CHEMICAL ENGINEERING TRANSACTIONS
VOL. 52, 2016
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Petar Sabev Varbanov, Peng-Yen Liew, Jun-Yow Yong, Jiří Jaromír Klemeš, Hon Loong Lam

ISBN 978-88-95608-42-6; **ISSN** 2283-9216
DOI: 10.3303/CET1652048

Water Recovery and Reuse in the Fractionation of Protein Hydrolysate by Ultrafiltration and Nanofiltration Membranes

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The fractionation of a protein hydrolysate obtained from tuna processing by-products by means of a membrane cascade integrating ultrafiltration (UF) and nanofiltration (NF) membranes was proposed in order to separate and purify the protein fraction between 1 and 4 kDa, which is the most interesting for nutraceutical purposes. A simulation model, based on mass balances and empirical equations for describing permeate flux and rejection of protein fractions, was developed and complemented with a simple cost estimation model. The product purity (49.3 %) and the process yield (62.6 %) were independent of the total water consumption of the process, but high water consumptions were required to maintain the total protein content of the stream below upper bounds that assured the absence of membrane clogging. The implementation of a water recovery system, based on an additional tight NF stage, implied improvements in both environmental and economic aspects of the process.

1. Introduction

The recovery and posterior reuse of water is a key aspect to be taken into consideration during the production processes by industries which manage biological-origin compounds. Most of these compounds require water as solvent and, similarly to the cases which employ organic solvents, effective measures to reduce water consumption and wastewater production must be implemented in order to look for more sustainable conditions in the food, pharmaceutical and nutraceutical sectors. The incorporation of closed-loop solvent recycling systems has demonstrated its usefulness to improve the solvent management, by avoiding fresh solvent consumption after recovery, purification and recirculation of previously used solvent (Abejón et al. 2015), so its applicability to water consuming separation processes was studied.

The production of fish protein hydrolysates appears as a promising route to add value to fish by-products due to their potential application as a source of interest peptide fractions. Relation between molecular weight and biological activity of the peptide fractions has been reported: fractions between 1 and 4 kDa are the most interesting for nutraceutical purposes. Therefore, the extraction and purification of this fraction from the hydrolysate is a key issue and appropriate fractionation must be carried out.

These research groups had previous experience with the design of membrane cascades to purify liquids (Abejón et al., 2012) and gases (Mourgues and Sanchez-Marcano, 2012) and decided to share the acquired knowledges to advance in the design of integrated membrane systems (combining UF and NF modules) for hydrolysate fractionation. Besides, the fractionation of a protein hydrolysate obtained from tuna processing by-products has been previously investigated by members of these research groups (Saidi et al., 2013). Therefore, the main objective of this work is the investigation of optimal membrane cascades to minimize the freshwater consumption required for the fractionation of protein hydrolysates and the potential implementation of water recovery systems to promote the reuse of water in the process.

Please cite this article as: Abejón R., Abejón A., Belleville M.-P., Garea A., Irabien A., Sanchez-Marcano J., 2016, Water recovery and reuse in the fractionation of protein hydrolysate by ultrafiltration and nanofiltration membranes, Chemical Engineering Transactions, 52, 283-288 DOI:10.3303/CET1652048

2. Case study

A pilot-scale installation designed to treat 200 L/h of tuna protein hydrolysate obtained after enzymatic hydrolysis of tuna by-products using Alcalase® (72 g/L protein concentration in the resulted stream) was chosen as case study. The separation process was based on two in-series membranes cascades (Figure 1), both of them including three stages: the first cascade with UF membranes (stages 1A, 2A and 3A) and the second one with NF membranes (stages 1B, 2B and 3B). The membrane cascades have been identified as very advantageous configurations to attain high purity permeates when poorly rejected solutes are present or exigent solute fractionation is required (Abejón et al., 2012).

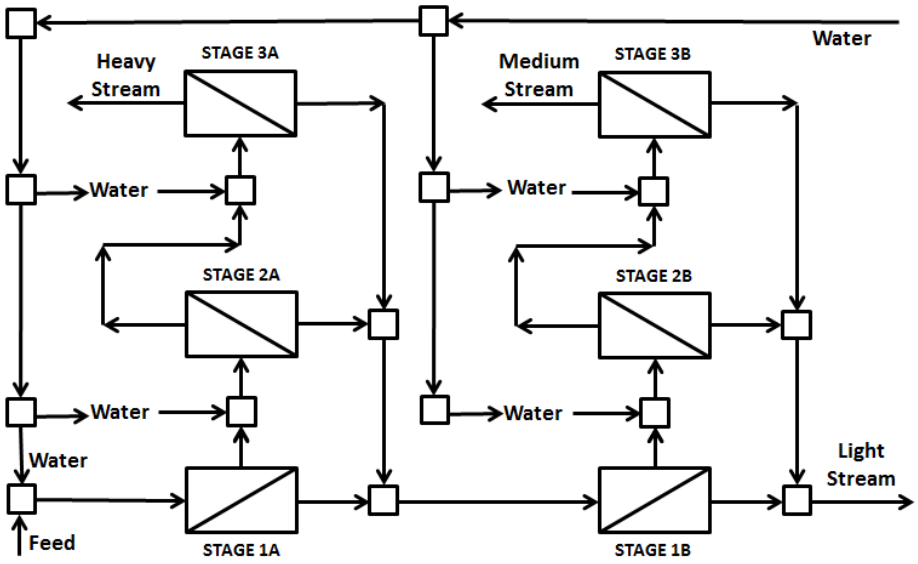

Figure 1: Scheme of a six-stage (3UF3NF) cascade

The total protein content of the hydrolysate can be divided into different protein fractions. In this case, five different fractions were defined, from ultra-heavy to ultra-light, where the medium fraction (molecular weights between 1 and 4 kDa) was the desired product, since it is the most interesting one from the nutraceutical point of view. Information about the molecular weight ranges that define the different protein fractions and the composition of the raw hydrolysate can be consulted in Table 1.

3. Process model

The performance of the selected ceramic UF membranes and the polymeric NF membranes for protein fractionation had been deeply investigated by previous experimental works (Saidi et al., 2013). These results have been adjusted to simple models and the required parameters have been calculated in order to be able to simulate the performance of the system.

On the one hand, Table 1 compiles the empirical functions that describe the three different types of relationships (constant, linear and quadratic) between applied pressure and the resulting rejection for each protein fraction.

Table 1: Composition of the protein hydrolysate from tuna processing by-products and simulated percentual rejections as functions of applied pressure (ΔP, bar)

Protein fractions	Molecular weight range (kDa)	Raw protein distribution (%)	UF rejection (%)	NF rejection (%)
UltraHeavy (UH)	> 7.0	11.5	100	100
Heavy (H)	4.0 - 7.0	3.0	96 - 7.75(ΔP)	100
Medium (M)	1.0 - 4.0	19.0	33	$-0.42(\Delta P)^2 + 7.7(\Delta P) + 58$
Light (L)	0.3 – 1.0	28.5	21	$-0.64(\Delta P)^2 + 13(\Delta P) + 15$
UltraLight (UL)	< 0.3	38.0	16	$-0.76(\Delta P)^2 + 16(\Delta P) - 28$

On the other hand, permeate fluxes have been adjusted to Darcy's law with variable membrane permeability, since they depend on the total protein content in the stream entering the membrane module. These are the developed equations for the UF membrane (Eq.1) and the NF membrane (Eq.2):

$$J_V = (30 - 1.7\sqrt{TP})\Delta P \quad (1)$$

$$J_V = (8.4 - 0.6\sqrt{TP})\Delta P \quad (2)$$

where J_V is the permeate flux (L/h m^2), TP the total protein concentration (g/L) and ΔP the applied pressure (bar). The proposed membrane cascades integrated membrane modules and mixers. The complete mathematical model that described these systems was formulated as follows by the appropriate equations based on mass balances. For the mixers, the total (Eq.3) and partial for total protein content (Eq.4) and protein fractions (Eq.5) mass balances were formulated, where F_{IN1} and F_{IN2} were the flows of the streams entering the mixer, F_{OUT} the flow of the leaving stream, TP_X the total protein concentration in the X stream and M_X^i the concentration of the i protein fraction in the X stream.

$$F_{IN1} + F_{IN2} = F_{OUT} \quad (3)$$

$$F_{IN1} \cdot TP_{IN1} + F_{IN2} \cdot TP_{IN2} = F_{OUT} \cdot TP_{OUT} \quad (4)$$

$$F_{IN1} \cdot M_{IN1}^i + F_{IN2} \cdot M_{IN2}^i = F_{OUT} \cdot M_{OUT}^i \quad (5)$$

Equivalent mass balances were formulated for the membrane modules: the total one Eq(6), the partial one for total protein content Eq(7) and the ones corresponding to the protein fractions Eq(8). In this case, the UP, PERM and RET subscripts represented the feed, permeate and retentate streams.

$$F_{UP} = F_{PERM} + F_{RET} \quad (6)$$

$$F_{UP} \cdot TP_{UP} = F_{PERM} \cdot TP_{PERM} + F_{RET} \cdot TP_{RET} \quad (7)$$

$$F_{UP} \cdot M_{UP}^i = F_{PERM} \cdot M_{PERM}^i + F_{RET} \cdot M_{RET}^i \quad (8)$$

Once the membrane transport equations and the mass balances were defined, the rest of the simulation model was easily developed. The two main characteristics of the permeate streams, the flow and the protein fraction concentrations, were calculated taking into account the membrane area of the corresponding stage and the permeability and rejection values. Finally, the recovery rates of the membrane stages were defined as the ratio between the permeate and feed streams.

The performance of the system was evaluated by two different parameters. The first one was the purity of the medium stream X^M, measured as the percentage of the medium protein fraction over the total protein concentration in this product stream Eq(9); and the second one was the process yield Y^M, defined as the percentage of the medium protein fraction in the feed hydrolysate that was recovered in the product medium stream Eq(10).

$$X^M = 100\frac{M_{MPROD}^M}{TP_{MPROD}} \quad (9)$$

$$Y^M = 100\frac{F_{MPROD} \cdot M_{MPROD}^M}{F_{FEED} \cdot M_{FEED}^M} \quad (10)$$

The simulation model was complemented with some economic considerations that allowed the assessment of the total costs of the process. The total costs TC were defined as the sum of the capital costs CC and the operation costs OC Eq(11). On the one hand, the capital costs attributable to membranes (CC_{MEMB}) or to the rest of the installation (CC_{INST}) were differentiated Eq(12). On the other hand, operation costs were itemized into energy (OC_{EN}), continuous consumption of freshwater (OC_W), maintenance (OC_M) and membrane cleaning (OC_{CLEAN}) costs Eq(13).

$$TC = CC + OC \quad (11)$$

$$CC = CC_{MEMB} + CC_{INST} \quad (12)$$

$$OC = OC_{EN} + OC_W + OC_M + OC_{CLEAN} \quad (13)$$

4. Results and discussion

Optimization software (GAMS) was employed to determine the optimal cascade configuration to minimize the water consumption (Rosenthal, 2016). The optimization results demonstrated that the product purity and the process yield were not influenced by the total water consumption of the system. The maximal purity that the proposed cascade was able to attain was 49.3 % and the corresponding yield of the process was 62.6 %. Consequently, it can be reduced without implications over the main parameters that characterize the process performance. Nonetheless, other restrictions must be taken into account: high total protein contents in the streams can cause problems in the membrane modules, mainly related to membrane clogging. Therefore, appropriate upper limits have to be defined in order to assure appropriate concentrations in the streams.
The influence of these defined upper limits over the minimal water consumption was analysed. Figure 2 shows the minimal water inlet flows for each of the auxiliary water streams depicted in Figure 1 as functions of the imposed total protein limit concentration.

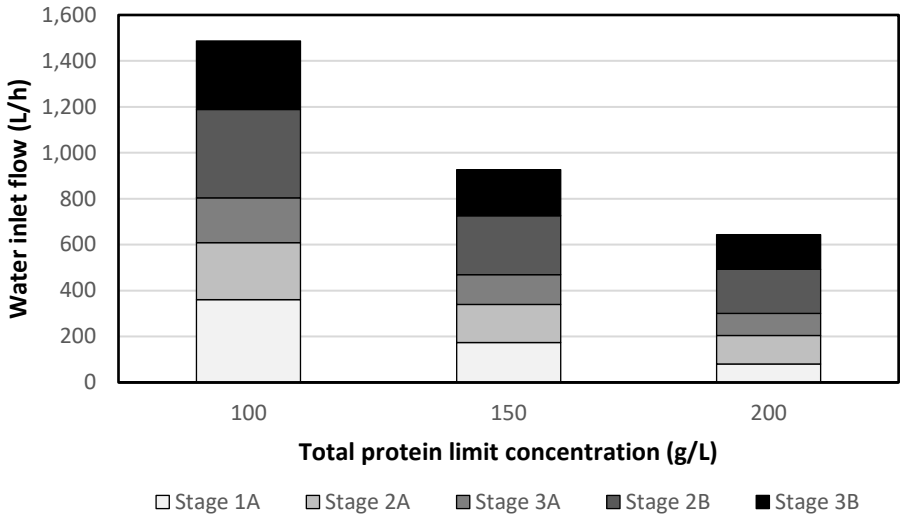

Figure 2: Total water consumption and contribution of each stage as functions of the maximal allowed total protein concentration

The results clearly drew attention to the great water consumption required to manage the fractionation process. Even for the highest considered limit (200 g/L), the total water inlet flow was above 640 L/h, more than three times the hydrolysate feed flow. Moreover, when a more conservative upper bound was selected such as 100 g/L, the resulting water consumption increase until more than 1,480 L/h.
A further analysis of the results revealed the importance of the water inlets to the first UF stage (Stage 1A) and the second NF stage (Stage 2 B). They were the streams that required more water to assure the upper limit concentration was not exceeded. However, the Stage1A water inlet was highly reduced when the limit was 200 g/L and other water streams became relevant. Nevertheless, all the water introduced to the process left the system within the light stream. As example, the flow of the light stream was 815 L/h for the 200 g/L limit, which corresponded to the total water inlet and 57.5 % of the hydrolysate feed stream. Taking into account that fact, the implementation of water recovery systems to recover water from that high-flow dilute stream and recirculate it back to the process became a promising proposal.
The scheme of the cascade that resulted after implementation of the water recovery system is shown in Figure 3. The water recovery stage was based on an additional tight NF stage (Stage 1C), which was fed by the dilute light stream. Tight NF has demonstrated its usefulness for almost total rejection of low molecular weight organic compounds in combination with high permeate flux as consequence of higher applied pressures (Dixon et al., 2011). Consequently, water with very low content in protein fractions could be recovered from the dilute light stream, which was directly recirculated back to the process to avoid the employment of a freshwater stream. In addition, a concentrated light stream was obtained.
The process under water recirculation conditions was optimized and the results confirmed the viability of the water recovery system. The total amount of water required to control the total protein content below the imposed limits did not change and the system was able to recover it from the light stream without any additional water inlet to the process. The tight NF membrane area required in the Stage 1C depended on the

imposed upper bound: from 7.0 m^2 for 200 g/L to 16.2 m^2 for 100 g/L. Nevertheless, in all the cases this membrane area was totally comparable to the dimension of the other NF stages incorporated in the cascade and it did not imply implementation problems.

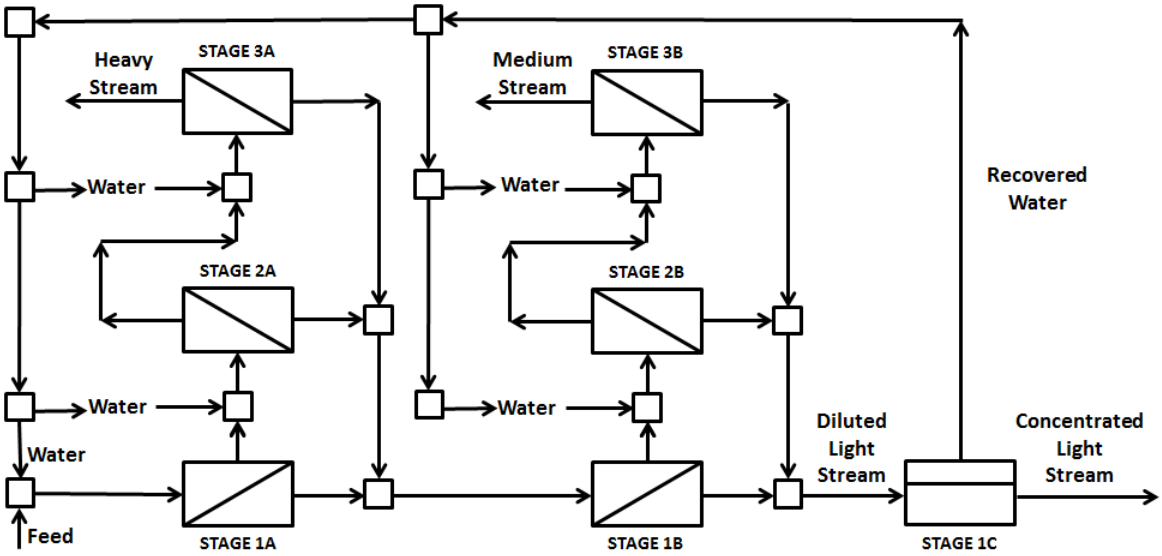

Figure 3: Scheme of a six-stage (3UF3NF) cascade with water recovery stage

The economic considerations of the process are shown in Table 2, which compiles the breakdown of the total costs attributable to the process. The economic results indicated that the capital costs were clearly higher than the operation costs: around 84 % of the total costs were due to the required capital investment. The UF stages contributed more to the capital costs than the NF ones, even including the additional tight NF stage for water recovery. It is well known that the ceramic UF membranes (González Alriols et al., 2014) are much more expensive than the polymeric NF membranes (Sannino et al., 2013) and the corresponding auxiliary installations and services follow up the same trend.

The operation costs were maintained below 5 $/d and they were almost equally distributed among the three main components: electrical energy, maintenance and membrane cleaning. Nevertheless, the proposed economic model was quite simple (particularly for the determination of the membrane cleaning costs). Therefore, future work will be performed to improve the cost estimation and apply it to real scale industrial installations.

Nonetheless, despite the simplicity of the proposed cost model, the economic savings caused by the water recovery system were out of any doubt. Preliminary works were carried out to obtain the economic evaluation of the fractionation process without the implementation of water recovery. As an illustrating example, the system with a total water inlet equal to 800 L/h resulted in total costs above 75 $/d, mainly because of the 44 $/d attributable to the continuous freshwater consumption.

Table 2: Economic breakdown of the proposed cascade with water recovery stage and control of the maximal total protein concentration

Costs ($/d)	Total protein limit concentration (g/L)		
	100	150	200
Total costs	31.1	25.4	23.6
Capital costs	26.1	21.3	19.9
UF membrane costs	6.4	5.2	4.8
NF membrane costs	4.3	3.6	3.5
Rest UF installation costs	12.8	10.4	9.5
Rest NF installation costs	2.6	2.1	2.1
Operation costs	5.0	4.1	3.8
Energy costs	1.9	1.2	0.9
Maintenance costs	1.3	1.1	1.0
Cleaning costs	1.8	1.8	1.8

5. Conclusions

The fractionation of a protein hydrolysate obtained from tuna processing by-products was proposed by means of UF and NF membrane cascades and the implementation of a water recovery system was evaluated. The proposed simulation model was based on empirical equations for solvent and solute transport through the membranes and the corresponding mass balances (overall and by components) for membrane modules and stream mixers. A simple economic model to assess the main costs of the process was included.

The optimization results calculated the minimal water consumption required to control the total protein concentration in the streams below upper bounds that assured the absence of membrane clogging. Total water consumptions between 4 and 8 times higher than the hydrolysate feed flow were required to maintain the imposed concentration limits. The product purity attained under those conditions by the fractionation process was 49.3 % and the corresponding yield was 62.6 %.

The incorporation of an additional tight NF stage was useful in recovering water from the dilute light stream of the process. This way, the consumption of freshwater was avoided by direct reuse of the recovered water. This upgraded process improved not only the environmental charges by reduction of the water footprint, but it also resulted in considerable economic savings.

Acknowledgments

This research has been financially supported by the Spanish Ministry of Economy and Competitiveness (MINECO) through CTQ2014-56820-JIN Project.

References

Abejón R., Garea A. Irabien A., 2012, Integrated countercurrent reverse osmosis cascades for hydrogen peroxide ultrapurification, Computers and Chemical Engineering, 41, 67-76.

Abejón R., Garea A. Irabien A., 2015, Organic solvent recovery and reuse in pharmaceutical purification processes by nanofiltration membrane cascades, Chemical Engineering Transactions, 43, 1057-1062.

Dixon M.B., Falconet C., Ho L., Chow C.W.K., O'Neill B.K., Newcombe G., 2011, Removal of cyanobacterial metabolites by nanofiltration from two treated waters, Journal of Hazardous Materials, 188, 288-295.

González Alriols M., García A., Muñoz V., Serrano L., Labidi J., 2014, Analysis of the performance of membrane ultrafiltration in the biorefinery by Aspen Plus simulation, Chemical Engineering Transactions, 39, 1711-1716.

Mourgues A., Sanchez-Marcano J., 2012, Theoretical considerations about a membrane process for helium purification in multichannel monoliths for high temperature nuclear reactors, Nuclear Engineering and Design, 247, 88-97.

Rosenthal J.E., 2016, GAMS: A user's guide, GAMS Development Corporation, Washington, DC.

Saidi S., Deratani A., Ben Amar R., Belleville M.P., 2013, Fractionation of a tuna dark muscle hydrolysate by a two-step membrane process, Separation and Purification Technology, 108, 28-36.

Sannino D., Sacco O., Chianese A., 2013, Determination of optimal operating condition in nanofiltration (NF) and reverse osmosis (RO) during the treatment of a tannery wastewater stream, Chemical Engineering Transactions, 32, 1993-1998.