# SYNTHESIS OF MEMBRANE PROCESSES FOR EFFLUENT TREATMENT AND METAL RECOVERY

## PASI – 2005

Iguazú,  16 - 25 August

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# OUTLINE

- Cleaner technologies with Membrane processes

- Non Dispersive Solvent Extraction Technology
    - Modelling
    - Semicontinuos Process - Design
    - Continuos Process - Design
    - Synthesis
        - Strategies for the MINLP formulation.
        - Binary variables space dimension and Initialization.
        - Bounds on the continuos variables.
- Conclusions

# CLEANER TECHNOLOGIES

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

(Recovery of metal, contaminant or valuable component)

MAIN ADVANTADGE

- Reduction of the amount of contaminant disposed finally into the environment.

# TRADITIONAL TECHNOLOGIES FOR EFFLUENT TREATMENT

Effluent, wastewater or underground water
is treated to remove the contaminant
which is frecuently transfered 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.

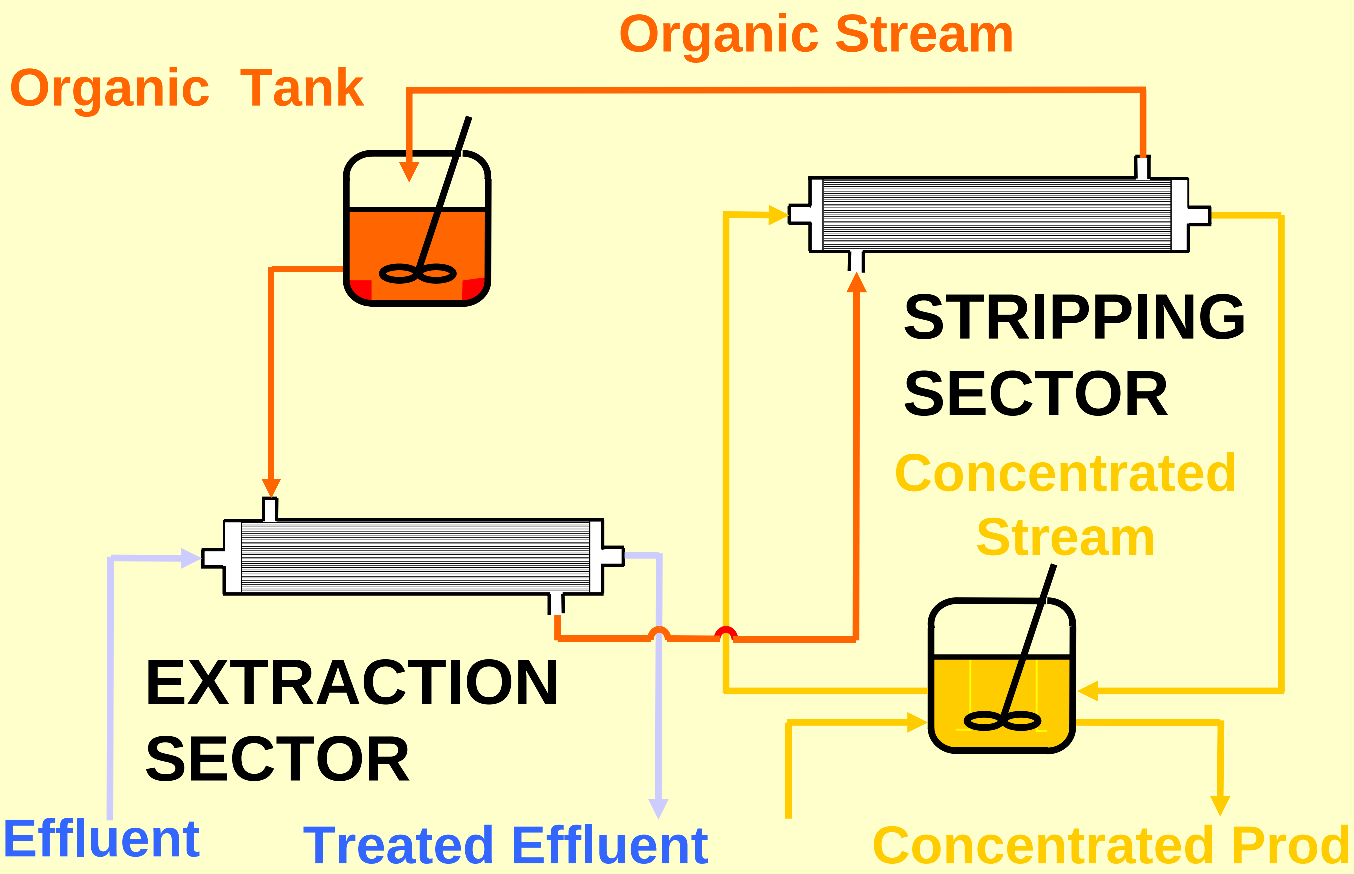
# NON DISPERSIVE SOLVENT EXTRACTION

- NDSX

✓ Optimization of new technologies
at the conceptual design stage
to analyse the economical viability
and promote its industrial application.

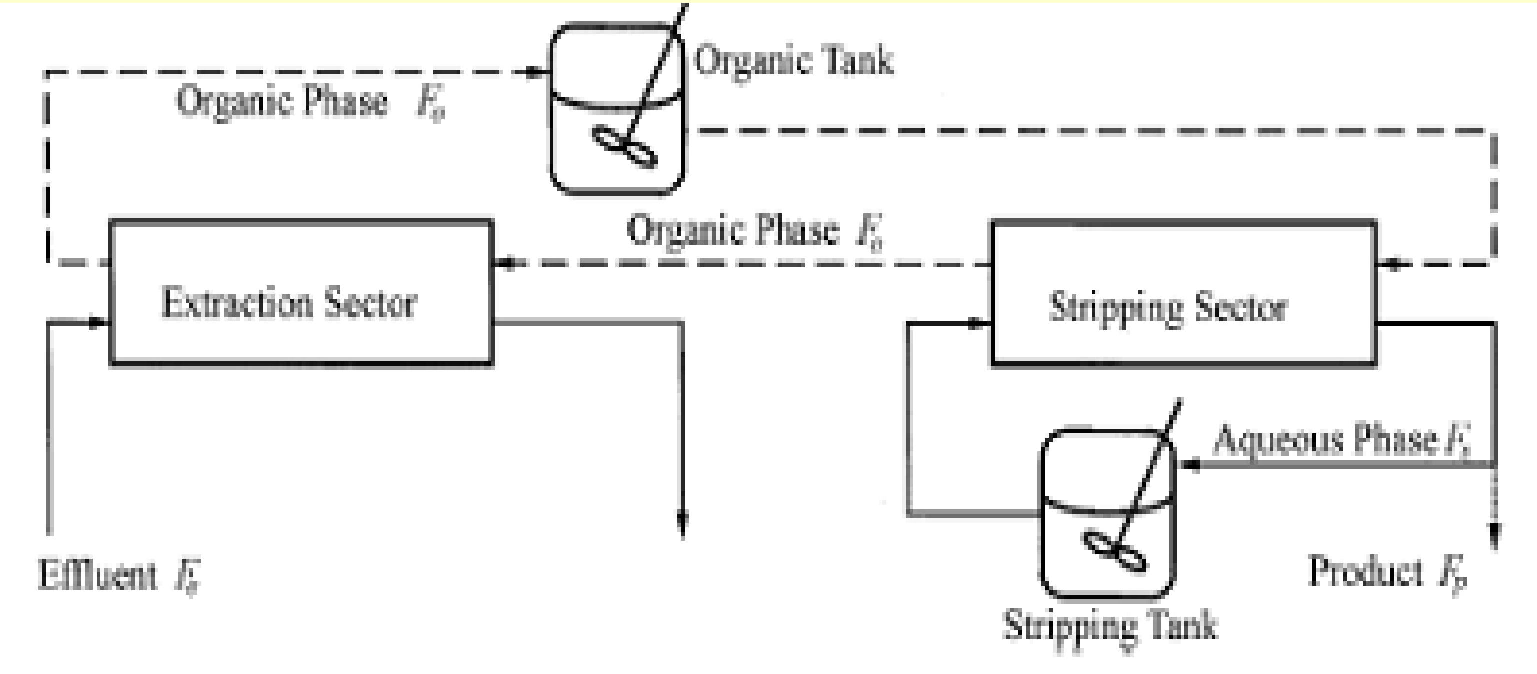
✓ Understand the behaviour of new processes,
define the best operating regions,
the best operating conditions,
and design new plants.

# NON DISPERSIVE SOLVENT EXTRACTION




Schematic Diagram - Cocurrent

# 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 re use 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.

# ORGANIC STREAM

- 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 re used.
- 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.
- Conectivity 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

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

Organic phase

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

Cocurrent operation

# STRIPPING SECTOR

Aqueous phase

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

Organic phase

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

Cocurrent operation

# SCALES and OPERATING MODE

- LABORATORY Batch
- PILOT PLANT Batch - Semicontinuos
- INDUSTRIAL APLICATIONS ( PSE )

Continuos – Semicontinuos - Batch ???

Define best operating mode !!!

Case dependent

Feed and product especifications ???

# 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

- **CONTINUOS**
- **BATCH**
- **SEMICONTINOUS**

| Sector | Stream | Process |
|---|---|---|
| Extraction | Aqueous | Continuos |
| Striping | Organic | Continuos |
| | Aqueous | Batch |

# SEMICONTINUOS PROCESS

- Feed and organic streams run in a continuos mode

- Stripping stream runs in a dicontinuos 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 SEMICONTINUOS 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 Chromiun composition in the organic stream.
  - Organic and stripping flow rates.

# DESIGN of the SEMICONTINUOS PROCESS

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

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

Problem formulated and solved in gOPT.

Initial work

***Eliceche, Alonso and Ortiz, (2000, 2000 a, 2001).***

***Galan, B.and I.E. Grossmann (1998), Optimal design of distributed wastewater treatment networks.***

# CONTINUOS PROCESS

Effluent, organic and concentrated streams
operate in a continuos 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.

***Eliceche, Corvalan and Ortiz, (2002, 2003, 2004)***

# CONTINUOS PROCESS

OPERATING MODE

- COUNTERCURRENT better than COCURRENT
- CONTINUOS and SEMICONTINUOS

A similar perfomance 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

- CONTINUOS 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

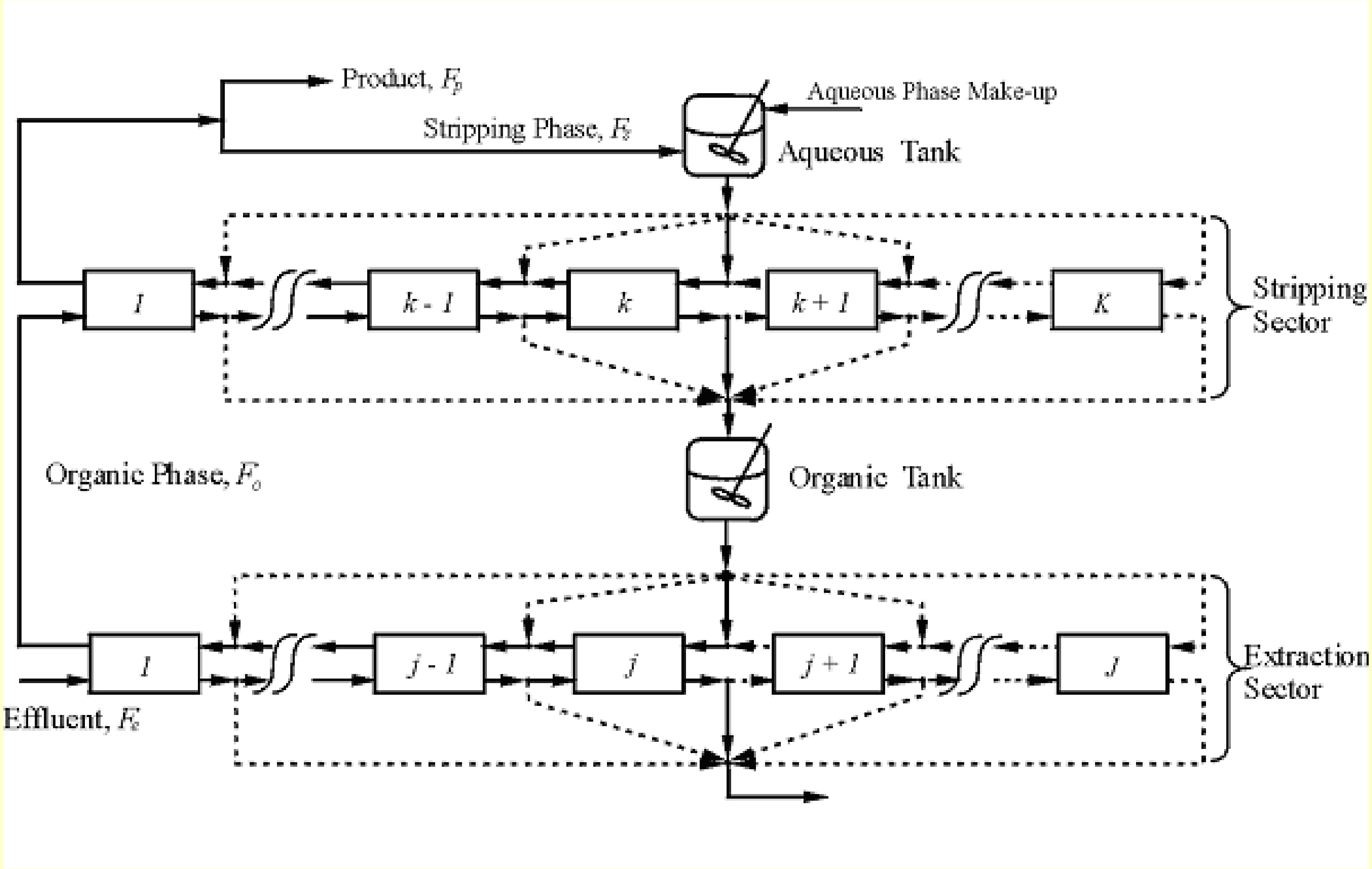
# OBJECTIVE FUNCTION

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

MINIMIZE THE TOTAL AREA.

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

# SUPERSTRUCTURE



# 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 continuos optimization variables.

- RIGOROUS MODELLING of each membrane module
  represented by a differential and algebraic system of
  equations (DAE) as equality constraints.

# Mixed Integer Diferential Optimization Problem

$$\min_{v,y} \quad \phi(x, v, y)$$

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

$$g(\dot{x}, x, w, v, y) \leq 0$$

$$I(x(0), x(L), y) = 0$$

$$x^{LB} \leq x \leq x^{UB}$$

$$w^{LB} \leq w \leq w^{UB}$$

$$v^{LB} \leq v \leq v^{UB}$$

$$y \in \{0,1\}$$

# 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 → MINLP problem.

Discretize the diferential 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

$$\underset{v}{Min}\ AT$$

$$
\begin{aligned}
s.t.: \quad & \boldsymbol{h}(\boldsymbol{x},\boldsymbol{w},\boldsymbol{v},\boldsymbol{y}) = \boldsymbol{0} \\
& \boldsymbol{g}(\boldsymbol{x},\boldsymbol{w},\boldsymbol{v},\boldsymbol{y}) \leq \boldsymbol{0} \\
& \boldsymbol{x}^{LB} \leq \boldsymbol{x} \leq \boldsymbol{x}^{UB} \\
& \boldsymbol{w}^{LB} \leq \boldsymbol{w} \leq \boldsymbol{w}^{UB} \\
& \boldsymbol{v}^{LB} \leq \boldsymbol{v} \leq \boldsymbol{v}^{UB} \\
& \boldsymbol{x} \in R^n \\
& \boldsymbol{y} \in [0,1]
\end{aligned}
$$

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

# NLP SOLUTION

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 Ae and Stripping As sectors.

Evaluate number of membrane modules in each sector

that provide the area required Ae and As.

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 continuos variables.

# NLP solution

| | Initial Pt. | Solution Pt. | MMN | LB | UB |
|---|---|---|---|---|---|
| **$F_o$** ($m^3\ h^{-1}$) | 0.500 | 0.112 | | 0.100 | 10 |
| **$F_s$** ($m^3\ h^{-1}$) | 0.500 | 0.100 | | 0.100 | 10 |
| **$A^E$** ($m^2$) | 1000 | 897.839 | **6.91** | 500 | 5000 |
| **$A^S$** ($m^2$) | 1000 | 909.208 | **6.99** | 500 | 5000 |
| **$C^E_{out}$** ($mol\ m^{-3}$) | | 1.923 | | 0.5 | 1.923 |
| **$C^S_{out}$** ($mol\ m^{-3}$) | | 384.615 | | 384.61 | |

# MINLP solution

| | Initial Pt. | Solution Pt. | LB | UB |
|---|---|---|---|---|
| **$F_o$** ($m^3$ $h^{-1}$) | 0.150 | 0.1335 | 0.100 | 1 |
| **$F_s$** ($m^3$ $h^{-1}$) | 0.150 | 0.1000 | 0.100 | 1 |
| **$A^E$** ($m^2$) | 910 | 910 ( **7** ) | 650 (6) | 1040 (8) |
| **$A^S$** ($m^2$) | 910 | 910 ( **7** ) | 650 (6) | 1040 (8) |
| **$C^E_{out}$** (mol $m^{-3}$) | 1.900 | 1.923 | | 1.923 |
| **$C^S_{out}$** (mol $m^{-3}$) | | 384.633 | 384.615 | |
| **NLP time,** sec | | 83.70 | | |
| **MIP time,** sec | | 2.59 | | |

Six binary variables

# NLP solution to formulate MINLP problem

- ASSOCIATED NLP PROBLEM SOLUTION
  provides crutial 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.

# REMARKS

- Membrane proccesses 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 usefull
  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 |

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