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Optimal Synthesis of an Emulsion Pertraction Process for the Removal of Pollutant Anions in Industrial Wastewater Systems

M. Fresnedo San Román[a], Eugenio Bringas[a], Inmaculada Ortiz[a*] and Ignacio E. Grossmann[b]

[a]Departamento de Ingeniería Química y Química Inorgánica
Universidad de Cantabria, 39005 Santander, Spain.

[b]Department of Chemical Engineering
Carnegie Mellon University, Pittsburgh, USA.

Abstract

This paper describes a synthesis model for the optimal design of an emulsion pertraction process for removal and recovery of pollutant anions from industrial wastewater. The goal is to separate with minimum area of membrane modules the anions in order to obtain an environmentally acceptable stream with minimum concentration and a stream in which the anion is concentrated for further processing. A superstructure is proposed which consists of a prespecified number of modules that are interconnected in all possible ways in order to account for all potential configurations. The selection of the optimal design from this superstructure is formulated as a NLP problem. The mathematical model for the continuous operation consists of a set of differential/algebraic equations. In order to formulate the proposed NLP optimisation model the differential equations are discretised using a first order backward finite difference scheme. The axial dimension of the module is divided into a series of intervals and the derivatives are expressed in terms of truncated Taylor series. The resulting model was implemented within the modelling system GAMS and solved with CONOPT. An example is presented to illustrate the capability of the proposed model.

Keywords: pertraction, emulsion, superstructure optimization, nonlinear programming.

1. Introduction

The increasing public concern about environment and the need of recycling and recovering are the driving force for the increasingly stringent regulations, in particular those related to industry. In these cases it is necessary to deploy new separation technologies in order to meet the regulations. One of the emerging technologies is the emulsion pertraction which combines the efficiency of the emulsion liquid membranes with the advantages of hollow fiber modules *(Hu and Wiencek, 1998).* A hollow fiber module is used to carry out the simultaneous extraction (EX) and back extraction (BEX) of a solute. The aqueous feed solution, containing the solute to be extracted, flows in continuous mode through the inner side of the hollow fibers. The stripping solution is dispersed into the organic phase forming the emulsion phase which flows in a recycling

mode. The solute is transferred from the aqueous feed solution to the organic phase which is embedded in the pores of the membrane (interfacial area). The solute is then transported into the droplets where the stripping phase is situated. Finally, the solute is recovered from the internal aqueous phase after emulsion breakage *(Wiencek and Hu, 2000).*

Emulsion pertraction can be applied for the selective recovery of different solutes such as high metals, Zn, Cd, Cr and Ni. This process is especially suitable for the selective removal of these metals at a low concentration level and concentrating them to a much higher level. Sometimes, depending of the solution pH, the metals are dissolved forming anionic species. In this work, we consider the removal of pollutant anions, such as chromium, from the industrial wastewater systems using emulsion pertraction technology *(Ho and Poddar, 2001).* We propose in this paper a nonlinear programming (NLP) model that is based on a superstructure containing four modules that are interconnected in all possible ways in order to account for all potential design configurations. The process is subject to several restrictions, including physical constraints, maximum and minimum flowrates, minimum concentration of the stripping solution at the end of the cycle for use and maximum concentration of the feed solution for disposal. The objective is to find the optimal configuration in which the total membrane area is minimized. The proposed mathematical model for the continuous operation consists of a set of partial and differential equations that takes into account the mass transport through the feed and membrane and two chemical reactions at the feed and stripping phase, in the droplets area. Additionally, splitters and mixers are introduced to enable the choice of the optimum configuration in both phases. The data for the chemical equilibrium constants and mass transfer coefficients for this process were obtained from the previous work by Ortiz et al. *(2003)*. The model parameters were obtained after the integration of the equations and comparison of experimental and simulated results. In order to formulate the proposed optimisation model as an NLP, the differential equations for the chromium mass balance for the phases in the membrane modules are discretised into a set of algebraical equations using a first order backward finite difference scheme. The axial dimension of the module is divided into a series of ten intervals and the derivatives are expressed in terms of truncated Taylor series. The resulting model was implemented within the modelling system GAMS and solved with CONOPT2.

2. Potential configurations of the emulsion pertraction process

Figure 1 shows the network superstructure for the aqueous feed solution that has embedded all possible configurations for the set of specified modules (four in this example). A similar scheme can be postulated for the emulsion phase in which the recirculation streams are not taken into account since this phase works in discontinuous mode. As seen in Fig. 1 the feed stream is divided by an initial splitter (S5) into streams that are directed to mixers (M1, M2, M3 and M4) at to the inlets of the modules and to the discharge point (M5). After each module, splitters (S1, S2, S3 and S4) are placed to direct the treated stream to recirculation or to final discharge *(Galán and Grossmann, 1998)*. The waste feed stream is characterised by a known flow rate, $F_a = 2.5\ m^3\ h^{-1}$ and a known concentration of a pollutant, $C_a^{in} = 7.7\ mol\ m^{-3}$ (400 ppm). An upper bound on

the concentration of the pollutant at the outlet of the aqueous stream is given by environmental regulations, $C_a^{out} \leq 0.00961$ mol m^{-3} (0.5 ppm).

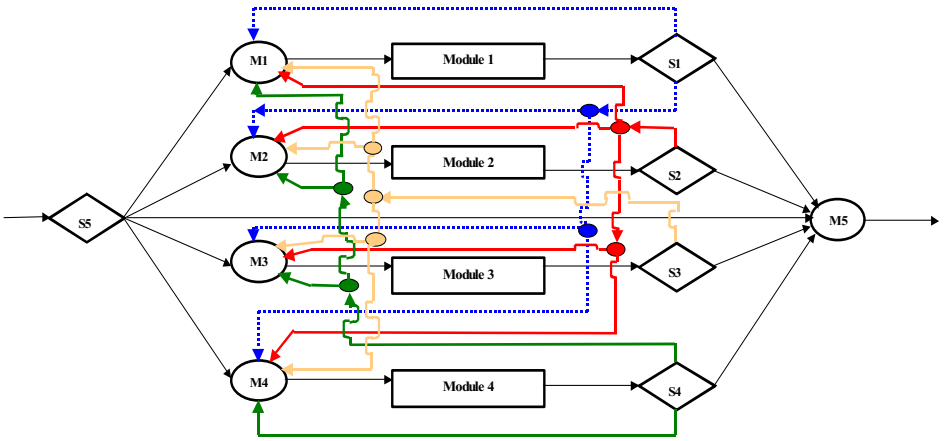

Figure 1. Network superstructure for the aqueous feed solution.

The emulsion is prepared by dispersing an aqueous sodium hydroxide solution of an initial concentration of 3000 mol m^{-3} in the organic phase at a volume ratio of 1:4. The organic solution consists of Isopar L in which the extractant Alamine 336 is dissolved together with emulsion modifiers *(Ortiz et al., 2003)*. The numbers of the splitters, mixers and modules or treatment units are equal than in the feed phase. In this case the emulsion and feed solution are in countercurrent flow. The concentration of the pollutant in the stripping stream required for reuse is expressed as a lower bound on the stripping concentration, $C_s^{out} \geq 385$ mol m^{-3} (20000 ppm).

At the exit of the superstructure, the emulsion phase is decanted; the organic phase containing chromium, is recycled. The stripping phase with the chromium concentration required for reusing is replaced by a new clean phase which is added to the organic phase forming the feed emulsion. On the other hand, other alternatives like a stream or part of it can be discharged into a sewerage directly without any treatment or recirculating of if same are considering negligible.

3. Optimal design of the emulsion pertraction process

In the previous section, the process network consists of splitters, mixers and treatments units (pertraction process). The pertraction model obtained by Ortiz et al. *(2003)*, consists of a set algebraical and differential equations. In order to formulate the model as an NLP the differential equations must be replaced by algebraic equations that are obtained through discretisation of the spatial variation of concentrations. The spatial variation of the concentrations within the module is discretised using a first order backward finite difference scheme. The resulting NLP optimisation model has the following form (P1):

$$
\begin{aligned}
&\underset{\boldsymbol{v}}{Min} \quad \Phi(\boldsymbol{x},\boldsymbol{v}) \\
&s.t.: \quad \boldsymbol{h}(\boldsymbol{x},\boldsymbol{v}) \;\; = \;\; \boldsymbol{0} \\
&\qquad \boldsymbol{g}(\boldsymbol{x},\boldsymbol{v}) \;\; \leq \;\; \boldsymbol{0} \\
&\qquad \boldsymbol{I}(\boldsymbol{x}(\boldsymbol{0}),\boldsymbol{x}(\boldsymbol{L}),) \;\; = \;\; \boldsymbol{0} \\
&\qquad \boldsymbol{x}^{LB} \;\leq\; \boldsymbol{x} \;\leq\; \boldsymbol{x}^{UB} \\
&\qquad \boldsymbol{v}^{LB} \;\leq\; \boldsymbol{v} \;\leq\; \boldsymbol{v}^{UB} \\
&\qquad\quad \boldsymbol{x} \in R^{n}
\end{aligned}
\tag{P1}
$$

where Φ is the total area of the four modules in the process, the outlet chromium concentration of the aqueous phase and the inlet chromium concentration in the organic phase, $\boldsymbol{h}$ represents the model equations associated to mass balances, mass transfer relationships and equipment connectivities, **g** includes inequalities related to chromium concentration for both the treated effluent and concentration stream for reuse. The vector $\boldsymbol{v}$ includes the optimisation variables for the design problem, such as the stream flowrates and membrane area needed in each sector, while the other variables are included in the vector $\boldsymbol{x}$. The initial conditions for the differential equations are given by $\boldsymbol{I}$. Upper and lower bounds were applied for all the variables in the optimisation problem. The specific optimization problem is shown below:

3.1 Objective function

$$\Phi = \sum_{m} A^{m} + C_{a}^{out} + C_{o}^{out} \qquad \forall m \in M \tag{1}$$

3.2 Pertraction model

In the discretisation of the differential equations the axial dimension is divided into a series of intervals (z) and the derivatives are expressed in terms of truncated Taylor series. The finite difference method yields the following non-linear algebraic equations,

$$F_{a,m} \cdot \frac{C_a^m(z+1) - C_a^m(z)}{\Delta z} = -\frac{A^m}{L^m} \cdot K_L \cdot \left(C_a(z) - C_a^*(z)\right), \quad \forall m \in M; \quad z = 0 \Rightarrow C_a^m = C_{a,m}^{out} \tag{2}$$

$$F_{o,m} \cdot \frac{C_o^m(z+1) - C_o^m(z)}{\Delta z} = -\frac{A^m}{L^m} \cdot K_L \cdot \left(C_a(z) - C_a^*(z)\right) + \frac{V_s^m \cdot H_r}{L^m} \cdot [OH]^2 \cdot C_o^m(z) \qquad \forall m \in M; \quad z = 0 \Rightarrow C_o^m = C_{o.m}^{in} \tag{3}$$

$$F_{s,m} \cdot \frac{C_s^m(z+1) - C_s^m(z)}{\Delta z} = \frac{V_s^m \cdot H_r}{L^m} \cdot [OH]^2 \cdot C_o^m(z), \qquad \forall m \in M; \quad z = 0 \Rightarrow C_s^m = C_{s,m}^{in} \tag{4}$$

The remaining equations, the values of the model parameters and the symbols used in the equations can be found in Ortiz et al. *(2003)*.

3.3 Mixers.

A mixer consists of a set of inlet streams *j* and outlet stream *i*.

$$F_{k,m} = \sum_{i} F_{k,j,i} \qquad i = m \tag{5}$$

$$\forall m \in M; \quad \forall k \in PH; \quad \forall i \in MX; \quad \forall j \in SP;$$

The chromium balance in the mixers for the phases that constitute the process is given by

$$C^{out}_{k,m} \cdot F_{k,m} = \sum_{i} C_{k,j,i} \cdot F_{k,j,i} \qquad i = m \tag{6}$$

$$\forall m \in M; \quad \forall k \in PH; \quad \forall i \in MX; \quad \forall j \in SP;$$

3.4 Sppliters.

A mixer consists of a set of inlet streams *i* and outlet stream *j*.

$$F_{k,m} = \sum_{j} F_{k,j,i} \qquad j = m \tag{7}$$

The chromium balance in the splitters for the phases that constitute the process is given by

$$C^{in}_{k,m} = C_{k,j,i} \qquad j = m \tag{8}$$

$$\forall m \in M; \quad \forall k \in PH; \quad \forall i \in MX; \quad \forall j \in SP;$$

For all cases PH represents the aqueous (a), organic (o) and stripping (s) phase; M represents the four membrane modules; MX represents the mixers and SP the splitters. The model given by equations (1)-(8) corresponds to an NLP model since equations (2)-(4) and (6) are non-linear. They were obtained using CONOPT2 as a solver in GAMS, and the computer time required was 3.9 seconds and 1046 iterations. Figures 2 and 3 show the optimal configuration of the effluent and emulsion phase.

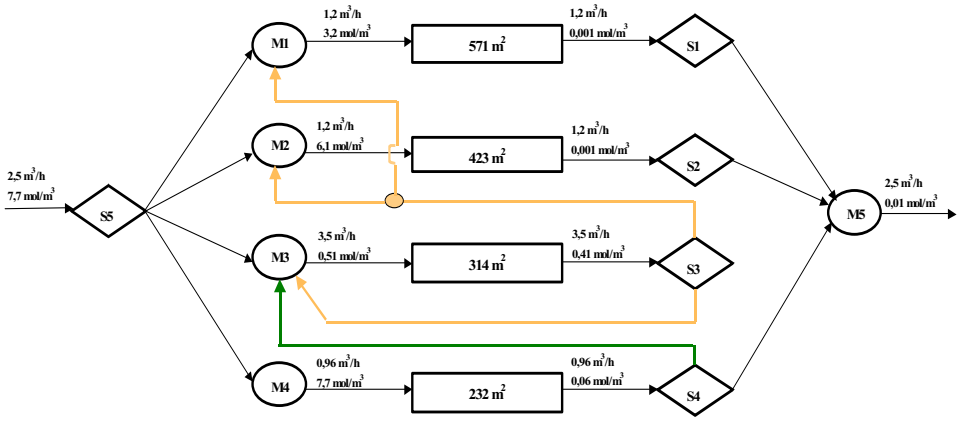

Figure 2. Optimal solution for the aqueous feed solution.

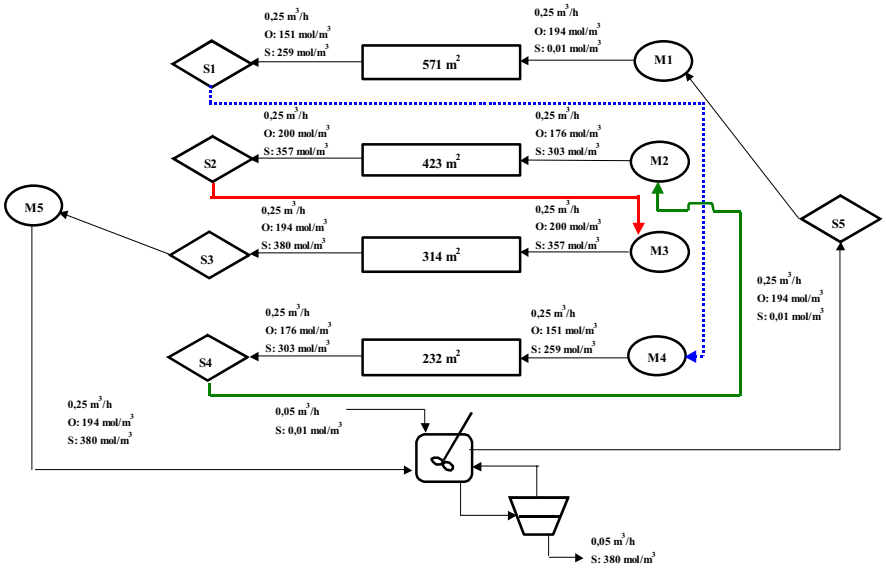

Figure 3. Optimal solution for the emulsion phase

The optimal structure obtained for the aqueous phase is a structure in parallel. On the other hand, for the emulsion a series structure is obtained. At the end of the of the cycle the emulsion phase is decanted, the stripping phase is separated and a new emulsion is obtained with a fresh stripping phase. In this case the flowrates are small due to the high chromium concentration required in the stripping solution. The total area of the membrane modules is 1540 m^2, which is lower than the one reported by Corvalán et al., *(2004)*.

5. Conclusions

This study has addressed the optimal synthesis of distributed emulsion pertraction process networks for the removal of pollutant anions in industrial wastewater systems. As was shown the proposed NLP model has the following abilities: i) getting a stream with a minimum chromium concentration for final disposal, ii) getting a stream with a high chromium concentration for industrial reuse , iii) minimizing the membrane area for reducing the costs of the process.

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