers[12] proposed to improve the overall yield (or reduce the requirement of fresh water) by increasing the ratio of surface and volume of mince particles using a 1 mm gap mince crusher in the mincing stage. They concluded that using 1 mm gap in the crushing stage, the total yield was increased 2% respect to the convention mincing (5 mm mince). Lin and Park[13] approached the water usage problem by investigating the water to mince ratio combined with more washing cycles and washing time. They found that the myosin heavy chain content, water retention, and whiteness of the washed mince decreased as the water to mince ratio decreased whereas increasing the number of wash cycles and time gave a higher moisture content product.

A review of the state of the art in the production technology of surimi gel indicates that no studies were found on the use of advanced mathematical programming techniques and conventional optimization algorithms for modeling and optimization purposes.

The purpose of this work is to develop a mathematical model for the optimization of the process configuration and the operation conditions of the continuous leaching process. As will be described later, the mathematical model is based on a superstructure formulation in order to include several process arrangements for simultaneous optimization. Conventional and countercurrent arrangements (Figure 2) including a hybrid arrangement which results from the combination of both arrangements are embedded and optimized simultaneously in order to the determine the best flow-pattern of the recycle streams, sizes of pieces of equipment, and operating conditions as well. The development and implementation of a mathematical model with these decisions is a challenge and novel task in the food processing industry.

The optimization model is based on a previous work in which simulation runs of the leaching process were performed for batch processing of surimi using *sábalo* (*Prochilodus platensis*) as raw material. Thus, the simulation model previously developed is now extended for optimization purposes, including several alternative recycle streams as optimization variables. In addition, the residence time, water volume fraction, agitation velocity, fluxes, and temperature are also considered as optimization variables.

GENERAL CHARACTERISTICS OF FISH PROTEINS

The eaten part of a fish specimen varies in accordance with the species, form, catch age, and time (after or before the swapping time) but represents approximately 45−50% of the whole fish weight. The fish muscle contains three groups of proteins:[14]

Sarcoplasmic proteins are soluble in water or in salt solution of low ionic strength and normally found in the cell plasma where they act as enzymes and oxygen carriers. They approximately comprise from 18 to 25% of total proteins.

Myofibrillar proteins are the largest proportion of muscle proteins, 70−79% of total proteins. The major components are myosin, actin, tropomyosin, and troponin.

Stroma proteins are those making up the connective tissues, surrounding the muscle fibers, and in the skin; they include collagen and elastin. These proteins comprise about 3−5% of total protein.

Myofibrillar proteins have functional properties, such as emulsifying properties, gel-forming ability, and water holding capacity.[15] Generally, fish myofibrillar protein is thermally and chemically less stable than chicken or mammal proteins.[16] 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.[17] Sarcoplasmic proteins have an adverse effect on the gel formation by interference in myosin cross-linking during gel matrix formation.[18] 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.[1,19] Also, this stage is more critical when fatty fish species are processed, either marine or freshwater, which entails a thorough wash treatment.

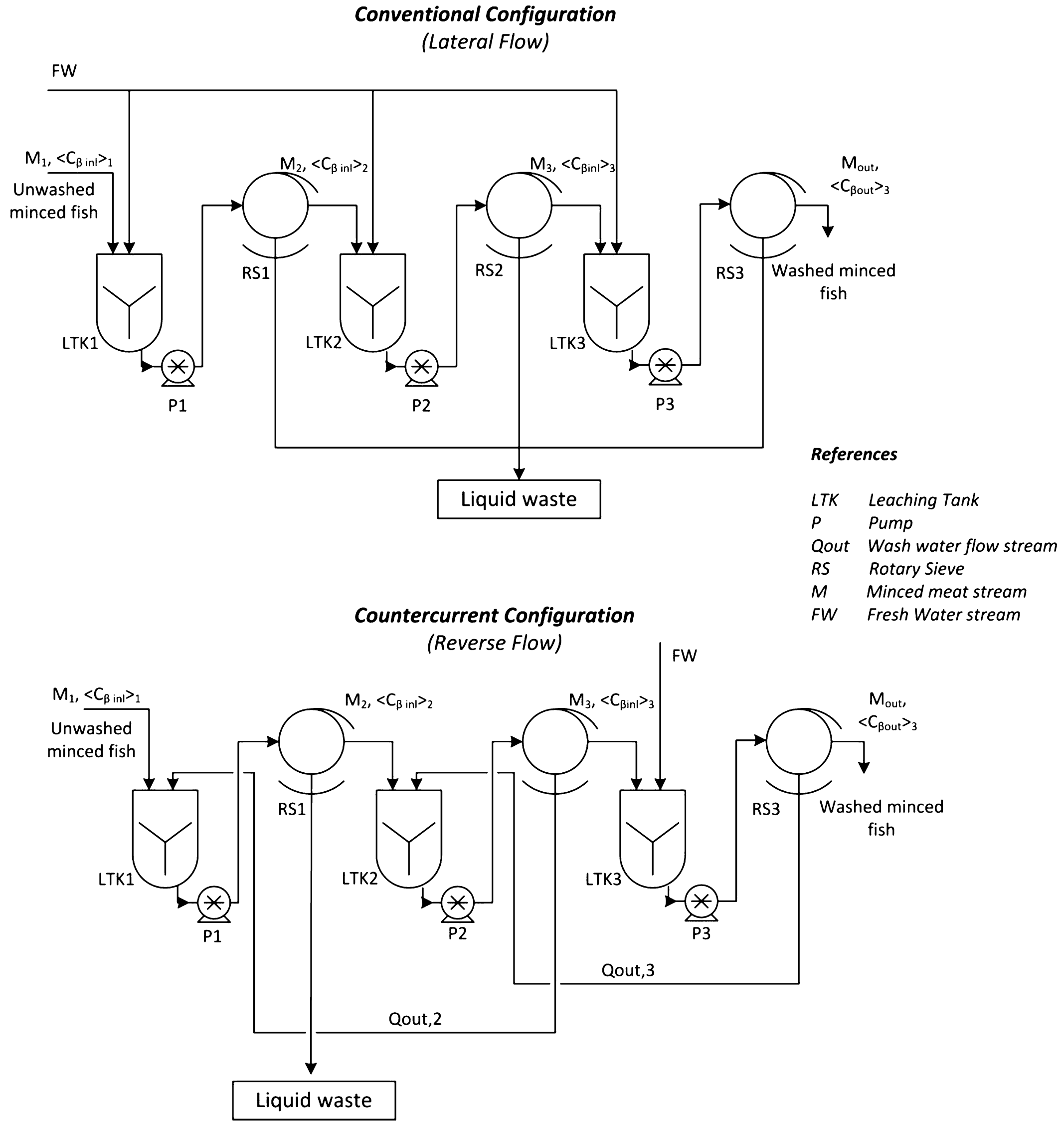

Figure 2. Conventional and countercurrent configurations.

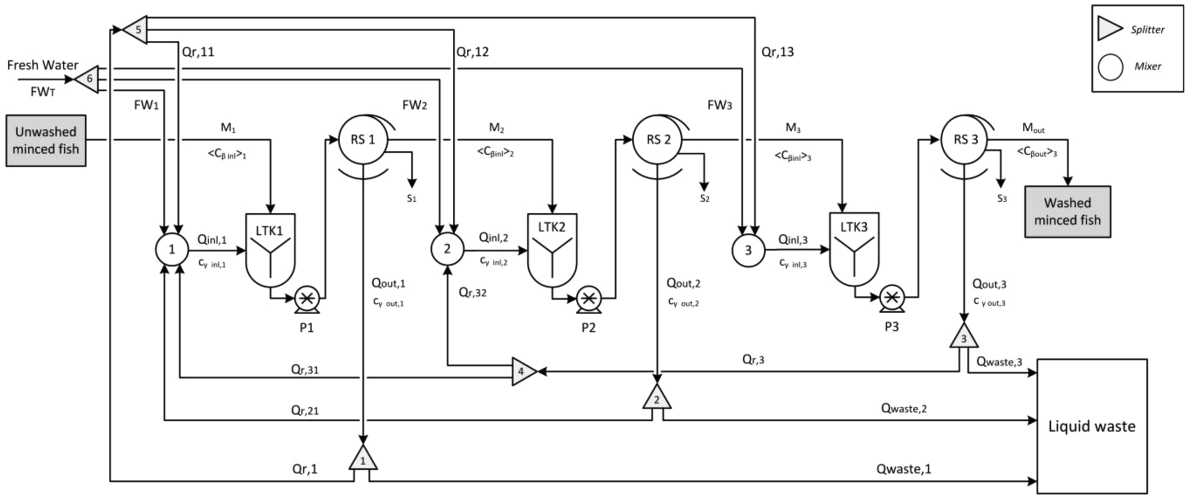

Figure 3. Superstructure of alternative configurations for the leaching process.

A significant loss of the functional properties of myofibrillar proteins can happen when protein denaturation occurs during frozen storage. Cryoprotectants have a beneficial effect on frozen storage, protecting the elasticity and cohesiveness of the gel.

Therefore, various cryoprotectants, such as sucrose, sorbitol, and polyphosphates, have been blended with surimi.[20] Sucrose and sorbitol improve the gel-forming ability, increase protein solubility, and decrease cooking loss.[21,22]

■ PROBLEM STATEMENT

Figure 3 shows the superstructure of alternative configurations under study. It embeds the conventional and countercurrent arrangements including also a hybrid alternative that may result from the combination of both arrangements. For instance, it includes the possibility of recycling wash water stream from the first cycle ($Q_{\mathrm{out},1}$) to the three leaching tanks (LTK). Summarizing, the wash water stream leaving each cycle ($Q_{\mathrm{out},c}$) may be divided into a recycle stream (Q_{r}) and a liquid waste stream ($Q_{\mathrm{waste},c}$). Also, the recycle stream coming from the first stage ($Q_{\mathrm{r},1}$) may be distributed to the three cycles ($Q_{\mathrm{r},11}$, $Q_{\mathrm{r},12}$, and $Q_{\mathrm{r},13}$), the recycle stream coming from the second stage ($Q_{\mathrm{r},21}$) to the first one, and the recycle stream coming from the third stage ($Q_{\mathrm{r},3}$) may be distributed to the first and second stages ($Q_{\mathrm{r},31}$ and $Q_{\mathrm{r},32}$).

The optimization problem can be stated as follows. Given the mass flow of minced fish (D_{p}) and the soluble protein extraction yield (Y_{EP}), that ensures an acceptable quality of surimi gel, the goal is to determine the best flow-patterns for fresh water and/or recycle streams (process configuration) and the optimal operating conditions (agitation velocity, water volume fraction, residence time, and temperature) which require a minimum amount of fresh washing water ($\mathrm{FW_T}$). In addition, the volume of each leaching tank ($V_{\mathrm{TK},c}$) is also obtained.

When continuous variables (flow rate of fresh water or recycle streams) take a zero value at a solution point, this means that the corresponding stream is removed from the superstructure.

■ PROCESS MODEL

The natural approach to handle mathematical models based in superstructure formulations are the mixed-integer linear programming (MINLP) techniques.[23−25] As mentioned earlier, the presence or not of recycle streams may be indicated by the values obtained from the model. For instance, if the recycle stream (Q_{r}) (Figure 3) is removed from the optimal solution, then its corresponding value of flow-rate will be zero. Therefore, an NLP model is enough to solve the superstructure illustrated in Figure 3 and the optimization problem previously stated.

The mathematical model will be developed based on the following assumptions.

Assumptions.

- Soluble proteins diffuse to the surface of each sphere according to Fick's second law
- Model 1D: temporal variations of total protein concentration in the radial direction are contemplated
- The size and shape of spherical particles and the density of the minced fish do not change during the leaching process
- The external surface of each sphere is supposed to be surrounded by the extractor solvent
- Only the soluble proteins diffuse from the minced fish to the surface. Then, sarcoplasmic proteins are transferred by convection in the interphase sphere-solvent.
- A uniform soluble protein concentration is considered in the solvent phase

Mathematical Model. On the basis of the above assumptions, the following optimization model is developed to optimize the superstructure of alternative configurations shown in Figure 3.

Leaching Stage Model. It is considered that the operative volume of the leaching tanks is 70% of the total volume:

$$V_{\mathrm{op},c} = 0.7V_{\mathrm{TK},c} \tag{1}$$

where the total volume ($V_{\mathrm{TK,T}}$) is given by

$$V_{\mathrm{TK,T}} = \sum_{c=1}^{3} V_{\mathrm{TK},c} \tag{2}$$

During the washing process in each cycle, the operative volume of the tank is filled by minced fish and washing water and is computed as follows:

$$V_{\mathrm{op},c} = V_{\mathrm{f},c} + V_{\mathrm{w},c} \tag{3}$$

The residence time of the minced fish during each washing stage is calculated as

$$\theta_c = \frac{V_{\mathrm{f},c}\rho_{\mathrm{f}}}{M_c} \tag{4}$$

The volume fractions of minced fish and solvent are calculated as follows:

$$\varepsilon_{\mathrm{f},c} = \frac{V_{\mathrm{f},c}}{V_{\mathrm{op},c}} \tag{5}$$

$$\varepsilon_{\mathrm{w},c} = \frac{V_{\mathrm{w},c}}{V_{\mathrm{op},c}} \tag{6}$$

where

$$\varepsilon_{\mathrm{f},c} + \varepsilon_{\mathrm{w},c} = 1 \tag{7}$$

The global and protein mass balances in each leaching stage (leaching tank and rotary sieve, as control volume) and balances in each mixer is given by

Mixer 1

$$\mathrm{FW}_1 + Q_{\mathrm{r},11} + Q_{\mathrm{r},21} + Q_{\mathrm{r},31} = Q_{\mathrm{inl},1} \tag{8}$$

$$Q_{\mathrm{r},11}c_{\gamma,1} + Q_{\mathrm{r},21}c_{\gamma,2} + Q_{\mathrm{r},31}c_{\gamma,3} = Q_{\mathrm{inl},1}c_{\gamma\mathrm{inl},1} \tag{9}$$

Leaching stage 1 ($c = 1$)

$$\begin{aligned} &M_1\langle c_{\beta\mathrm{inl}}\rangle_{\mathrm{EP},1} + Q_{\mathrm{inl},1}c_{\gamma\mathrm{inl},1} \\ &\quad = Q_{\mathrm{out},1}c_{\gamma\mathrm{out},1} + M_2\langle c_{\beta\mathrm{out}}\rangle_{\mathrm{EP},1} + S_1\langle c_{\beta\mathrm{out}}\rangle_{\mathrm{EP},1} \end{aligned} \tag{10}$$

$$M_1 = M_2 + S_1 \tag{11}$$

Mixer 2

$$\mathrm{FW}_2 + Q_{\mathrm{r},12} + Q_{\mathrm{r},32} = Q_{\mathrm{inl},2} \tag{12}$$

$$Q_{\mathrm{r},12}c_{\gamma\mathrm{out},1} + Q_{\mathrm{r},32}c_{\gamma\mathrm{out},3} = Q_{\mathrm{inl},2}c_{\gamma\mathrm{inl},2} \tag{13}$$

Leaching stage 2 ($c = 2$)

$$\begin{aligned} &M_2\langle c_{\beta\mathrm{inl}}\rangle_{\mathrm{EP},2} + Q_{\mathrm{inl},2}c_{\gamma\mathrm{inl},2} \\ &\quad = Q_{\mathrm{out},2}c_{\gamma\mathrm{out},2} + M_3\langle c_{\beta\mathrm{out}}\rangle_{\mathrm{EP},2} + S_2\langle c_{\beta\mathrm{out}}\rangle_{\mathrm{EP},2} \end{aligned} \tag{14}$$

$$M_2 = M_3 + S_2 \tag{15}$$

Mixer 3

$$\mathrm{FW}_3 + Q_{\mathrm{r},13} = Q_{\mathrm{inl},3} \tag{16}$$

$$Q_{\mathrm{r},13}c_{\gamma\mathrm{out},1} = Q_{\mathrm{inl},3}c_{\gamma\mathrm{inl},3} \tag{17}$$

Leaching stage 3 ($c = 3$)

$$M_3\langle c_{\beta\mathrm{inl}}\rangle_{\mathrm{EP},3} + Q_{\mathrm{inl},3}c_{\gamma\mathrm{inl},3} = Q_{\mathrm{out},3}c_{\gamma\mathrm{out},3} + M_{\mathrm{f}}\langle c_{\beta\mathrm{out}}\rangle_{\mathrm{EP},3} + S_3\langle c_{\beta\mathrm{out}}\rangle_{\mathrm{EP},3} \tag{18}$$

$$M_3 = M_{\mathrm{f}} + S_3 \tag{19}$$

In the previous equations, it is considered that 2% in the first stage and 1% in the second and third stages of minced fish is lost in the rotary sieve. Therefore

$$M_2 = 0.98M_1 \tag{20}$$

$$M_3 = 0.99M_2 \tag{21}$$

$$M_{\mathrm{f}} = 0.99M_3 \tag{22}$$

Also, at each stage is satisfied that

$$Q_{\mathrm{inl},c} = Q_{\mathrm{out},c} \tag{23}$$

Splitter Mass Balances.

Splitter 1

$$Q_{\mathrm{out},1} = Q_{\mathrm{r},1} + Q_{\mathrm{waste},1} \tag{24}$$

Splitter 2

$$Q_{\mathrm{out},2} = Q_{\mathrm{r},21} + Q_{\mathrm{waste},2} \tag{25}$$

Splitter 3

$$Q_{\mathrm{out},3} = Q_{\mathrm{r},3} + Q_{\mathrm{waste},3} \tag{26}$$

Splitter 4

$$Q_{\mathrm{r},3} = Q_{\mathrm{r},31} + Q_{\mathrm{r},32} \tag{27}$$

Splitter 5

$$Q_{\mathrm{r},1} = Q_{\mathrm{r},11} + Q_{\mathrm{r},12} + Q_{\mathrm{r},13} \tag{28}$$

Splitter 6

$$\mathrm{FW}_{\mathrm{T}} = \sum_{c=1}^{3} \mathrm{FW}_c \tag{29}$$

Extraction Process. The kinetic model of soluble protein extraction from spherical particles of minced fish is described as follows:

$$(1 - \varepsilon_{\mathrm{w},c})\frac{1}{D_{\beta\gamma}}\frac{\partial c_{\beta,c}(r,t)}{\partial t} = \frac{\partial^2 c_{\beta,c}}{\partial r^2} + \frac{2}{r}\frac{\partial c_{\beta,c}}{\partial r}, \quad 0 < r < R \tag{30}$$

$$c_\beta = \langle c_{\beta\mathrm{inl}}\rangle_c, \qquad t = 0, \forall\ 0 \le r \le R \tag{31}$$

$$\frac{\partial c_{\beta,c}(r,t)}{\partial r} = 0 \qquad r = 0, \forall\ t > 0 \tag{32}$$

$$-D_{\beta\gamma}\frac{\partial c_{\beta,c}}{\partial r} = k_{c\gamma,c}(c_{\gamma\mathrm{i},c} - c_{\gamma\mathrm{out},c}), \qquad r = R, \forall\ t > 0 \tag{33}$$

Equation 30 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) in the washing solution (γ) per cycle, c. Equation 31 assumes homogeneous initial concentration of proteins in the mince. Equation 32 corresponds to the boundary condition at the surface of each sphere and states that there is no mass transfer in the meat sphere. Equation 33 represents the interfacial soluble proteins flux, where $k_{c\gamma,c}$ is the global mass transfer coefficient in the solvent phase in each stage, $c_{\gamma\mathrm{i},c}$ is the concentration of soluble proteins at the interphase solid−solvent, and $c_{\gamma,c}$ is the concentration of soluble proteins of the washing solution phase at the outlet of each leaching tank.

It is therefore necessary to clarify that despite the residence time per cycle is an optimization variable, the whole model of the continuous leaching process is a steady-state model.

The semiempirical equation of Polson[26] was used to estimate the protein diffusion coefficient, $D_{\beta\gamma}$, which is recommended for biological solutes:

$$D_{\beta\gamma} = \frac{9.40e - 15T}{\mu_{\mathrm{w}}(\mathrm{Mw}_\gamma)^{1/3}} \tag{34}$$

Suspension of solid particles during leaching in an agitated system can be assumed as a fluidized bed.[27] The overall mass transfer coefficient was calculated using the correlation proposed by Geankoplis[27] for fixed beds and also valid for fluidized beds of spheres in the Reynolds number range of 10−4000:

$$J_D = \frac{0.4548}{\varepsilon_{\mathrm{c}}}Re^{-0.4069} \tag{35}$$

$$kc_{\gamma,c} = \frac{J_D v_c}{Sc^{2/3}} \tag{36}$$

where

$$Re_c = \frac{Dp\rho_\gamma v_c}{\mu_\gamma} \tag{37}$$

and

$$Sc = \frac{\mu_\gamma}{D_{\beta\gamma}\rho_\gamma} \tag{38}$$

Equations 30, 32, and 33 were discretized using the central finite difference method (CFDM) using the explicit second-order accurate method in both space and time. The number of discretization nodes used for the time-domain and spatial-domain were, respectively, 50 and 10.

The equilibrium of soluble proteins concentration under diluted assumption is expressed as

$$c_{\gamma i} = Kc_{\beta i} \tag{39}$$

The average concentration of total proteins in phase β, after the leaching process, is computed as follows:

$$\langle c_{\beta\mathrm{out}}\rangle_c = 3A\int_0^R c_\beta/(\mathrm{AR}), \qquad t = \theta_c \tag{40}$$

The initial concentration of protein in the washed minced fish is equal to the final protein concentration of the previous cycle (Figure 3). Then, the following constraints are considered:

$$\langle c_{\beta\mathrm{out}}\rangle_c = \langle c_{\beta\mathrm{inl}}\rangle_{c+1}, \qquad c = 1, 2 \tag{41}$$

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 unwashed mince:

$$Y_T\% = \frac{\langle c_{\beta \mathrm{inl}} \rangle_1 - \langle c_{\beta \mathrm{out}} \rangle_3}{\langle c_{\beta \mathrm{inl}} \rangle_1}\% \tag{42}$$

Sarcoplasmic proteins are 25% of the total protein present in the muscle; this percentage corresponds to the maximum of removable protein.[28,29] 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:

$$Y_{EP}\% = \frac{\langle c_{\beta \mathrm{inl}} \rangle_{EP,1} - \langle c_{\beta \mathrm{out}} \rangle_{EP,3}}{\langle c_{\beta \mathrm{inl}} \rangle_{EP,1}}\% \tag{43}$$

where

$$\langle c_{\beta 0} \rangle_{EP,1} = 0.25 \langle c_{\beta 0} \rangle_1 \tag{44}$$

Objective Function. The objective function, OF, consists of minimizing the total fresh water consumption:

$$\min \mathrm{OF} = \min \mathrm{FW_T} \tag{45}$$

Summarizing, the optimization problem state:

- min $\mathrm{FW_T}$ (v_c, T, θ_c, ε_c, $V_{\mathrm{op},c}$, $Q_{\mathrm{out},c}$, $Q_{\mathrm{waste},c}$, $Q_{r,c}$, Y_{EP}); subject to eqs 1−44

The optimization model is implemented in GAMS (General Algebraic Modeling System) and involves 2999 constraints (equalities and inequalities) and 2209 variables. The generalized reduced gradient algorithm CONOPT 2.041 was here used as a nonlinear programming (NLP) solver.[30]

RESULTS AND DISCUSSION

In this section, simulated and optimized results are presented and discussed through four case studies. The first case study deals with the model validation. The remaining case studies discuss optimal results and configurations obtained for different design goals. The complexity of solving the optimization problem depends on the case studies, and it increases as the freedom degree of the model increases. Case study 2 addresses the simplest optimization problem, and case study 3 discusses the most complex optimization problem. Finally, a sensitivity analysis is also discussed in case study 4.

Table 1 lists the model parameter values used to perform the simulations and optimizations.

Table 1. Model Parameter Values

parameter	value
particle diameter, D_p [m]	0.005
crude protein concentration, $\langle c_{\beta 0} \rangle_1$ [mg/mL]	183
distribution constant, K [dimensionless]	0.006
protein's molecular weight, Mw_β [kDa]	50
density of the minced fish, ρ_{fish} [kg/m^3]	1041
unwashed minced fish mass stream, M_1 [kg/s]	1.305

A processing plant with a production capacity of 10 tons of frozen surimi on an 8-h day basis is considered for the optimization problem. Therefore, according to the yield values at the different stages of the whole process presented in Figure 1, the leaching process requires 23.5 ton per working day of minced fish. Then, considering that the total time for the leaching stage is 5 h/day, the mass flow of unwashed minced fish is 1.305 kg/s.

Case Study I: Model Validation. In order to verify the proposed model, output results obtained by the model are compared with the experimental data. Certainly, experimental measures at laboratory scale using three extraction cycles were performed in order to validate the mathematical model that predicts the percentage of extraction from the total proteins (Y_T) and soluble proteins (Y_{EP}). Due to the fact that there is no experimental data available of surimi processing plants operating in a continuous mode, the mathematical model used to predict the kinetic of extraction, which involves eqs 30−44 and is the most essential part of the complete mathematical model, was verified. Therefore, the kinetic model of soluble protein extraction is validated comparing the predicted values by the model with the available experimental data. Only for model verification, the mathematical model was here used as a simulator in a predictive manner. For this, it was necessary to fix the model degree-of-freedom. In addition, in order to reproduce the experimental results, the recycle streams were removed from the model by setting the corresponding values of flow-rates to zero.

The experiments were carried out using sábalo (*Prochilodus platensis*) as raw material. Surimi was prepared at laboratory scale using a washing tank of 0.02 m^3, following a common procedure, as illustrated in Figure 1. Sábalo, is a warm-water fish species and, therefore, can tolerate a higher processing temperature than cold-water fish species without a reduction in protein functionality.[28] Therefore, the washing water temperature was set to 18 °C.

Table 2 compares the experimental and output results of the model.

Table 2. Experimental and Validation Model Values

	experimental	model validation
volume fraction of solvent, ε_c [dimensionless]	0.777	0.777[a]
water temperature, T [°C]	18	18[a]
residence time, θ_c [s]	277	277[a]
protein's diffusion coefficient, $D_{\beta\gamma}$ [m^2/s]	4.366×10^{-11}	4.366×10^{-11}[a]
global mass transfer coefficient, $kc_{\gamma,C}$ [m/s]	7.54×10^{6}	7.54×10^{-6}[a]
Agitation velocity, v_c [m/s]	0.15	0.15[a]
percentage of extracted proteins from the total protein content, Y_T [%]	10.710	10.528
percentage of extracted protein from the soluble protein content, Y_{EP} [%]	42.938	42.111

[a] Values fixed for the model verification.

As shown, the obtained results clearly reveal a good agreement between experimental and simulated extraction yield values. The differences between them for Y_T and Y_{EP} are, respectively, 1.69% and 1.92%.

Once the kinetic model was successfully verified, the conventional continuous process was simulated using three leaching tanks of 2.225 m^3 for which 3.816 m^3/s (1.272 m^3/s per leaching stage) of fresh water is necessary in order to obtain a soluble protein extraction percentage, Y_{EP}, of 42.111% in 277 s of residence time/stage for processing the required mass rate of raw material presented in Table 1. The corresponding flowrate of wastewater stream is 22896 m^3/d.

Case Study II: Optimal Configuration and Operating Conditions for Fresh Water Consumption Minimization. In this section, the proposed mathematical model is solved in order to determine the optimal operating conditions to minimize

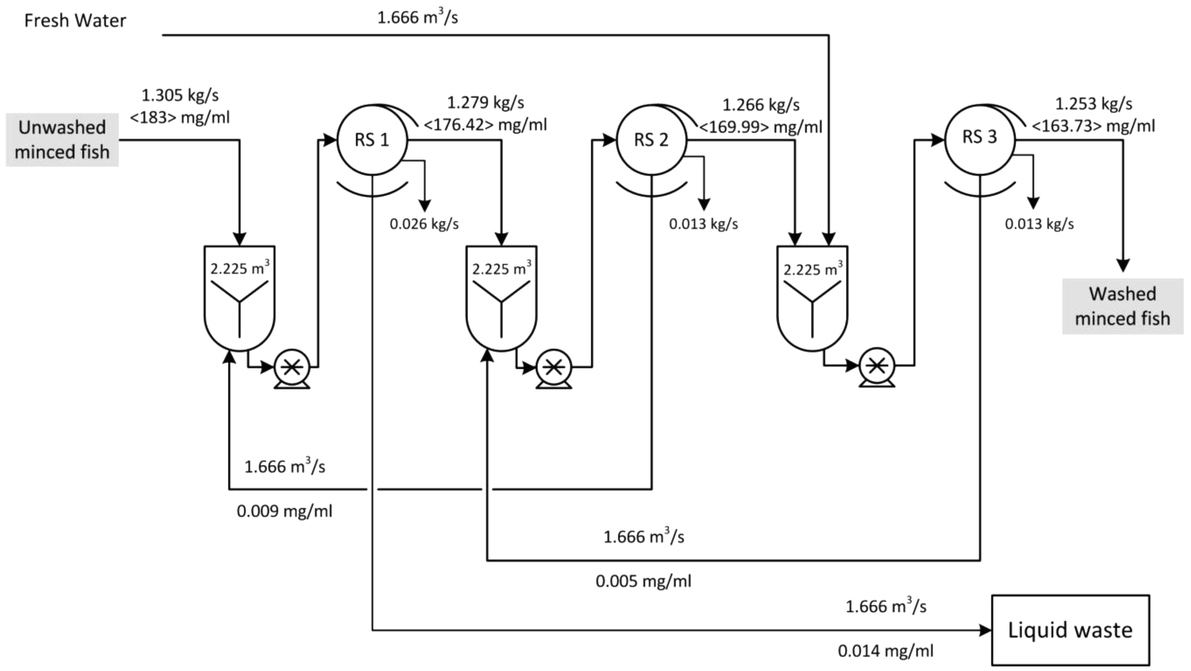

Figure 4. Optimal configuration for fresh water consumption minimization.

the water consumption required during the leaching process and guarantee the same extraction yields assumed in the model validation (case study 1). In contrast to the previous case, the possibility of recycle streams is considered and its selection and flowrates are optimization variables while the volumes of the tanks and residence times are keeping constant. Thus, the operating conditions listed in Table 2 are used as input data.

Figure 4 presents both the optimal configuration and operating conditions. Figure 5 shows the variation with time of the crude protein concentration in the particle in each of the stages. As shown, the countercurrent leaching arrangement was selected from the superstructure model as the optimal configuration to obtain Y_{EP} = 42.111%. According to Figure 4, the fresh water is only supplied to the third leaching stage and the flow stream emerging from the first stage is directly discharged as liquid waste. This flow pattern is consistent with the results published in the works of Green and Lanier[8] and Park and Lin.[2] As shown, the stream coming from the first stage and the recycle were not selected because their corresponding driving forces are not strong enough for the extraction process.

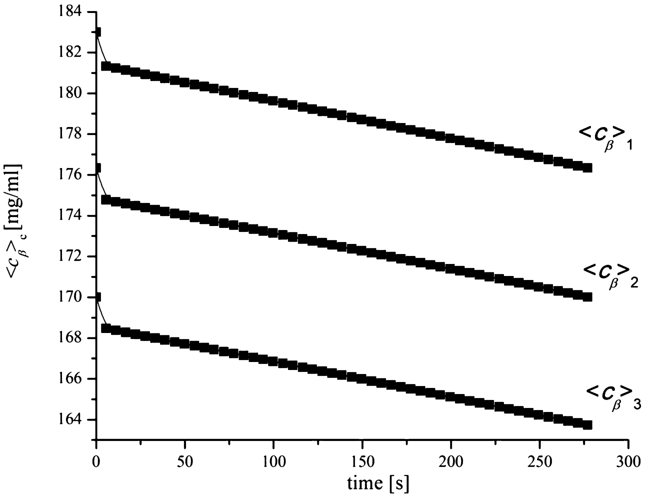

Figure 5. Variation with time of the crude protein concentration in the particle in each of the stages (case study 2).

The fresh water requirement is 1.666 m^3/s; hence, significant reductions in the fresh water requirement, and therefore in the liquid waste to be treated, are achieved in comparison to the previous case (56.34%).

Then, the same optimization problem was solved but now considering the total volume and the volume of the each leaching tank as optimization variables. As a result, the same arrangement but with a nonuniform volume distribution was obtained. In fact, the optimal volume corresponding to each leaching tank is 2.307 (tank 1), 2.261 (tank 2), and 2.239 m^3 (tank 3), with an optimal total volume of 6.807 m^3. Thus, the fresh water consumption for the nonuniform distribution is 0.886 m^3/s lower than that required for the uniform distribution of a total volume of 6.675 m^3; certainly, it was reduced from 1.666 to 0.78 m^3/s (53.18%).

Case Study III: Influence of the Wash Water Temperature, Average Soluble Protein Extraction, and Overall Water to Meat Ratio on the Process Configuration and Fresh Water Consumption. During surimi processing, especially when marine fish species are used as raw material, the wash water temperature ranges from 5 to 10 °C.[1,6] Also, during the manufacturing of surimi using different fish species, the average soluble protein extraction is about 60%.[2,8] Finally, the overall water to meat ratio used for washing generally corresponds to water volume fractions from 0.7 to 0.9.

According to that mentioned above, the wash water temperature, the average soluble protein extraction, and the overall water to meat ratio are now considered as optimization variables. Thus, the optimization problems proposed in this section differ from the previous one on the number of optimization variables considered. Certainly, the input data presented in Table 2 are now optimization variables, increasing the degrees of freedom. Table 3 lists the lower and upper bounds

Table 3. Lower and Upper Bounds for the Main Optimization Variables

variable	lower bound	upper bound
agitation velocity, v [m/s]	0.05	0.3
water temperature, T [°C]	5	10
leaching tank volumes, $V_{\mathrm{TK},c}$ [m^3]	1	5
total volume, $V_{\mathrm{TK,T}}$ [m^3]	3	10
percentage of extraction from soluble proteins, Y_{EP} [%]	60	100
volume fraction of solvent, $\varepsilon_{w,c}$ [adim]	0.7	0.9

used for new optimization variables which are imposed using the following inequality constraints:

- Washing temperature [°C]: $T \geq 5$; $T \leq 10$
- Percentage of extraction from soluble proteins [%]: $Y_{\mathrm{EP}} \geq 60$
- Volume fraction of solvent, [dimensionless]: $\varepsilon_{\mathrm{w},c} \geq 0.7$; $\varepsilon_{\mathrm{w},c} \leq 0.9$

As a result, two optimal configurations were obtained. Figure 6 and Table 4 present the optimal results of the main optimization variables. Despite the fresh water consumption being identical in both configurations, the flow-rate and composition of each stream and size of leaching tanks are different. The first optimal configuration, hereafter named as structure A, is formed by a hybrid configuration, in which the fresh water feed is supplied to the third leaching tank, the outlet flow stream from the third stage is completely recycled to the second one, the emerging flow stream from the second to the first cycle, and also part of the outlet flow stream from the first stage is recycled to itself. The second optimal configuration, hereafter named as structure B, is the countercurrent leaching, as was explained in the previous case study.

Figure 7 presents the variation with time of the crude protein concentration in the particle in each of the stages for both structures (A and B). As shown, it almost decreases linearly as the time increases. From Figures 5 and 7, it can be concluded that, despite the discretization method used (explicit second order discretization in time), oscillations or divergence of the solution were not observed and also the stability criteria of the finite difference method has been checked in each case study. In addition, a total implicit discretization method has been also used in order to check the crude protein profiles (results not shown) and similar results have been obtained.

Table 4 reports the residence time corresponding to each stage. As indicated, the total residence time corresponding to the three cycles is 2 s less for the countercurrent leaching (structure B). As shown, for both cases (structures A and B), the volume fraction of solvent and the water temperature as well as the agitation velocity reached the imposed bounds (upper or lower), and different distribution of the tank volumes, flow rates, and residence times were obtained (Figure 6 and Table 4).

Finally, it is should be mentioned that structure B is more preferred than structure A when the fresh washing water consumption is minimized because it is more easy to operate. For this reason, the countercurrent configuration is only analyzed in the following section. However, a complete and detailed objective function including costs, maintenance, and operability aspects should be considered in order to select the final flowsheet. These aspects will be taken into account in future works.

Solution Strategy. Different Initialization Points. In general, the benefit of the proposed superstructure is that it allows the discovery of novel configurations or eventually more than one solution for a same optimization problem, that in advance may be difficult to identify. It should be mentioned from a mathematical programming point of view, that a complete and detailed objective function including costs, maintenance, reliability, and operability aspects should be considered in order to select the final flowsheet. Depending on the objective function used for optimization, one configuration will be preferred over the other one. For instance, a complete objective function involving the investment and operating cost of each piece of equipment (for example, investment of mixers and splitters) will lead to a unique optimal solution if no new nonconvexities are introduced and then structure B will be selected. However, if aspects such as reliability, maintenance, and safety are considered, then structure A may be preferred over structure B. This aspect largely exceeds the aim of this work.

Finally, it should be mentioned from the solution strategy point of view that the proposed model was solved using several initializations. Once the first optimal solution was found (structure A, hybrid arrangement), then the model was solved several times in order to get a better solution. Precisely, the model was solved using different initializations and imposing an upper bound on the objective function. The value of the imposed upper bound was the water consumption obtained for the hybrid configuration. Independently of the initialization used, a same optimal solution was obtained (structure B, pure countercurrent arrangement). In this sense, the proposed model is being extended in order to include the remaining process stages and an objective function that includes several trade-offs (cost, maintenance, reliability, and operability).

Case Study IV: Influence of the Total Volume, Extraction Yield, and Number of Stages on the Fresh Water Consumption (Countercurrent Arrangement). In this case study, a sensitivity analysis is presented in order to show the influence of the total volume of leaching tanks and extraction yield of soluble protein (model parameters) on the minimum fresh water consumption. For this, the same optimization problem proposed in the previous section was solved by varying their lower and upper bounds.

Table 4. Optimal Main Process Variable Values

variable	value	
	structure A	structure B
volume of minced fish [m^3]		
$V_{\mathrm{fish},1}$	0.363	0.425
$V_{\mathrm{fish},2}$	0.733	0.708
$V_{\mathrm{fish},3}$	1.004	0.967
volume of washing water [m^3]		
$V_{\mathrm{w},1}$	0.847	0.992
$V_{\mathrm{w},2}$	1.711	1.652
$V_{\mathrm{w},3}$	2.342	2.256
percentage of extraction from soluble proteins, Y_{EP} [%]	60[a]	60[a]
volume fraction of solvent, ε_c [dimensionless]	0.7[a]	0.7[a]
water temperature, T [°C]	10[b]	10[b]
residence time [s]		
θ_1	290	339
θ_2	597	576
θ_3	825	795
agitation velocity, v_c [m/s]	0.3[b]	0.3[b]
total volume, $V_{\mathrm{TK,T}}$ [m^3]	10[b]	10[b]

[a] Lower bound. [b] Upper bound.

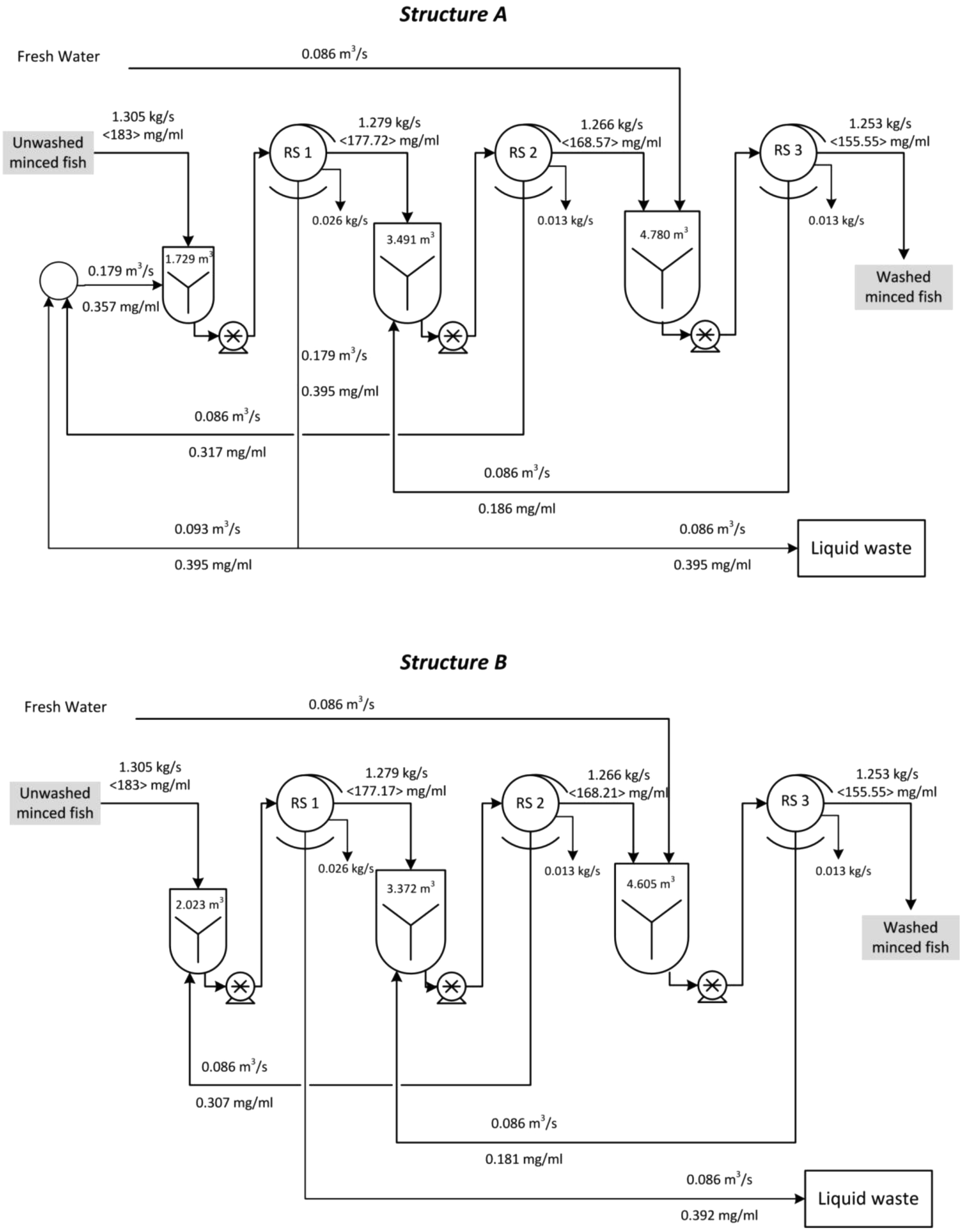

Figure 6. Optimal configurations and process variable values.

Table 5 presents the optimal results corresponding to different total volumes. As observed, the fresh water consumption (FW_T) significantly decreases as the total volume ($V_{TK,T}$) increases. This is because of the fact that the higher total volumes tank the higher residence times resulting in lower fresh water consumptions. For instance, FW_T required for $V_{TK,T}$ = 8 m^3 is 90.69% higher than that required for $V_{TK,T}$ = 10 m^3. However, the total residence time ($\ominus_{Total}$), required for $V_{TK,T}$ = 8 m^3 is 19.76% lower than that required for $V_{TK,T}$ = 10 m^3. Then, the difference between the FW_T required for 12 and 14 m^3 is 18.86%. Thus, the minimal fresh water requirement decreases with the increasing of tank total volume following an exponential decay law. Here, a sharp trade-off between water consumption and volume required is showed.

As expected and shown in Table 5, the extraction yield of soluble protein (Y_{EP}) and the volume fraction of solvent reached their lower bounds (60% and 0.7).

In contrast to this, the agitation velocity (v_c) and water temperature (T) reached their upper bounds (0.3 m/s and 10 °C). Certainly, the higher temperatures and agitation velocities, the lower fresh water requirements. This is explained on the basis that the extraction rate is significantly improved as the agitation velocity and temperature increase.

Then, the influence of the number of leaching cycles on the FW_T for Y_{EP} = 60% (lower bound) and total volume of 8 m^3 was

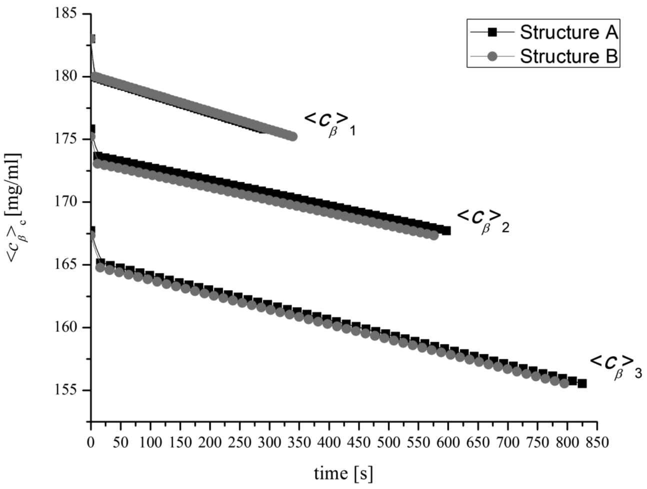

Figure 7. Variation with time of the crude protein concentration in the particle in each of the stages (case study 3).

Table 5. Optimal Main Process Variable Values with Different Total Volumes

	total volume, $V_{TK,T}$ [m^3]			
variable	8	10	12	14
fresh water consumption, FW_T [m^3/s]	0.164	0.086	0.063	0.053
percentage of extraction from soluble proteins, Y_{EP} [%]	60^a	60^a	60^a	60^a
leaching tank volume [m^3]				
$V_{TK,1}$	1^a	2.024	3.307	4.338
$V_{TK,2}$	2	3.371	3.937	4.662
$V_{TK,3}$	5^b	4.605	4.756	5^b
residence time [s]				
θ_1	167	339	554	726
θ_2	342	576	673	797
θ_3	863	795	821	863
agitation velocity, v_c [m/s]	0.3^b	0.3^b	0.3^b	
volume fraction of solvent, ε_c [dimensionless]	0.7^a	0.7^a	0.7^a	0.7^a
water temperature, T [°C]	10^b	10^b	10^b	10^b

[a]Lower bound. [b]Upper bound.

Table 6. Optimal Main Process Variable Values for Y_{EP} = 60% (lower bound) and Total Volume of 8 m^3

	3 stages	2 stages	1 stage
leaching tank volume [m^3]			
$V_{TK,1}$	1^a	N/A	N/A
$V_{TK,2}$	2	3	N/A
$V_{TK,3}$	5^b	5^b	8^b
residence time [s]			
θ_1	167	N/A	N/A
θ_2	342	513	N/A
θ_3	863	863	1381
fresh water consumption, FW_T [m^3/s]	0.164	0.320	0.983

[a]Lower bound. [b]Upper bound.

also investigated and the optimal results are presented in Table 6. It can be observed that the fresh water consumption decreases when the number of stages increases due to the fact that more recycle streams are available, reducing both the fresh water requirement and the liquid waste stream. Therefore, the trade-off between operating costs and fixed investment is clearly evidenced.

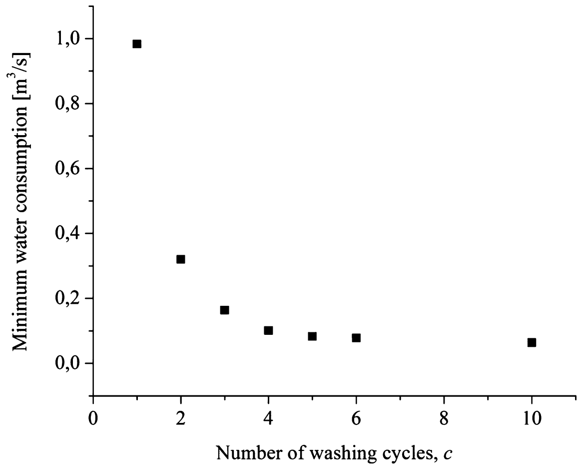

Figure 8. Influence of the number of stages on the minimum water consumption for Y_{EP} = 60% (lower bound) and total volume of 8 m^3.

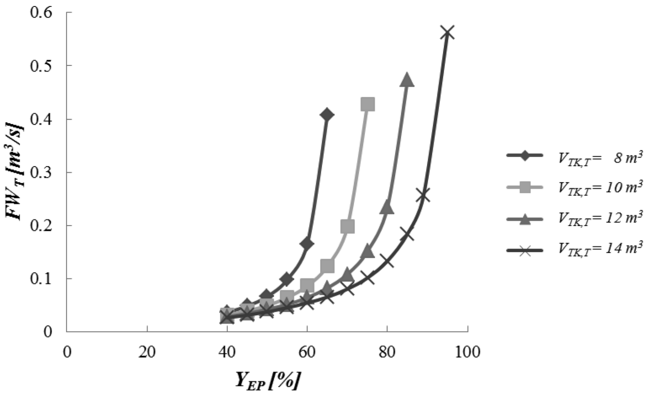

Figure 9. Optimal points of minimal fresh water consumption for different minimal soluble protein extracion yields.

The influence of the number of stages on the minimum water consumption is also analyzed in Figure 8. The results presented in Figure 8 clearly show that using four or more stages minimum water consumption is expected. But, this consumption does not vary considerably from the third to fourth stage. Therefore, as a first approximation, three stages are assumed in this work, which is a reasonable value from an industrial application point of view. An MINLP program will be implemented in a further work in order to obtain the number of stages that minimizes the water consumption. In this case four stages will be proposed as the maximum number of cycles.

Finally, Figure 9 represents optimal points that relate, for a given total volume (8, 10, 12, and 14 m^3), the minimal fresh water consumption to the minimal soluble protein extracion yields from 40 to 100% .

From Figure 9, the following conclusions can be drawn:

- From Y_{EP} = 40 to 50%, $V_{TK,T}$ has a slight effect on the FW_T and Y_{EP}. In contrast to this, from YEP = 50%, a significant difference on FW_T is observed.
- Soluble protein extracion yields are limited by the total volume used for the leaching. For instance, for $V_{TK,T}$ = 8 m^3 the maximum soluble protein that can be extracted is 65% for which the minimal fresh water requeriment is 0.407 m^3.
- For a given value of FW_T higher than 0.2 m^3/s, the amount of soluble protein that can be extracted (Y_{EP}) increases linerly with the increasing of $V_{TK,T}$.

- For a given value of $V_{TK,T}$, the minimal values of FW_T increase exponentially with the increasing of Y_{EP}.

CONCLUSIONS

Significant advances on the modeling, simulation, and optimization of the leaching process in the manufacturing process of surimi gel were presented. A superstructure formulation that embeds not only known process arrangements (conventional and countercurrent) but also hybrid configurations is proposed for simultaneous optimization. The proposed superstructure was modeled as a nonlinear programming mathematical model (NLP) and implemented into the optimization environment GAMS. In addition, a phenomenological model for the leaching process was developed and successfully implemented and includes the kinetic model of soluble protein extraction within spherical particles of minced fish. Despite the steady state process considered, a set of differential equations is used to describe the diffusion process. The central finite difference method (CFDM) using the second-order accurate method in both space and time was used for discretization.

First, the model that predicts the kinetic of extraction [eqs 30−44] was successfully verified by comparing the output results with experimental data at laboratory scale. Then, the complete optimization model [eqs 1−45] was solved in order to determine not only the best process arrangement but also the optimal operating conditions and volume of each leaching tank ($V_{TK,1}$, $V_{TK,2}$, and $V_{TK,3}$) to reach a given percentage of extraction of soluble proteins (Y_{EP}) at minimum fresh water requirement (FW_T). An interesting result from the superstructure optimization presented in case study 3 reveals that, for a given Y_{EP} and total volume of leaching tank ($V_{TK,T}$), the same minimum fresh water requirement (FW_T) is obtained with different leaching arrangements and with different distributions of flowrates, leaching tank volumes, and residence times. Certainly, the first optimal configuration (structure A) is formed by a hybrid configuration, in which the fresh water feed is supplied to the third leaching tank, the outlet flow stream from the third stage is completely recycled to the second one, the emerging flow stream from the second to the first cycle, and also part of the outlet flow stream from the first stage is recycled to itself. The second optimal configuration (structure B) is the countercurrent leaching, and it is more preferred than structure A because it is easier to operate. However, a complete and detailed objective function including costs, maintenance, and operability aspects should be considered in order to select the final flowsheet. These aspects will be taken into account in future works, in which the remaining unit operation of the process will be also included.

Also, a sensitivity analysis was conducted in order to study the influence of the total volume of leaching tanks ($V_{TK,T}$), number of leaching cycles, and extraction yield of soluble protein (Y_{EP}) on the minimum fresh water consumption (countercurrent arrangement). As expected, for a given percentage of extraction from soluble proteins, the fresh water consumption (FW_T) significantly decreases, following an exponential decay law, as the total volume ($V_{TK,T}$) increases.

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Notes

The authors declare no competing financial interest.

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NOMENCLATURE

A = area (m^2)
c = concentration (mg/mL)
D_p = particle's diameter (m)
$D_{\beta\gamma}$ = mass diffusivity (m^2/s)
FW = fresh water flow stream (m^3/s)
FW_T = total fresh water consumption (m^3/s)
J_D = Chilton and Colburn factor
k_c = global mass transfer coefficient (m/s)
K = distribution constant
Mw = molecular weight (kDa)
M = mass flow rate of minced fish (kg/s)
Q_{inl} = inlet flow stream (m^3/s)
Q_{out} = outlet flow stream (m^3/s)
Q_r = recycle flow stream (m^3/s)
R = sample radius (m)
r = variable radius (m)
S = lost minced fish mass stream (kg/s)
T = temperature (°C)
t = time (s)
v = agitation velocity (m/s)
V_{TK} = leaching tank volume (m^3)
V_{op} = operative volume of the leaching tank (m^3)
V_f = volume of minced fish (m^3)
V_w = volume of washing water (m^3)
Y = percentage of extraction (%)

Dimensionless Groups

Re = Reynolds's number
Sc = Schmidt's number

Greek Symbols

ε = volume fraction of solvent (dimensionless)
ρ = density (kg/m^3)
μ = viscosity ($N\cdot s/m^2$)
θ = residence time (s)
θ_T = total residence time (s)

Subscripts

β = proteins presented in minced fish
γ = proteins presented in solvent phase
c = cycle
EP = from the removable proteins
f = minced fish
i = at interface
inl = inlet
out = outlet
T = from total proteins

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