SYNTHESIS OF MEMBRANE PROCESSES FOR EFFLUENT TREATMENT AND METAL RECOVERY

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OUTLINE

• Cleaner technologies with Membrane processes

• Non Dispersive Solvent Extraction Technology
  Modelling
  Semicontinuous Process - Design
  Continuous Process - Design
  Synthesis
  Strategies for the MINLP formulation.
  Binary variables space dimension
  and Initialization.
  Bounds on the continuous variables.

• Conclusions
CLEANER TECHNOLOGIES

SIMULTANEOUS
WATER TREATMENT
and RECOVERY of CONTAMINANT
FOR RECYCLING AND INDUSTRIAL REUSE

(Recovery of metal, contaminant or valuable component)

MAIN ADVANTAGE

- Reduction of the amount of contaminant disposed finally into the environment.
Effluent, wastewater or underground water is treated to remove the contaminant which is frequently transferred to another phase, gas, liquid or solid.

- Further treatment of this phase is needed before final disposal. Associated economical cost.

- The contaminant is finally disposed into the environment. Associated environmental impact.
Optimization of new technologies at the conceptual design stage to analyse the economical viability and promote its industrial application.

Understand the behaviour of new processes, define the best operating regions, the best operating conditions, and design new plants.
NON DISPERSIVE SOLVENT EXTRACTION

Schematic Diagram - Cocurrent

Organic Tank -> Organic Stream

EXTRACTION SECTOR

Treated Effluent -> Effluent

STRIPPING SECTOR

Concentrated Stream

Concentrated Prod
NON DISPERSIVE SOLVENT EXTRACTION

Schematic Diagram - Countercurrent
SEPARATION OBJECTIVES

• Maximum contaminant composition in the treated effluent for final disposal.

• Minimum contaminant concentration in the product

✓ for recycling and reuse in the same plant that generated the effluent

✓ or industrial reuse in other site.
CLEANER TECHNOLOGIES with MEMBRANE PROCESSES for WATER TREATMENT and SIMULTANEOUS RECOVERY for RECYCLING and REUSE

• SAVINGS IN ROW MATERIAL CAN ALSO BE EXPECTED DUE TO RECOVERY, RECYCLING AND REUSE.

• REDUCE FINAL DISPOSAL

The main difference with a traditional technology is that the CONTAMINANT is simultaneously RECOVERED and CONCENTRATED to be RECYCLED and REUSED in an industrial site.
The organic stream extract the contaminant from the effluent in the extraction sector.

The contaminant is back extracted from the organic stream in the stripping sector.

The organic stream is recycled between the extraction and stripping sectors.

The organic solvent is recycled and reused.

There is no need of solvent disposal.
MODELLING OF MEMBRANE PROCESSES

• Mass Transfer equations
  in the Aqueous and Organic phases
  of each membrane module
  in the Extraction and Stripping sectors.

• Organic and concentrated tanks.

• Connectivity equations.
Cr (VI) EQUILIBRIUM REACTION

Extraction

$$CrO_4^{2-} + 2(Al)Cl \Leftrightarrow (Al)_2CrO_4 + 2Cl^-$$

Stripping

Extraction sector

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

Stripping sector

$$H = \frac{C_s}{C_{oi}^s}$$
EXTRACTION SECTOR

Aqueous phase

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

Organic phase

\[
\frac{dC_o^E}{dz} = \frac{A^E}{F_o L^E} K_m (C_{oi}^E - C_o^E) \quad C_o^E(0) = C_o^s(L^S)
\]

Cocurrent operation
STRIPPING SECTOR

Aqueous phase

\[
\frac{dC_s}{dz} = \frac{A^S}{F_s L^S} K_m (C^S_o - C^S_{oi}) \quad C_s(0) = C_s^T
\]

Organic phase

\[
\frac{dC^S_o}{dz} = \frac{A^S}{F_o L^S} K_m (C^S_o - C^S_{oi}) \quad C^S_o(0) = C^E_o(L^E)
\]

Cocurrent operation
SCALES and OPERATING MODE

- LABORATORY  Batch
- PILOT PLANT  Batch - Semicontinuous
- INDUSTRIAL APLICATIONS ( PSE )
  Continuos – Semicontinuos - Batch  
  Define best operating mode  
  Case dependent 
  Feed and product specifications
CONFIGURATIONS

• **COCURRENT or COUNTERCURRENT** mode of operation between the Aqueous and Organic Streams in the membrane module.

• **SERIES and / or PARALLEL** arrangement of membrane modules in the Extraction and Stripping sectors.
MODE OF OPERATION

- CONTINUOUS
- BATCH
- SEMICONTINUOUS

<table>
<thead>
<tr>
<th>Sector</th>
<th>Stream</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction</td>
<td>Aqueous</td>
<td>Continuos</td>
</tr>
<tr>
<td>Striping</td>
<td>Organic</td>
<td>Continuos</td>
</tr>
<tr>
<td></td>
<td>Aqueous</td>
<td>Batch</td>
</tr>
</tbody>
</table>
SEMICONTOINUOUS PROCESS

• Feed and organic streams run in a continuous mode.

• Stripping stream runs in a discontinuous mode until the minimum composition required in the concentration tank is achieved for industrial reuse of the product.

MODELLING

Derivatives of the stripping composition with respect to time are needed.

The modelling equations are posed as a DAE system of equality constraints.
DESIGN of the SEMICONTINUOUS PROCESS

OPTIMIZATION PROBLEM

Objective function

Minimize total membrane area \((Ae+As)\)

Separation objectives and operating conditions as equality constraints.

Optimization variables

- **Design Variables**
  Extraction and stripping membrane areas.
  Volume of the concentrated tank.

- **Operating variables**
  Initial Chromium composition in the organic stream.
  Organic and stripping flow rates.
DESIGN of the SEMICONTINUOUS PROCESS

Sensitivity analysis of the extraction and stripping areas effluent and product compositions with respect to operating conditions.

Initial chromium composition in the organic phase is the most important operating variable.

Problem formulated and solved in gOPT.

Initial work

CONTINUOUS PROCESS

Effluent, organic and concentrated streams operate in a continuous mode.

Objective function
Minimize total membrane area

Optimization variables

DESIGN
Extraction and Stripping areas

OPERATING
Organic and stripping flowrates

Maximum effluent composition
and minimum concentrated composition
as inequality constraints.

CONTINUOUS PROCESS

OPERATING MODE

• COUNTERCURRENT better than COCURRENT

• CONTINUOUS and SEMICONTINUOUS

A similar performance is observed in terms of total area required to achieve the maximum allowed composition in the effluent and the minimum required concentration in the product.
SYNTHESIS of a NDSX PROCESS

- CONTINUOUS MODE of OPERATION
- COUNTERCURRENT
- MODULES in SERIES in the EXTRACTION and STRIPPING SECTOR
- CALCULATE the NUMBER of MEMBRANE MODULES required in the STRIPPING and EXTRACTION SECTORS
OBJECTIVE FUNCTION

MINIMIZE THE NUMBER OF MEMBRANE MODULES USED in the EXTRACTION and STRIPING SECTORS.

MINIMIZE THE TOTAL AREA.

THE COST OF MEMBRANE MODULES IS THE MAIN CONTRIBUTION TO CAPITAL AND OPERATING COST.
SUPERSTRUCTURE OPTIMIZATION

- **DESIGN VARIABLES**
  BINARY VARIABLES are used to select the number of membrane modules in the stripping and extraction sectors.

- **OPERATING VARIABLES**
  ORGANIC and STRIPPING FLOW RATES are the continuous optimization variables.

- **RIGOROUS MODELLING** of each membrane module represented by a differential and algebraic system of equations (DAE) as equality constraints.
Mixed Integer Differential Optimization Problem

\[
\begin{align*}
\text{Min} & \quad \phi ( x, v, y ) \\
\text{s.t.} & \quad h ( \dot{x}, x, w, v, y ) = 0 \\
& \quad g ( \dot{x}, x, w, v, y ) \leq 0 \\
& \quad I ( x(0), x(L), y ) = 0 \\
& \quad x_{LB} \leq x \leq x_{UB} \\
& \quad w_{LB} \leq w \leq w_{UB} \\
& \quad v_{LB} \leq v \leq v_{UB} \\
& \quad y \in \{ 0, 1 \}
\end{align*}
\]
Mixed Integer Diferential Optimization Problem

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 $z$, $w$ is the set of algebraic distributed variables such as the inter phase concentration along the modules, $v$ is the set of non distributed variables such as aqueous or organic flow rates, and $y$ is the set of binary variables.

The mass balances, equilibrium, operating and interconnecting equations are represented by a set of differential and algebraic equations. equalities $h$ and inequalities $g$, and initial conditions $I$. 
MINLP PROBLEM

Transform the MIDO problem \(\rightarrow\) MINLP problem.
Discretize the differential equations using Ortogonal Colocation on Finite Elements

Objective function
Minimize the the total membrane area

Optimization variables:

DESIGN Binary variables to select the number of membrane modules in the extraction and stripping sectors.

OPERATING Organic and stripping flowrates.
MINLP PROBLEM

\[ \begin{align*}
\text{Min} & \quad AT_v \\
\text{s.t.} & \quad h(x, w, v, y) = 0 \\
& \quad g(x, w, v, y) \leq 0 \\
& \quad x^{LB} \leq x \leq x^{UB} \\
& \quad w^{LB} \leq w \leq w^{UB} \\
& \quad v^{LB} \leq v \leq v^{UB} \\
& \quad x \in \mathbb{R}^n \\
& \quad y \in [0,1]
\end{align*} \]

FORMULATE and SOLVE the MINLP problem in GAMS.

Corvalan, Ortiz and Eliceche (2005), Synthesis of NDSX plant for effluent treatment and metal recovery. Alonso et al. (2001)
MINLP PROBLEM FORMULATION

• DEFINE NUMBER OF BINARY VARIABLES to be used.

• INITIALISATION AND BOUNDING STRATEGIES TO INCREASE ROBUTNESS AND EFFICIENCY.

✓ Find reasonable bounds for the number of membrane modules required in the extraction and stripping sectors

✓ Solve an associated NLP problem
Objective function
Minimize total membrane area in the extraction and stripping sectors.

Continuos optimization variables
- Extraction and stripping areas.
- Organic and stripping flowrates.

Evaluate optimum membrane area required in the Extraction $A_e$ and Stripping $A_s$ sectors.

Evaluate number of membrane modules in each sector that provide the area required $A_e$ and $A_s$. Each membrane module has 130 $m^2$. 
SELECT NUMBER OF BINARY VARIABLES

NLP solution provides information to select the number of binary variables to be used in MINLP problem.

Develop strategies to calculate the number of binary variables to be included in the extraction and stripping sectors.

When the number of binary variables increase in the MINLP problem formulation the robustness to find a solution decreases.

Reduce the dimension of the binary variable vector ($y$). Bounds on the continuous variables.
### NLP solution

<table>
<thead>
<tr>
<th></th>
<th>Initial Pt.</th>
<th>Solution Pt.</th>
<th>MMN</th>
<th>LB</th>
<th>UB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_o$ (m$^3$ h$^{-1}$)</td>
<td>0.500</td>
<td>0.112</td>
<td></td>
<td>0.100</td>
<td>10</td>
</tr>
<tr>
<td>$F_s$ (m$^3$ h$^{-1}$)</td>
<td>0.500</td>
<td>0.100</td>
<td></td>
<td>0.100</td>
<td>10</td>
</tr>
<tr>
<td>$A^E$ (m$^2$)</td>
<td>1000</td>
<td>897.839</td>
<td>6.91</td>
<td>500</td>
<td>5000</td>
</tr>
<tr>
<td>$A^S$ (m$^2$)</td>
<td>1000</td>
<td>909.208</td>
<td>6.99</td>
<td>500</td>
<td>5000</td>
</tr>
<tr>
<td>$C^E_{out}$ (mol m$^{-3}$)</td>
<td>1.923</td>
<td></td>
<td>0.5</td>
<td>1.923</td>
<td></td>
</tr>
<tr>
<td>$C^S_{out}$ (mol m$^{-3}$)</td>
<td>384.615</td>
<td></td>
<td>384.61</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### MINLP solution

<table>
<thead>
<tr>
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<th>Initial Pt.</th>
<th>Solution Pt.</th>
<th>LB</th>
<th>UB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_0$ (m³ h⁻¹)</td>
<td>0.150</td>
<td>0.1335</td>
<td>0.100</td>
<td>1</td>
</tr>
<tr>
<td>$F_s$ (m³ h⁻¹)</td>
<td>0.150</td>
<td>0.1000</td>
<td>0.100</td>
<td>1</td>
</tr>
<tr>
<td>$A^E$ (m²)</td>
<td>910</td>
<td>910 (7)</td>
<td>650 (6)</td>
<td>1040 (8)</td>
</tr>
<tr>
<td>$A^S$ (m²)</td>
<td>910</td>
<td>910 (7)</td>
<td>650 (6)</td>
<td>1040 (8)</td>
</tr>
<tr>
<td>$C^{E}_{out}$ (mol m⁻³)</td>
<td>1.900</td>
<td>1.923</td>
<td></td>
<td>1.923</td>
</tr>
<tr>
<td>$C^{S}_{out}$ (mol m⁻³)</td>
<td></td>
<td>384.633</td>
<td>384.615</td>
<td></td>
</tr>
<tr>
<td>NLP time, sec</td>
<td></td>
<td>83.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MIP time, sec</td>
<td></td>
<td>2.59</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Six binary variables
NLP solution to formulate MINLP problem

• ASSOCIATED NLP PROBLEM SOLUTION provides crucial information to improve the formulation of the MINLP problem.

• Different strategies can be generated to formulate the MINLP problem. Dimension of the binary variable space. Initialization and bounding.
• Membrane processes are likely to be selected in hybrid processes with other technologies.

• Identify operating regions where less membrane area is required.

• The methodology presented can also be useful to define the optimum separation work to be carried out by membrane processes in a hybrid context.
NOMENCLATURE

\[ C \] Solute Concentration, mol/m^3
\[ C_{in} \] Effluent Inlet Concentration, mol/m^3
\[ F \] Flowrate, m^3/h
\[ K_m \] Membrane mass transfer coefficient, m/h
\[ L \] Fibre Length, m
\[ z \] Axial distance, m
\[ A \] Effective surface area, m^2

Superscript

\[ E \] Extraction module
\[ E_j \] Extraction module \( j \)
\[ S \] Stripping module
\[ S_k \] Stripping module \( k \)
\[ T \] Tank

Subscripts

\[ e \] Extraction phase
\[ s \] Stripping phase
\[ o \] Organic phase
\[ oi \] Organic interface
REFERENCES


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