Synthesis of a Non Dispersive Solvent Extraction Plant for Effluent Treatment and Metal Recovery

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Abstract

A Nonlinear Mixed Integer Programming approach is presented to select the number of membrane modules required in the extraction and stripping sectors of a Non Dispersive Solvent Extraction Plant for effluent treatment and metal recovery. The differential equations that model each membrane module are discretized using orthogonal collocation on finite elements leading to an algebraic system of equations. Binary variables are used to select the number of membrane modules in the extraction and stripping sectors. A superstructure with hollow fibre membrane modules in series in the extraction and stripping sectors is presented. A Mixed Integer Non Linear Programming problem is formulated in GAMS to optimise the superstructure.

An initialisation strategy for the solution of the Mixed Integer Non Linear Programming problem is presented. The solution of the non linear programming problem, with the extraction and stripping areas rounded up to the nearest superior integer number of membrane modules for both sectors is used as the initial point. This initialisation reduces significantly the time required to solve the MINLP problem leading in most cases to the optimal solution.

Keywords: Selective membranes, Cr(VI) recovery, synthesis.

1. Introduction

The purpose of this work is to present the methodology developed for the synthesis of the membrane modules required in the extraction and stripping sectors of a Non Dispersive Solvent Extraction (NDSX) plant in order to evaluate the feasibility of its industrial application. This is a cleaner technology because the contaminant Cr(VI), is extracted from the effluent in the extraction sector and it is simultaneously re extracted and concentrated for industrial reuse in the stripping sector. Therefore the amount of Cr(VI) disposed into the environment is significantly reduced compared to more conventional technologies.

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Membranes technologies have become a viable alternative to conventional separation processes. A relative new separation technology based on membranes is the Non Dispersive Solvent Extraction (NDSX) that treats an aqueous stream extracting the contaminant and simultaneously recovering and concentrating the contaminant in another aqueous stream. This concentrated stream is a product for industrial re use of the contaminant in the same plant that generated the effluent or somewhere else.

The NDSX process is based on the facilitated transport of solutes by a carrier that pumps a specific solute against its own concentration gradient through the membrane as it happens in many biological process.

Although there are several studies on the performance of NDSX technology, only recently the optimisation of this process has been attempted. The simulation of this technology for Cr(VI) recovery was first implemented by Alonso and Pantelides (1996). Galan and Grossman (1998) presented the synthesis of the extraction sector of a NDSX process using a simplified and algebraic model for the membrane model. The optimal operating conditions of a pilot plant operating in semi continuous and continuous mode have been analysed by Eliceche et al. (2000,2002). Alonso et al. (2001) proposed a superstructure for the semi continuous operation of a NDSX plant with four modules in both extraction and stripping sectors. The membrane modules modelling correspond to a continuous operation and the design specifications are not handled as inequalities constraints but added as penalty functions to the objective function.

Corvalan et al. (2004) presented the design of a NDSX plant solving a non linear programming problem showing that the counter current operations has a better performance that the co current operation between the aqueous and organic phases.

In this work a superstructure containing membrane modules in series in the extraction and striping sectors is presented for the continuous operation. The rigorous modelling for the membrane modules presented by Corvalan (2004) is used in this work. Due to the fact that binary variables are required for the selection of the membrane modules and that a differential and algebraic system of equations models each membrane module a Mixed Integer Differential Optimization (MIDO) problem arises. The MIDO problem is reformulated as a mixed integer non linear programming (MINLP) problem discretizing the differential equations with an Orthogonal Collocation on Finite Elements method.

The initialisation strategy developed is based in the solution of a non linear programming problem, Corvalan et al.(2004), were the real values of the membrane areas obtained for the extraction and stripping sectors are rounded to the nearest superior integer number of membrane modules in both sectors. This initialisation strategy reduces significantly the computing time required to obtain a solution leading in many cases to the optimal solution.

2. Description of a Non Dispersive Solvent Extraction plant

The hollow fibre membrane modules are the main equipment in the in the extraction or in the stripping sectors of a non-dispersive solvent extraction process as shown in Figure 1. The aqueous phase run through the lumen of the hollow fibres, and the organic phase containing the extractant flows on the shell side. The organic solution wets the porous wall of the hydrophobic fibre. The organic phase F_o extracts the contaminant from the effluent in the extraction sector. The contaminant is reextracted from the organic phase and concentrated in an aqueous phase, in the stripping sector. The organic stream leaving the extraction module is fed into the stripping sector, and the organic stream leaving the stripping module is recycled to the extraction sector. The stripping aqueous solution flowrate, F_s , takes the solute from the organic stream and is fed to the stripping tank for further recycling to the stripping module The recovered contaminant, extracted from the effluent, leaves the plant in the concentrated product stream F_p. An equivalent aqueous solution flowrate, free of contaminant enters the stripping tank.

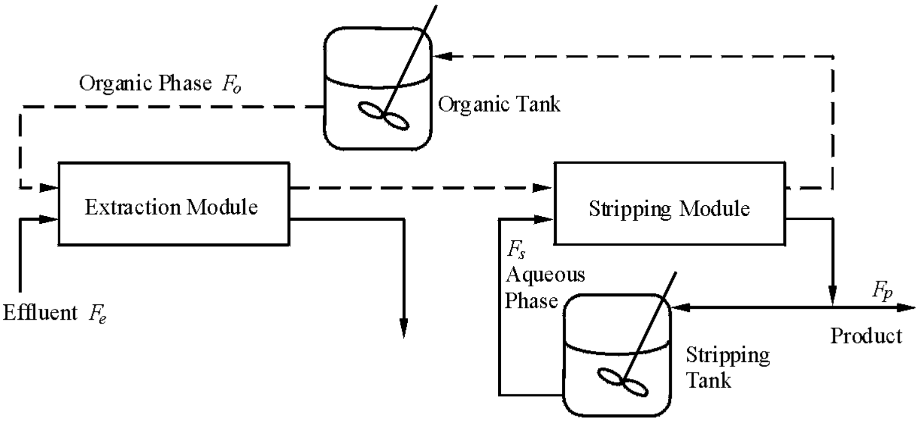

Figure 1- Non dispersive solvent extraction schematic diagram.

The model for the NDSX process involves the mass transport, balances and chemical equilibrium in each membrane module in the extraction and stripping sectors for both aqueous and organic phases. The differential and algebraic system of equations can be found in Corvalan et al. (2004).

3. Superstructure and optimisation problem

The superstructure presented in Figure 2 contains a series of membrane modules for the extraction and stripping sectors with the aqueous and organic phases running in a counter current mode. These two options are the best alternatives compared to modules arranged in parallel and aqueous and organic phases running in a co current mode, and for that reason are included in the superstructure.

A Differential Algebraic system of equations model the mass transport along the membrane module length, in the aqueous and organic phases for the extraction and stripping sectors, as described in Corvalan (2004). To optimise the superstructure presented in Figure 2, binary variables are introduced to select the number of membrane modules in the extraction and stripping sectors.

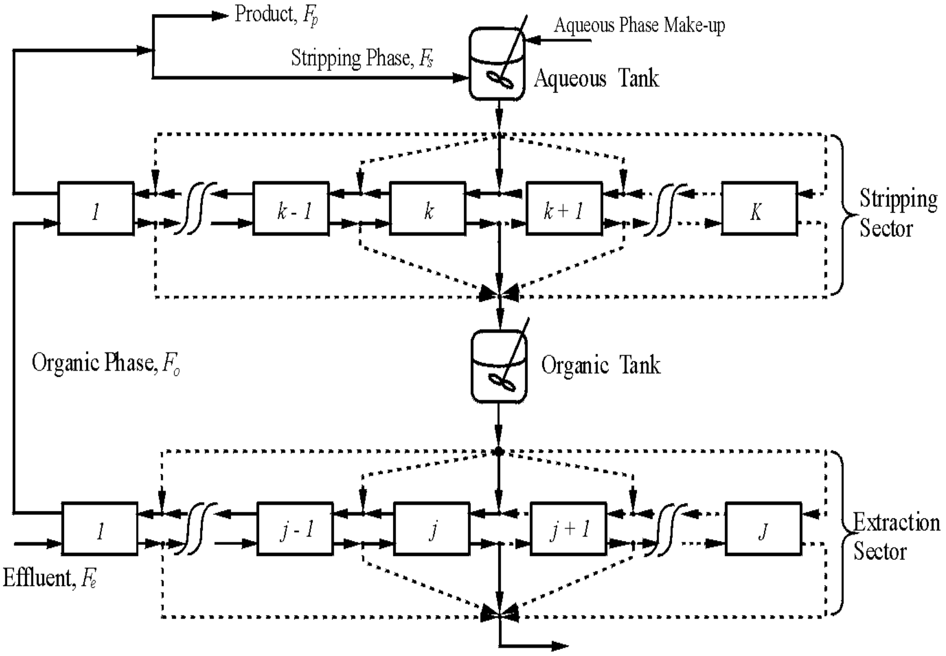

Figure 2 – Non Dispersive Solvent Extraction Superstructure

The formulation of the Mixed Integer Differential Optimisation (MIDO) problem to optimise the superstructure is formulated as follows in P1:

$$
\begin{aligned}
& \underset{v,y}{Min}\ \phi(x,v,y) \\
& s.t.: \quad \begin{aligned}[t]
& h(\dot{x},x,w,v,y) = 0 \\
& g(\dot{x},x,w,v,y) \leq 0 \\
& I(x(0),x(L),y) = 0 \\
& x^{LB} \leq x \leq x^{UB} \\
& w^{LB} \leq w \leq w^{UB} \\
& v^{LB} \leq v \leq v^{UB} \\
& y \in \{0,1\}
\end{aligned}
\end{aligned}
\qquad \text{(P1)}
$$

Where x represents the set of differential distributed variables such as the aqueous and organic concentration profiles, being $\dot{x}$ the derivative of x with respect to the module axial position z (with $z \in [0, L]$), w is the set of algebraic distributed variables, such as the interphase concentration along the modules, and v is the set of non distributed variables, for example, the aqueous or organic flowrates. The mass balances, equilibrium and interconnection relationships are represented by the set of differential and algebraic equalities ***h*** and inequalities ***g***, and the initial conditions and the connectivity between the modules are given by ***I***.

The differential equations are discretized using Orthogonal Collocation on Finite Elements, so the Mixed Integer Differential Optimisation (MIDO) problem is reformulated as a MINLP problem. The MINLP problem is formulated and solved in GAMS. The objective function used in this work has been the minimization of the total area of the extraction and stripping sectors. The cost of the membrane modules is the most significant contribution to the total cost of the plant.

4. Case study of Cr(VI) recovery and concentration

The synthesis of an industrial plant for the treatment of contaminated underground water with Cr(VI) and its recovery for industrial re use is presented in this work. The feed flow rate and Cr(VI) composition are: 1 m^3/h and 13.462 mol/m^3. The maximum Cr(VI) composition in the treated underground water is 1.923 mol/m^3 and the minimum Cr(VI) concentration in the product for industrial reuse is 384.615 mol/m^3. These two separation targets are posed as inequality constraints in the MINLP problem.

The membrane areas for the extraction and stripping sectors in the NLP problem solution point are reported in Table 1, together with the corresponding real number of membrane modules (7.79 and 14.21), each membrane module has 130 m^2 . The initial point for the number of membrane modules in the extraction and stripping sectors to solve the MINLP problem correspond to the nearest superior integer number of membrane modules found as the NLP solution for each sector (8 and 15). The solution point has the same number of membrane modules in both sectors than the initial point indicating that the initialisation strategy is a good one. The initial point correspond to the module j and k of the extraction and stripping sectors of the superstructure in Fig. 2. Binary variables are introduced for modules $j-1, j, j+1, k-1, k$ and $k+1$. Thus in principle only six binary variables are required regardless of the number of modules involved in each sector. This strategy reduces significantly the dimension of the binary variable vector in the MINLP problem that would be otherwise have a dimension of approximately $j+k$ binary variables (22 in this example).

Table 1: MINLP problem initialisation strategy with the NLP solution, Sol Pt (solution point), Ini Pt (Initial point)

	NLP problem		MINLP problem	
Area- modules	Sol Pt m^2	Sol Pt modules	Ini Pt modules	Sol Pt modules
Extraction sector	1013	7.79	8	8
Stripping sector	1848	14.21	15	15

The MINLP problem was solved using CPLEX for the Mixed Integer Linear sub problem and CONOPT for the NLP sub problem, requiring 51 seconds to find the solution with eight DICOPT iterations in GAMS.

5. Conclusions

The synthesis approach presented for the initialisation and solution of the MINLP problem facilitates the synthesis of industrial plants and the evaluation of the cost associated with the separation targets required. The initialisation strategy developed is based in the solution of a Non linear programming problem were the optimal real values of the membrane areas obtained for the extraction and stripping sectors are rounded to the nearest superior integer number of membrane modules in both sectors. This initialisation strategy reduces significantly the computing time required to obtain a solution leading in many cases to the optimal solution.

The separation work and therefore the number of membrane modules depends on the level of contamination of the under ground waterwater, and the two separation targets: the maximum Cr(VI) composition in the treated underground water and the minimum Cr(VI) composition required in the concentrated product for its industrial reuse. The knowledge of the relative cost of this technology compared to other alternative technologies, will allow the definition of separation regions for which a cleaner technology such as NDSX would be competitive at the conceptual design stage to promote its industrial application.

References

Alonso, A. and C. Pantelides, 1996, Modelling and simulation of integrated membrane processes for recovery of Cr(VI) with Aliquat 336, Journal of Membrane Science 110,151.

Alonso, A.I., A. Lassahn and G. Gruhn , 2001, Optimal design of non-dispersive solvent extraction processes, Computers and Chemical Engineering, 25, 267.

Brooke, A.; Kendrick, D.; Meeraus, A.; Raman, R. GAMS: A user guide*;* Scientific Press: Palo Alto, CA, 1992.

Corvalán, S.M., I. Ortiz and A.M. Eliceche, 2004. Design of an Industrial Membrane Plant for the Treatment of Industrial Effluents, Computers and Chemical Engineering, Vol 28/1-2, pp 103-109.

Eliceche, A.M.; A.I. Alonso and I. Ortiz, 2000, Optimal operation of selective membrane separation processes for wastewater treatment, Computers and Chemical Engineering, 24, 2115.

Eliceche A., S. Corvalán and I. Ortiz, 2002, Continuous operation of membrane processes for the treatment of industrial effluents, Computers and Chemical Engineering, 26, 4, 555-561.

Galan, B.and I.E. Grossmann, 1998, Optimal design of distributed wastewater treatment networks. Ind. Engng. Chem. Res., 10, 4036.

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