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Optimization of ionic liquid recycling in Ionic Liquid-based Three Phase Partitioning processes

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Abstract

The economic viability of Ionic Liquid-based Three Phase Partitioning (ILTPP) processes, which have been proposed to recover proteins from waste streams, highly depends on the recyclability of the salt and, especially, the ionic liquid used in this technique. For this reason, the economic optimization of the recovery of ILTPP reagents is carried out, considering the main operational costs (reagents and energy). Results show that the process configuration with which costs are minimized is based on the use of vacuum evaporation to remove water from the salt-rich phase of the process. Therefore, the increase of salt concentration is not an economically efficient alternative to recycle the ionic liquid, even though this alternative is usually proposed in the literature. The optimum costs vary between 51.5 – 307 € kg protein^{-1} for almost all protein concentrations in the feed stream, which are significantly lower than the lowest price reported for the target protein (lactoferrin), so ILTPP processes seem to be economically viable. In addition, the price of reagents and energy has very little influence on the optimum solutions, because very large changes of prices are required to modify the obtained results.

Keywords: protein recovery, ionic liquid consumption, recycle, operating cost.

1. Introduction

The major bottleneck of the economic and technical viability of protein production processes is downstream processing, since the conventional methods to purify these biomolecules are time and cost consuming (Pei et al., 2009). In this way, Ionic Liquid-based Three Phase Partitioning (ILTPP) has been proposed as a novel technique to recover proteins at the liquid-liquid interface formed by ternary systems ionic liquid/salt/water, which combines the use of Ionic Liquid-based Aqueous Two Phase Systems (ILATPS) with results that are characteristic of Three Phase Partitioning (TPP) (Alvarez-Guerra and Irabien, 2014). However, the development of ILTPP processes highly depends on the consumption of the reagents involved, and especially of ionic liquid, because of its relative high price.

For this reason, the net consumption of ionic liquid in this process has been assessed in previous works, concluding that between 0.8 and 5% of the ionic liquid cannot be reused, depending on experimental conditions. Therefore, two additional steps to enhance the ionic liquid recyclability have been considered: the increase of the salt concentration to reduce the ionic liquid fraction in the waste stream, and the water removal by means of evaporation to increase the fraction of liquid phases that can be recirculated in the process (Alvarez-Guerra et al., 2014a). Nevertheless, the previous studies have assessed these additional recovery steps individually.

The aim of this work is the economic optimization of the ionic liquid recovery in ILTPP processes so that the costs associated with this recycling, which constitute the objective function, are minimized. This approach makes it possible to analyze simultaneously all the different alternatives to recycle the ionic liquid in the most efficient way: the individual additional recovery steps previously mentioned, a combination of them or the performance of the process without any of these steps. The target protein considered in this work for its recovery by means of ILTPP is lactoferrin, a high-added value whey protein which stands out due its nutraceutical properties (Wakabayashi et al., 2006).

2. Mathematical formulation

Figure 1 shows the general block diagram of the ILTPP process, which considers the alternatives proposed in previous works simultaneously (Alvarez-Guerra et al., 2014a). Therefore, once the protein recovery has been carried out in the first separation tank, the overall salt mass fraction may be increased to reduce the fraction of ionic liquid present in the salt-rich phase. Furthermore, a fraction of the water present in the salt-rich phase can be removed to increase the fraction of ionic liquid and salt contained in this phase that is recirculated, keeping the overall mass of the system constant. Nevertheless, the consideration of these additional recovery steps in the general diagram of the process does not imply that these alternatives to enhance the ionic liquid recyclability are actually included in the process, since they will be discarded if the amount of extra salt added or the fraction of water evaporated is equal to zero.

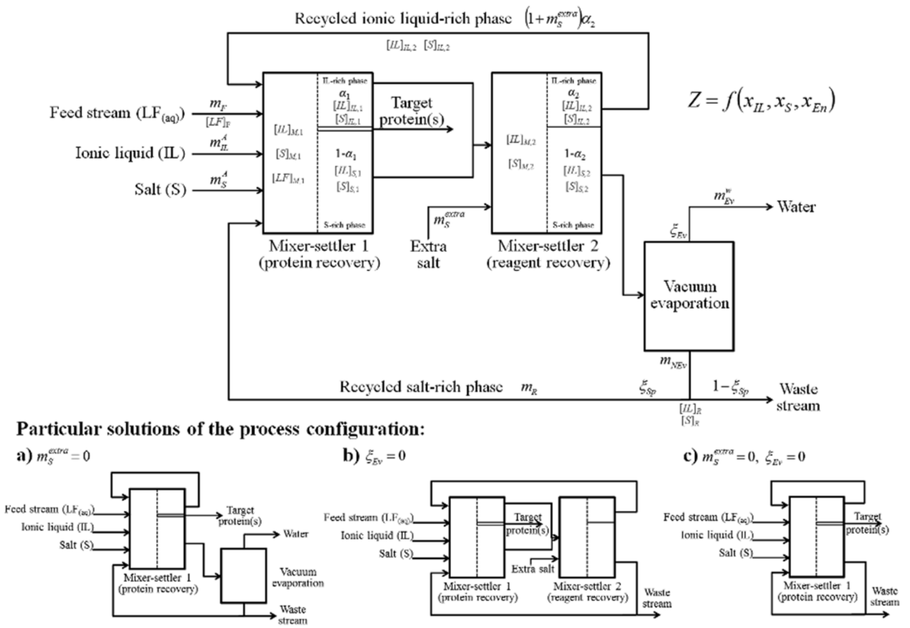

Figure 1-General block diagram and particular solutions of the ILTPP process.

The optimization of the ionic liquid recovery is based on the minimization of operating cost of the process associated with this objective. For this purpose, the three main operating costs related to the ionic liquid recyclability are: the net consumption of both ionic liquid and salt and the energy required to carry out the vacuum evaporation. However, due to the relative simplicity of the equipment involved in the process, investment costs are considered to be neglected. In fact, for a production of 1 t LF y^{-1} and an amortization period of 10 y, the maximum fixed costs related to the equipment that is added to the process in the different particular solutions of the process configuration are estimated to be around 6 € kg LF^{-1}, according to the Guthrie's modular method (Biegler et al., 1997). These maximum fixed costs only represent around 10 % of the minimum operating costs obtained at high protein concentrations in the feed stream, as shown in the next section. Consequently, results demonstrate the applicability of the previous assumption. Therefore, the mathematical model for the optimization of the ionic liquid recovery is formulated as Figure 2 shows.

Min $$Z = f_{LF}\left(\sum_i c_i x_i + c_{En} x_{En}\right) \quad (1)$$

s.t.

$$x_i = 0.01(1-\xi_{Sp})[i]_R m_{NEv} \quad (2)$$

$$x_{En} = \frac{m_{Ev}^w RT \ln\left(P_{out}/P_{in}\right)}{M^w \eta_m \eta_c} + \lambda_{Ev}^w m_{Ev}^w \quad (3)$$

$$m_{IL}^A + m_S^A + m_F + \left(1+m_S^{extra}\right)\alpha_2 + m_R = 1 \quad (4)$$

$$[i]_{M,1} = 100 m_i^A + [i]_{IL,2}\left(1+m_S^{extra}\right)\alpha_2 + [i]_R + m_R \quad (5)$$

$$[IL]_{M,2} = \frac{[IL]_{M,1}}{1+m_S^{extra}} \quad (6)$$

$$[S]_{M,2} = \frac{[S]_{M,1} + 100 m_S^{extra}}{1+m_S^{extra}} \quad (7)$$

$$m_{NEv} = (1-\xi_{Ev})\left(1+m_S^{extra}\right)(1-\alpha_2) \quad (8)$$

$$m_{Ev}^w = \xi_{Ev}\left(1+m_S^{extra}\right)(1-\alpha_2) \quad (9)$$

$$m_R = \xi_{Sp} m_{NEv} \quad (10)$$

$$[i]_R = [i]_{S,2} / (1-\xi_{Ev}) \quad (11)$$

$$[IL]_{S,j} = a_S \exp\left(b_S [S]_{S,j}\right) \quad (12)$$

$$[IL]_{IL,j} = a_{IL}[S]_{S,j} + b_{IL} \quad (13)$$

$$[S]_{IL,j} = d_{IL} \quad (14)$$

$$\frac{[IL]_{M,j} - [IL]_{IL,j}}{[S]_{M,j} - [S]_{IL,j}} = \frac{[IL]_{S,j} - [IL]_{M,j}}{[S]_{S,j} - [S]_{M,j}} \quad (15)$$

$$\alpha_j = \frac{[S]_{S,j} - [S]_{IL,j}}{[S]_{S,j} - [S]_{M,j}} \quad (16)$$

$$\xi_{Ev} \le 0.01\left(100 - [IL]_{S,2} - [S]_{S,2}\right) \quad (17)$$

$$x_i, \xi, m, \alpha \le 1 \quad (18)$$

$$[i] \le 100 \quad (19)$$

$$x, \xi, m, \alpha, [i] \ge 0 \quad (20)$$

$$x, \xi, m, \alpha, [i] \in \Re^n$$

Figure 2-Mathematical model for the optimization of the ionic liquid recovery. Notation: x_i is the net consumption of i; x_{En} is the energy consumption required for water removal by means of vacuum evaporation; $[i]$ is the mass fraction of i expressed as percentage; m is the mass fraction of the stream with respect to the total input streams in the first piece of equipment; α is the mass fraction of the ionic liquid-rich phase; ξ is the fraction of the stream evaporated (ξ_{Ev}) or split (ξ_{Sp}); f_{LF} is a conversion factor to express the cost per kg of target protein (lactoferrin, LF) recovered; η_m and η_c are the motor and compressor efficiencies; i denotes the component (IL: ionic liquid; S: salt) and j denotes the number of the mixer-settler (1 and 2: pieces of equipment where the protein recovery and the reagent recovery take place, respectively). Further details about the notation of the variables can be found in Figure 1.

The energy consumption is equal to the latent heat added to the system to keep temperature constant during evaporation and the energy required to create vacuum so that evaporation can be carried out at room temperature. For the last purpose, a vacuum pump is used that is modeled as a compressor that works isothermally due to the relatively low mass flow (McCabe et al., 2005). The compressor is modeled according to Biegler et al. (1997) for the case in which P_{out} = 1 atm and $P_{in} = P^o_{w,\,25\,^oC}$. Regarding the constraints of the optimization problem, Eq. 4 and 5 show the overall mass balance and the mass balance to IL and S, respectively, which assures the constancy of the total mass and composition of the system. Eq. 6-11 are also mass balances to connect the streams and compositions among the different pieces of equipment. The thermodynamic equilibrium characterization of the ILTPP systems which allows the determination of the composition and phase ratio in the mixer-settlers is introduced by means of Eq. 12-16 (Alvarez-Guerra et al., 2014b). It should be noted that in this work $[S]_{IL,j}$ is considered to be constant, since at very high mass fraction of ionic liquid this variable shows a relatively low variability with system composition. Eq. 17 introduces the idea that the maximum fraction that can be evaporated from the salt-rich phase is equal to its water content, since the other components are not volatile (salt and ionic liquid). Eventually, a complete recovery of lactoferrin at the liquid-liquid interface in the first mixer settler, where the concentration of this protein is equal to 0.016 wt% (Alvarez-Guerra et al., 2014b), is assumed in the model.

The optimization problem, which is non-linear (NLP), is solved by means of the CONOPT solver of GAMS (v. 23.3.3). MINOS solver is also used to check the sensitivity of the solution to the resolution algorithm, obtaining almost identical results.

3. Results and discussion

The minimum operation costs of ILTPP process are assessed for different protein concentrations in the feed stream ($[LF]_F$ = 0.32 – 2.00 g kg^{-1}; Alvarez-Guerra et al., 2014a) using BmimTfO and NaH_2PO_4 as ionic liquid/salt system. Table 1 shows the values of the main variables and parameters fixed in the optimization model. The values of other parameters that characterized the thermodynamic equilibrium of the BmimTfO/NaH_2PO_4 system have been previously reported by Alvarez Guerra et al. (2014b).

Table 1-Values of the main variables and parameters fixed in the optimization model.

f_{LF}	6250 kg kg^{-1} [a]	d_{IL}	0.5 % [a]
c_{IL}	895 € kg^{-1} [b]	$[IL]_{M,1}$	26.3 % [a]
c_S	47.5 € kg^{-1} [b]	$[S]_{M,1}$	23.3 % [a]
c_{En}	0.12 € kWh^{-1} [c]	P_{in}	0.0313 atm [e]
η_m	0.9 [d]	λ_{Ev}^{w}	2430 kJ kg^{-1} [e]
η_c	0.8 [d]	T	298.15 K

[a] Alvarez-Guerra et al. (2014b); [b] Commercial suppliers; [c] Foro Nuclear (2014); [d] Biegler et al. (1997); [e] Yaws (2014)

Figure 3 shows the values of the objective function (the main operating cost of the ILTPP process) for different values of $[LF]_F$. In the range 335.3-2000 mg kg^{-1}, moderate costs are obtained (within the range 51.5 – 307 € kg LF^{-1}), which correspond to the vacuum evaporation of water from the salt-rich phase. Therefore, the lower the protein concentration, the higher the cost, because a higher fraction of water must be evaporated to achieve the complete recovery of both the ionic liquid and the salt. In this case, $m_S^{extra} = 0$, which corresponds to the process configuration of Figure 1.a. However, for $[LF]_F \leq 335.2$ mg LF kg^{-1}, ionic liquid and salt losses are obtained and $m_S^{extra} > 0$, so operating costs increase dramatically. This region is strongly related to that previously reported by Alvarez Guerra et al. (2014a) for which water evaporation could not recycle all the reagents, even though in the present work this behaviour is exhibited for a slightly broad range of concentrations due to the combination of vacuum evaporation and increase of salt concentration ($m_S^{extra} > 0$).

Even though the price of LF is very variable depending on the commercial supplier and the quantity purchased, 600 € kg^{-1} is approximately the cheapest price that can be found for this protein. For this reason, ILTPP seems to be an economically viable process, because the price of lactoferrin is clearly higher than its main operating costs for the reagent recovery when only vacuum evaporation is performed. In fact, for $[LF]_F > 850$ mg LF kg^{-1}, the analyzed operating costs represent a lower percentage than 20 % of the lowest price reported for LF. Nevertheless, for the production of commercial LF, additional up- or downstream processes not included in the ILTPP may be required, which might imply additional costs.

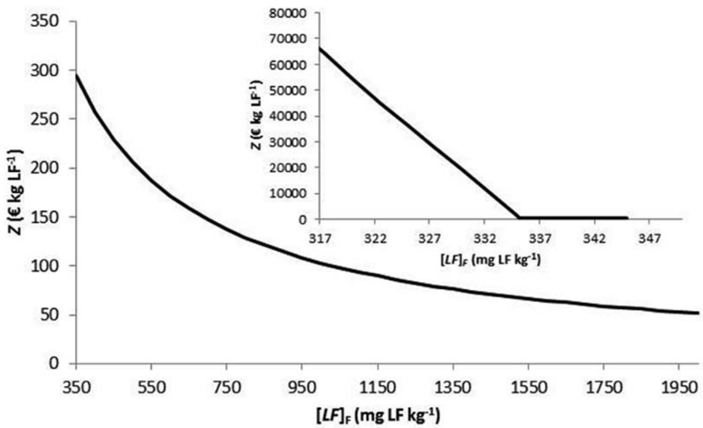

Figure 3-Minimum operating costs of the ILTPP process at different protein concentrations in the feed stream.

Due to the uncertainties associated with the cost of the reagents (ionic liquid and salt) and energy, which are the coefficients of the objective function, a sensitivity analysis is carried out. According to previous trends, it is expected a decrease of the price of reagents (especially the ionic liquid) and an increase of the cost of energy, so their coefficients are multiplied or divided by different factors as follows:

$$Z = f_{LF}\left[\frac{1}{f_{\mathrm{Re}}}\left(c_{IL}x_{IL} + c_S x_S\right) + f_{En}c_{En}x_{En}\right] \tag{21}$$

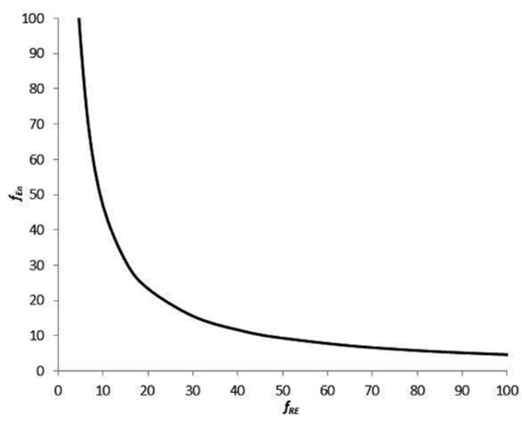

Figure 4-Combinations of the maximum values of f_{Re} and f_{En} for which $m^S_{extra}=0$.

It is observed that the maximum value of the product $f_{Re}{\cdot}f_{En}$ for which $m_S^{extra} = 0$ (i.e., evaporation remains as the unique reagent recovery step) is kept constant at 468 for all the protein concentrations in the feed stream. Therefore, at least an increase of f_{Re} or f_{En} higher than 468 will be required to change the optimum solution exclusively based on the use of vacuum evaporation to enhance the recovery of reagents. In this sense, Figure 4 graphs the combinations of the maximum values of f_{Re} and f_{En} for which $m_S^{extra} = 0$.

As a consequence, water removal by means of evaporation is a clear more advantageous alternative to recycle the ionic liquid and salt, even when significant changes in the price of reagents and energy occur. In this way, not only is the increase of salt concentration less effective in terms of ionic liquid recovery, but it also leads to higher operating costs, even though this approach is usually suggested in the literature to recycle the ionic liquid (Deng et al., 2009; Li et al., 2010) according exclusively to thermodynamic data.

4. Conclusions

The minimization of operating costs related to the recyclability of ILTPP reagents involves exclusively the water removal from the salt-rich phase by means of vacuum evaporation for almost all protein concentrations in the feed stream. Moreover, this optimum solution is very little sensitive to the price of reagents or energy, leading to operating costs that are significantly lower that the price of the protein to be recovered (lactoferrin), which may assure the economic viability of ILTPP processes.

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