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Optimal design of membrane processes for wastewater treatment and metal recovery

Sergio M. Corvalan^a, Inmaculada Ortiz^b, Ana M. Eliceche^{a,*}

^a Chemical Engineering Department, Universidad Nacional del Sur, Plapiqui-Conicet, Camino La Carrindanga km 7, 8000 Bahía Blanca, Argentina

^b Dpto. de Química, Universidad de Cantabria, 39005 Santander, Spain

Abstract

Different continuous operating modes of a nondispersive solvent extraction (NDSX) process with membrane modules of hollow fibre for wastewater treatment and metal recovery are evaluated. Cocurrent and countercurrent flow of aqueous and organic phases in the membrane modules with alternative product extraction locations for the removal and recovery of hexavalent chromium from wastewater are studied. The design of NDSX process in a countercurrent continuous operation is addressed for the first time in this work and the improvement achieved is reported. The membrane area required in the countercurrent operation is reduced significantly compared with the cocurrent operation, requiring also less investment in pumps and pumping cost leading to the minimum total cost. Thus a significant improvement in the design of this new and cleaner technology is presented.

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1. Introduction

The synthesis, design and operation of the nondispersive solvent extraction (NDSX) technology need to be addressed in order to promote and evaluate the economic viability of its industrial application. In this work the design of different configurations is presented with a rigorous model of the mass transfer in the hollow fibre of the membrane modules. As a case study the extraction of hexavalent chromium Cr(VI) from wastewater and its recovery for industrial reuse is presented, which poses a real challenge for pollution prevention and has a wide range of applications of industrial interest.

Separation processes based upon reversible chemical complexation, offer possibilities of high mass transfer and selective extraction. The chemical pumping of a relatively diluted solute against its concentration gradient by a carrier, known as coupled transport (Cussler, 1971), allows the extraction of pollutants from industrial wastewaters and their concentration in another phase, because of the reversibility of the chemical reaction with

the carrier or extractant. As the contaminant can be recycled and re-used, the amount of pollutant sent off finally into the environment is reduced leading to a new and cleaner technology than the existing ones.

Extraction processes using supported liquid membranes are of particular interest due to their versatility. While in conventional-practice solvent extraction processes rely on dispersion, in microporous membrane-based NDSX the dispersion of a phase into another is eliminated, and both are contacted through the pores of the fibre. With the NDSX technology, limitations of conventional liquid extraction such as flooding, intimate mixing and requirement of density difference are overcome. In the last years, extensive studies on dispersion-free solvent with the use of microporous membrane have been carried out by Prasad and Sirkar (1988), D'Elia, Dahuron and Cussler (1986), Wickramasinghe, Semmens and Cussler (1992) and Yang and Cussler (1986). Ho and Sirkar (1992) presented a general review of the NDSX technology, and more recently, Gabelman and Hwang (1999) provided an overview of hollow fibre contactors and de Gyves and de San Miguel (1999) reviewed the applications for metal separations.

Decisions regarding the selection of the operating mode, process configuration, size of equipment and

* Corresponding author. Tel.: +54-291-486-1700; fax: +54-291-486-1600.

E-mail address: meliceche@plapiqui.edu.ar (A.M. Eliceche).

Nomenclature

C	solute concentration (mol m^{-3})
C_{in}	effluent inlet concentration (mol m^{-3})
CT	total carrier concentration (mol m^{-3})
F	flowrate ($\text{m}^3 \text{h}^{-1}$)
H	stripping distribution coefficient
K	extraction equilibrium constant
K_m	membrane mass transfer coefficient (m h^{-1})
L	fibre length (m)
r	ratio of the length to the area of the membrane modules
z	axial distance (m)
A	effective surface area (m^2)
Superscripts	
E	extraction module
S	stripping module
T	tank
Subscripts	
e	extraction phase
p	product
s	stripping phase
o	organic phase
oi	organic interface

operating conditions need to be addressed in order to promote their industrial application. A large number of studies of this technology have been mentioned in the literature, but there is still little information on the analysis and optimisation of these processes with a rigorous modelling.

Alonso and Pantelides (1996) carried out the simulation of the NDSX process to extract and re-use Cr(VI) in a batch mode. An analysis to validate the models with the performance of an NDSX pilot plant in the semicontinuous mode is reported by Alonso, Galan, Gonzalez and Ortiz (1999). Galan and Grossmann (1998) presented the synthesis of a cocurrent extraction sector using a simplified model for the membranes. The optimisation of a NDSX pilot plant, operating in a cocurrent semicontinuous mode, was presented by Eliceche, Alonso and Ortiz (2000) and the optimisation of the cocurrent continuous mode was presented by Eliceche, Corvalán and Ortiz (2002). Alonso, Lasshan and Gruhn (2001) implemented the synthesis of a cocurrent flow in the membrane modules and a semi-continuous process using a time independent model.

The countercurrent flow of the aqueous and organic phases in the extraction and stripping sectors is evaluated in this work for the first time. Previous work with NDSX technology for effluent treatment and Cr(VI) recovery has considered the cocurrent flow between the aqueous and organic phases in the membrane modules. The objective function to be minimised is the total membrane area required in the extraction and stripping sectors. The organic and stripping flowrates and the

membrane areas are evaluated solving a nonlinear programming problem including the differential equations that represent the contaminant composition profiles in the membranes. The separation targets are the maximum contaminant composition in the treated wastewater and minimum contaminant composition in the product for further re-use, which are posed as inequality constraints.

The membrane area required in the countercurrent flow is significantly smaller than the area required for the cocurrent flow. Thus the improvement achieved by the countercurrent operation and different product extraction locations has been quantified and it is reported. In the countercurrent operation, the reduction in areas is simultaneously achieved with lower organic and stripping flowrates, thus reducing the investment cost in pumps and the operating cost of pumping leading to the minimum total cost configuration.

The sensitivity of the total area for different configurations, with respect to the organic and stripping flowrates is also analysed.

2. Countercurrent configuration for wastewater treatment and metal recovery process

The separation process involves mass transport phenomena coupled with selective chemical reactions that can lead to different metal fluxes in the extraction and back-extraction or stripping steps.

The main components of a NDSX process are the membrane modules in the extraction and stripping

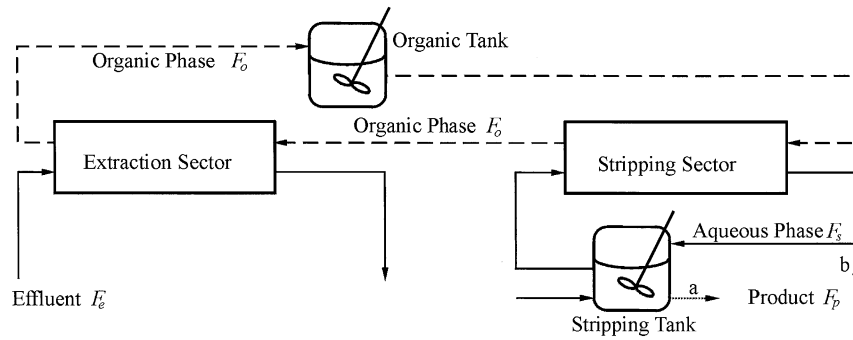


Fig. 1. NDSX countercurrent operation with product extraction before and from the stripping tank.

sectors, as shown in Fig. 1. The aqueous phase runs through the lumen of the hollow fibers, while the organic phase containing the extractant runs by the shellside. The membrane is hydrophobic and the phase contact takes place at the membrane interface.

The metal is extracted from the effluent stream F_e and transferred to the organic phase F_o in the extraction sector. The organic stream F_o leaves the extraction sector heading to the stripping sector, where the metal is back extracted from the organic phase and transferred to the aqueous stream F_s . The organic phase flows in a close circuit without leaving the process. A small overpressure on the aqueous phase over the organic phase is maintained, in order to avoid the contamination of the aqueous phase with the organic solution. The aqueous stream F_s leaves the stripping sector and goes to the aqueous tank. Finally, the product stream F_p containing the concentrated metal is removed from the stripping tank. The same flowrate of stripping aqueous solution with no chromium is added to the tank in order to replace the amount of solution removed from the system by the product stream.

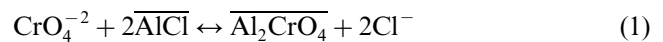
The aqueous and organic phases in the membrane module can run either in a countercurrent flow as shown in Fig. 1, or in cocurrent flow by reversing the organic phase flow. The product stream concentrated in the contaminant can be removed from the stripping tank (option a) or before entering the stripping tank (option b) as shown in Fig. 1.

The four configurations analysed in this work are the countercurrent and cocurrent flows inside the membrane modules with product extraction before entering the stripping tank and from the stripping tank.

3. Continuous countercurrent model of the NDSX process

The plant is designed for the removal of hexavalent chromium and its recovery for industrial re-use. The first step to model the process involves the mathematical representation of the chemical equilibrium at the membrane interfaces, in both the extraction and stripping processes.

The extraction and stripping reaction between the solute Cr(VI) and the organic carrier (quaternary ammonium salt Aliquat 336 dissolved in kerosene) is represented by:



Alonso, Galan, Irabien and Ortiz (1997) have shown that an ideal behaviour could be assumed for the aqueous phase while a non-ideal behaviour of the organic phase should be taken into account in the equilibrium expression, resulting in the following expression for the chemical equilibrium:

$$K = \frac{4C_{oi}^E(C_{in} - C_e^E)^2}{C_e^E(CT - 2C_{oi}^E)^2}(0.001CT)^{0.6} \quad (2)$$

where C_{in} is the initial Cr(VI) in the effluent and CT is the total carrier concentration.

As the chlorine concentration in the stripping aqueous solution is maintained high (1000 mol m^{-3}) in order to favour the stripping process, the change in Cl^- and AlCl concentration can be neglected along the modules. For that reason the chemical equilibrium can be well described by a distribution coefficient defined as the ratio of the equilibrium concentrations in the aqueous and organic phases as has been experimentally checked by Ortiz, Galán and Irabien (1996):

$$H = \frac{C_s}{C_{oi}^S} \quad (3)$$

The Cr(VI) mass balances in the organic and aqueous phases in the extraction and stripping process are modelled assuming that the main resistance to the solute transport lies in the microporous membrane, therefore, mass transfer resistances at the aqueous and organic phases are neglected. It is also assumed that the reactant species are in equilibrium in the whole interface.

The countercurrent operation with product removal before entering the stripping tank, as shown in Fig. 1, is represented by the following set of differential and algebraic equations.

3.1. Extraction sector

Aqueous stream

$$\frac{dC_e}{dz} = -\frac{A^E}{F_e L^E} K_m (C_{oi}^E - C_o^E), \quad C_e(0) = C_{in} \quad (4)$$

Organic stream

$$\frac{dC_o^E}{dz} = -\frac{A^E}{F_o L^E} K_m (C_{oi}^E - C_o^E), \quad C_o^E(0) = C_o^S(L^S) \quad (5)$$

3.2. Stripping sector

Aqueous stream

$$\frac{dC_s}{dz} = \frac{A^S}{F_s L^S} K_m (C_o^S - C_{oi}^S), \quad C_s(0) = C_s^T \quad (6)$$

Organic stream

$$\frac{dC_o^S}{dz} = \frac{A^S}{F_o L^S} K_m (C_o^S - C_{oi}^S), \quad C_o^S(0) = C_o^E(L^E) \quad (7)$$

3.3. Stripping tank

$$(F_s - F_p)C_s(L^S) = F_s C_s^T \quad (8)$$

In the extraction sector, $z \in [0, L^E]$ and in the stripping sector, $z \in [0, L^S]$. The ratio r , of the length to the area of the membrane modules in the extraction and stripping sectors is kept constant.

$$\frac{L^E}{A^E} = \frac{L^S}{A^S} = r \quad (9)$$

4. Formulation of the design problem

For a given configuration, the objective is to find the minimum membrane area to achieve the separation specifications, such as the maximum allowed metal composition in the wastewater leaving the plant and minimum metal concentration required in the product for further reuse. The membrane area is the most important contribution to the total cost. The design is formulated as the following non-linear programming problem:

$$\text{Min}_v (A^E + A^S)$$

$$\text{s.t. } h(x, \dot{x}, w, v) = 0$$

$$I(x, v) = 0$$

$$g(x, v, w) \leq 0$$

$$x^L \leq x \leq x^U$$

$$w^L \leq w \leq w^U$$

$$v^L \leq v \leq v^U \quad (\text{P1})$$

The algebraic and differential equations (1)–(9) are formulated as equality constraints h . The differential equations initial conditions are indicated as the equality constraints I ; and the separation targets such as maximum concentration of the treated wastewater and minimum product concentration are posed as inequality constraints g . Different operating constraints such as the allowed ratios between organic and aqueous flowrates in the membrane modules are also included as inequality constraints g .

The vector v represents the set of optimisation variables, such as the organic and stripping flowrates, the extraction (A^E) and stripping (A^S) membrane areas. The vector x represents the differential distributed variables like the aqueous and organic concentration in the modules, while \dot{x} represent their derivatives with respect to the module axial position z . The vector w represents the algebraic distributed variables such as the interface concentrations along the modules. Upper and lower bounds on vectors x , w and v are indicated by superscript U and L , respectively.

5. Case study for Cr(VI) removal and recovery

The design of an industrial plant for the treatment of wastewater contaminated with Cr(VI) and its recovery as a product for further re-use is studied in this work. A wastewater flowrate of $1 \text{ m}^3 \text{ h}^{-1}$ with an inlet Cr(VI) concentration of $13.462 \text{ mol m}^{-3}$ is treated in the plant. The maximum Cr(VI) concentration allowed in the treated wastewater is 1.923 mol m^{-3} and the minimum Cr(VI) concentration in the product for industrial reuse is $384.615 \text{ mol m}^{-3}$.

According to experimental work the ratio between these streams must be constrained to:

$$0.1 \leq \frac{F_s}{F_o} \leq 10 \quad (10)$$

This inequality constraint is included in the vector g of problem P1.

Lower and upper bounds for both the organic and stripping streams are 0.1 and $10 \text{ m}^3 \text{ h}^{-1}$, respectively, while 0.001 and $0.500 \text{ m}^3 \text{ h}^{-1}$ are used as lower and upper bounds for the product stream.

The system of differential equations is solved using a second order orthogonal collocation polynomial approximation over 50 finite elements in gPROMS (2002).

The optimum design for each configuration is obtained solving problem P1 with the optimisation code gOPT of gPROMS, which requires in the order of 6 s and 15 iterations in a Pentium III 700 MHz workstation.

6. Analysis of the design of alternative configurations

In a previous work, Eliceche et al. (2002) studied the optimal operation of a pilot plant running in the cocurrent mode with product extraction from the stripping tank. For the design of a plant at a bigger scale the following four configurations were considered: countercurrent with product removal from the stripping tank and before entering the stripping tank and cocurrent with product removal from the stripping tank and before entering the stripping tank. The differential and algebraic equations that model the process change slightly for each configuration, basically modifying the connectivity equations. The optimal design of the four configurations is reported in Table 1. The separation constraints related to the maximum Cr(VI) concentration of the treated wastewater and the minimum product concentration for reuse are always active at the optimum solution of problem P1. The inequality constraint formulated in the equation (10) is also active in the configurations of the second and third column of Table 1.

The objective is to minimise the total area, thus the best configuration corresponds to the countercurrent flow with product extraction before the stripping tank. It has the smallest stripping and extraction areas and low organic and stripping flowrates. Therefore, it has the minimum total cost due to minimum investment cost

Table 1
Optimal design of four configurations: BT (extraction before tank), FT (extraction from tank)

Optimisation	Countercurrent	Countercurrent	Cocurrent	Cocurrent
Variables	Product BT	Product FT	Product BT	Product FT
F_o ($\text{m}^3 \text{h}^{-1}$)	0.121	0.121	1	10
F_s ($\text{m}^3 \text{h}^{-1}$)	0.1	1.213	0.1	10
F_p ($\text{m}^3 \text{h}^{-1}$)	0.030	0.030	0.030	0.030
A^E (m^2)	897.791	1136.685	988.371	1058.735
A^E increment%	0	26.61	10.09	17.93
A^S (m^2)	909.158	1175.306	1892.892	2328.511
A^S increment%	0	29.27	108.20	156.12
Total area ($A^S + A^E$)	1806.949	2311.991	2881.263	3387.246
$(A^S + A^E)$ increment%	0	27.95	59.46	87.46

in membrane modules and pumps and minimum operating pumping cost. Thus the industrial plant should be designed for this configuration that has the smallest required total area. A significant reduction of 47% in the total area has been achieved with respect to the cocurrent mode with extraction from the stripping tank being used in the pilot plant previously analysed by Eliceche et al. (2002). This configuration not only has the biggest total required area but the optimum operating conditions for the organic and stripping flowrates are at the upper bound requiring more investment in pumps and in pumping costs.

The stripping area is more sensitive to the operating mode than the extraction area. The stripping area required in the cocurrent operation doubles the stripping area required in the countercurrent operation. It can also be observed that extraction before the stripping tank is a better option than the extraction from the stripping tank.

7. Total area as a function of the stripping and organic flowrates

In Figs. 2–5, the required area is shown as a function of the organic and stripping flowrates for the configurations mentioned previously. The total area is calculated using the optimum solution reported in Table 1 as the base case for each configuration, then the organic

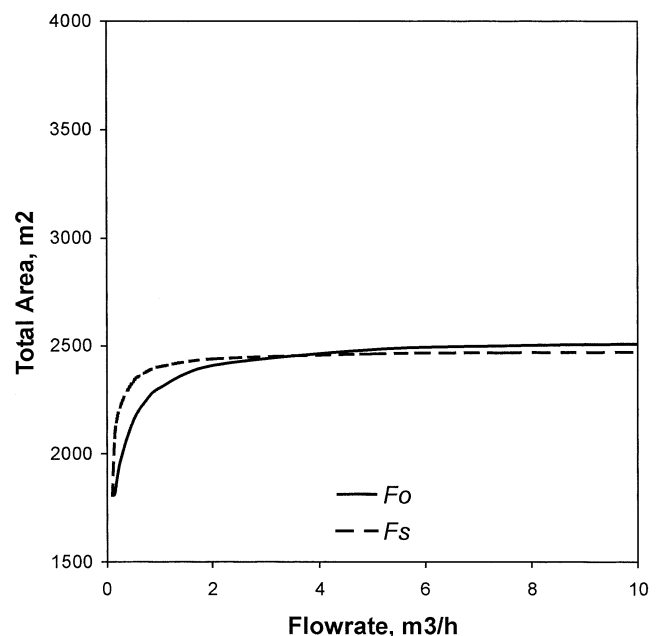


Fig. 2. Countercurrent operation with product extraction before the stripping tank.

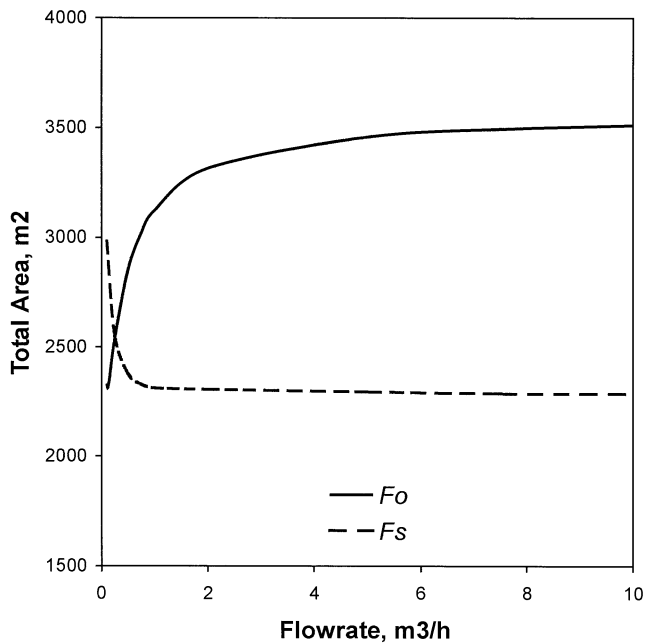


Fig. 3. Countercurrent operation with product extraction from the stripping tank.

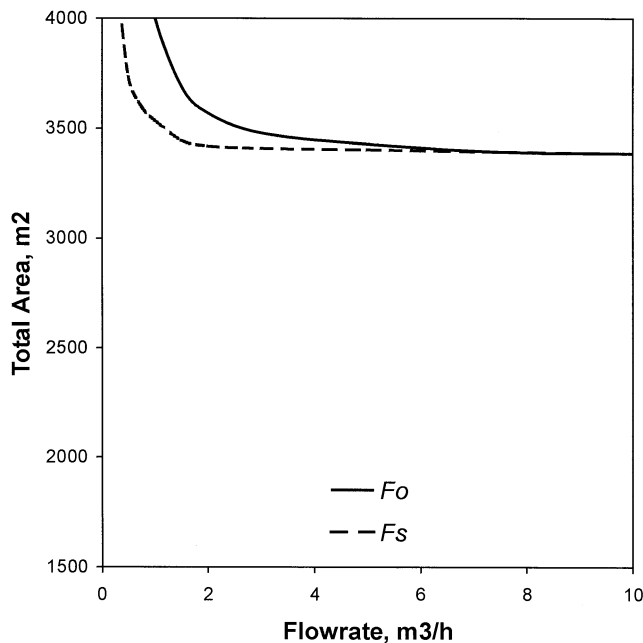


Fig. 5. Cocurrent operation with product extraction from the stripping tank.

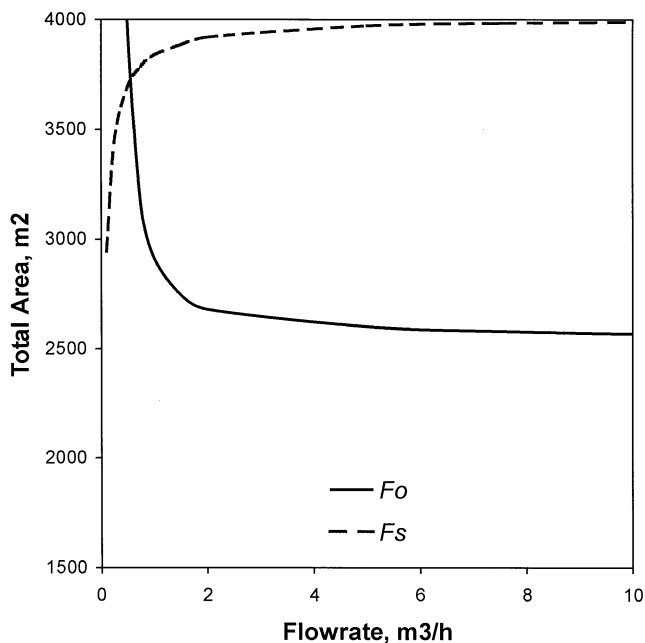


Fig. 4. Cocurrent operation with product extraction before the stripping tank.

and stripping flowrates change one a time, keeping the other one constant and equal to the optimum value.

It can be observed that the countercurrent operation (Figs. 2 and 3) requires less total area than the cocurrent operation (Figs. 4 and 5). The countercurrent operation with product extraction before the stripping tank is the

best configuration and it is better than the cocurrent operation with product extraction before the stripping tank in all the operating range, with flow rates varying from 0.1 to $10 \text{ m}^3 \text{ h}^{-1}$.

The minimum total required area for the countercurrent operation with product extraction before the stripping tank, Fig. 2, occurs at the lower bounds of the organic and stripping flowrates. As the organic and stripping flowrates decrease, the driving force for mass transfer in the extraction and stripping membrane modules increase requiring less area. Significant increments in the area can be observed with the organic and stripping flowrates increasing from 0.1 to $1 \text{ m}^3 \text{ h}^{-1}$, while the area increases very slowly for organic and stripping flowrates changing from 2 to $10 \text{ m}^3 \text{ h}^{-1}$.

The minimum total area for the cocurrent operation with product extraction from the stripping tank is at the upper bounds for the organic and stripping flowrates, as shown in Fig. 5. When the organic and stripping flowrates decrease the driving force for mass transfer in the membrane modules decrease and the area required increases. When the organic and stripping flowrates decrease from 10 to $4 \text{ m}^3 \text{ h}^{-1}$ the area increases slowly but when the flowrates decrease from 4 to $0.1 \text{ m}^3 \text{ h}^{-1}$ the area increments are significant. This configuration has the highest investment cost in membrane and pumps and also in the operating cost of pumping.

When the product is extracted before the stripping tank (Figs. 2 and 4) the area decreases when the stripping

flowrate decreases. If the product is extracted from the stripping tank (Figs. 3 and 5) the area increases as the stripping flowrates decreases. In the countercurrent operation (Figs. 2 and 3) the area decreases as the organic flowrate decreases and in the cocurrent operation (Figs. 4 and 5) the area increases as the organic flowrate decreases.

8. Conclusions

In this work the optimum design and analysis of different configurations including the countercurrent flow has been presented for the first time. At the conceptual design stage of new and cleaner technologies, this is a crucial step for promoting their industrial applications, gaining process insight simultaneously. The optimum design for each configuration is obtained solving a nonlinear programming problem that includes the differential equations that model the extraction and stripping sectors. Parameters obtained at the laboratory and pilot plant scale are used in the membrane models. The numerical results reported, for wastewater treatment for Cr(VI) removal and recovery for industrial reuse, quantify the significant improvement that can be achieved at earlier design stages. The cocurrent operation with product extraction from the stripping tank requires 87% more membrane area than the countercurrent operation with product extraction before the stripping tank. The cost of membranes is high, therefore, important reductions in membrane areas would help to improve the economic viability of this technology. This option has also low organic and stripping flowrates, with low fixed pump and pumping costs. It, therefore, has the minimum total cost.

The total area shown in Figs. 2–5, indicate the optimum operating regions for different configurations and the required total area sensitivity to changes in the organic and stripping flowrates.

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