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# OPTIMAL DESIGN OF MEMBRANE-HYBRID SYSTEMS FOR WASTE REDUCTION

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ABSTRACT

A systematic procedure is devised to tackle the design of membrane-hybrid systems for waste reduction. A membrane-hybrid system corresponds to any separation network that employs reverse-osmosis modules, booster pumps, turbines and mass exchangers (e.g. extractors, adsorption columns, ion exchangers, etc.). The proposed approach provides a generally-applicable framework for simultaneously screening all potential separation processes of interest. The problem is formulated as an optimal synthesis task. The solution to this task provides the minimum-cost hybrid configuration, types and sizes of reverse-osmosis units, mass exchangers, pumps and turbines. It also identifies the best distribution of streams and waste reduction loads. A case study is tackled to illustrate the applicability of the devised procedure.

## INTRODUCTION

Waste reduction is any industrial activity that aims at controlling the release of environmentally-unacceptable materials to the environment. In many cases, the implementation of recycle/reuse policies for the recovery of hazardous species provides an economically-viable option for waste minimization. In addition to its favorable environmental impact, the adoption of this waste-recovery approach can lead to significant energy and material savings and may even provide income from the salable wastes. The imposed separation levels combined with the various thermodynamic properties of the waste streams may necessitate the use of multiple mass-exchange as well as membrane-separation devices. It is, therefore, necessary to develop a systematic technique for simultaneously screening all the different separation processes that can be used in a recycle/reuse network. In this context, process-synthesis techniques can provide powerful tools for systemizing design decisions. In particular, two useful tools that have been recently developed can be effectively employed in designing membrane-hybrid systems; namely the synthesis of mass-exchange networks "MEN's" and reverse-osmosis networks "RON's".



The essence of the MEN methodology (1)-(4) is to generate the optimal network of mass-exchanger units (e.g. absorbers, extractors, adsorption columns) that can selectively transfer certain hazardous species from a set of rich (waste) steams to a set of lean streams (mass-separating agents "MSA's"). Several computer-aided process-synthesis techniques were employed to develop the MEN design procedures. In particular, the notion of a mass-exchange "pinch point" has been instrumental in assessing thermodynamic limitations on waste-reduction tasks as well as identifying minimum utility consumption without prior commitment to the network structure.

In the context of dilute aqueous waste separations, reverse osmosis "RO" is destined to play an important role. The availability of numerous types of strongly selective membranes makes it possible to accomplish very high separation levels for virtually all hazardous species (5)-(8). Since RO does not involve phase changes, its energy consumption is normally moderate. By virtue of their size compactness, RO systems can be conveniently added to existing plant structures to accommodate any prospective environmental regulations. While the behavior of individual RO modules has been extensively studied in the past three decades, very little attention has been directed towards the task of designing systems of multiple RO modules. Since an RO process typically involves the use of several (in some cases hundreds of) units, the complex problem of optimally designing these systems should be thoroughly investigated. In response to this need, the problem of synthesizing RON's has been recently introduced (9). The design task involves the systematic identification of the optimal arrangement of the units, size(s) and type(s) of the RO modules to be employed (hollow fiber, tubular and/or spiral wound), distribution of the streams, energy consumption and recovery, and separation loads.

The purpose of this work is to develop a systematic procedure for designing mass-exchange/reverse-osmosis hybrid networks for waste-reduction applications. The two design tools for synthesizing MEN's and RON's will be integrated. The problem will be formulated as an optimal-synthesis task whose objective is to identify the minimum-cost combination of mass exchangers, RO units, pumps and turbines. In addition, all unit sizes, stream distribution and waste-recovery loads will be optimally identified. A case study will be addressed to demonstrate the applicability of the proposed procedure.



## PROBLEM DESCRIPTION

### Problem Statement

The problem of designing a reverse-osmosis/mass-exchange hybrid system for waste reduction can be stated as follows: Given are

(i) a set $W = \{i | i = 1, N_w\}$ of waste streams

(ii) a set $S = \{j | j = 1, N_{SO} + N_{SR}\}$ of MSA's, which consists of a subset $SO = \{j | j = 1, N_{SO}\}$ of once-through MSA's (for which there is no economic or environmental motivation to regenerate/recycle them, and a subset $SR = \{j | j = N_{SO} + 1, N_{SO} + N_{SR} + 1\}$ of regenerable (recyclable) MSA's for which there is an economic and/or environmental impetus to regenerate the MSA's and/or recover solutes.

(iii) a set $H = \{k|k = 1, N_H)$ of regenerants which can be used in regenerating the recyclable MSA's.

Synthesize a cost-effective hybrid system of mass exchangers, RO units, pumps and energy-recovery devices that can separate each of the waste streams into an environmentally acceptable product (lean or permeate) stream and a retentate (rich or reject) stream in which the undesirable species is concentrated. Given also are:

- The flowrate of each waste stream, $F_i^w$, its pressure, $P_i^w$, and composition, $x_i^w$.
- A lower bound on the flowrate of each lean stream (a minimum required flowrate of product), $F_i^{l,min}$, i.e.

$$F_i^l \geq F_i^{l,min} \qquad i\epsilon W \tag{1}$$

- An upper bound on the concentration of the undesirable key compound in each lean stream as given by an environmental regulation, $x_i^e$, i.e.

$$x_i^l \leq x_i^e \qquad i\epsilon W \tag{2}$$

- The supply and target compositions, $u_j^s$ and $u_j^t$ respectively, for each once-through MSA.
- An upper bound, $L_j^c$, on the flowrate available for each MSA, i.e.

$$L_j \leq L_j^c \qquad j\epsilon S \tag{3}$$

- The supply and target compositions, $z_k^s$ and $z_k^t$ respectively, for each regenerating agent.
- An upper bound, $M_k^c$, on the flowrate available for each regenerating agents, i.e.

$$M_k \leq M_k^C \qquad k\epsilon H \tag{4}$$

## Problem Representation

In approaching the aforementioned design task, it is necessary to devise a structural representation of the system which is capable of embedding all possible configurations of interest. This representation should be rich enough to account for all the system elements including mass exchangers, regeneration units, RO modules, booster pumps and energy-recovery devices and distribution of all streams. The proposed representation is inspired by the "state-space approach" that has been recently proposed (10)-(12) for the synthesis of mass, heat and distillation networks. The system is conceptualized as being composed of six boxes: a stream-distribution box "SDB", a mass-exchange box, a regeneration box, a pressurization/depressurization matching box "PDMB", a reverse-osmosis stream-distribution box "ROSDB", a reverse-osmosis matching box "ROMB". The objective of the SDB and the ROSDB is to span the necessary space for the distribution of all the streams. In the mass-exchange network, the undesirable species is transferred from the waste streams to the MSA's. The recyclable MSA's are then regenerated in the regeneration network. Furthermore, the role of the PDMB and the ROMB is to embed all potential matching states for the streams associated with pumps/turbines and RO modules.



Each stream entering the SDB passes through an inlet junction. Thus, the SDB has a set $J1 = \{i \mid i = 1, N_w\}$ of inlet junctions for the waste feed streams, a set $J2 = \{q \mid q = 1, N_{RO}\}$ of inlet junctions for the reject streams entering the SDB. Furthermore, the SDB features a set $J4 = \{n \mid n = 1, N_o + 2N_w)$ of outlet junctions. Each stream entering the SDB is split into $N_o + 2N_w$ "substreams" each of which connects an inlet and an outlet junctions. Each of the first $N_o$ outlet junctions is assigned to an outlet stream whose flowrate, pressure and composition are denoted by $F_n$, $P_n$ and $x_n$, respectively. These streams proceed to the mass-exchange box. On the other hand, the streams leaving the next $N_w$ outlet junctions of the SDB represent the lean (product) streams leaving the network. Their flowrates, pressures and compositions are represented by $F^l_i$, $P^l_i$ and $x^l_i$, respectively, where $i = 1,2,\ldots,N_w$. Similarly, the concentrated rich (retenate) streams leave the next $N_w$ outlet junctions of the SDB. These streams have flowrate, pressures and compositions denoted by $F_i^c$, $P_i^c$ and $x_i^c$, respectively, where $i = 1,2,\ldots,N_w$.

The streams leaving the first $N_w$ outlet junctions of the SDB are fed to the mass-exchange box where they may be contacted with MSA's with the objective of transferring the undesirable species. The recyclable MSA's are forwarded to the regeneration box whereby the MSA's can be regenerated via direct contact with regenerants and recirculated back to the mass-exchange box.

The waste streams leaving the mass-exchange box are next fed to the PDMB. Each stream enters the PDMB via an inlet junction, then passes through a pump followed by a turbine and eventually leaves the PDMB through an outlet junction. At most, one of the sequential pump and turbine exists in the solution. Within the PDMB, the pressure of any stream may change to become $P^i_n$ after the pump and $P^o_n$ after the energy-recovery device.



Each stream leaving the PDMB passes to an inlet junction $n \epsilon JI = \{n | n = 1, N_o\}$ of the ROSDB and, then, splits into $N_{RO}$ "substreams" emanating from that junction to the $N_{RO}$ outlet junctions. Subsequently, one stream leaves each outlet junction $q \epsilon JO = \{q | q = 1, N_{RO}\}$ to form a feed stream to the ROSDB. The flowrate, pressure and composition of a stream leaving the qth outlet junction of the ROSDB are designated as $F^f_q$, $P^f_q$ and $x^f_q$, respectively.

Each feed stream entering the ROMB via an inlet junction is assigned to one of the $N_{RO}$ reverse-osmosis modules in the ROMB. Each stage, q, consists of a number, $N^S_q$, of parallel and identical RO modules. Depending upon the optimal solution, each of these RO stages may exist or vanish. In addition, $N^S_q$ is an unknown variable whose value can be determined via optimization. Subsequently, each feed stream entering the qth RO unit is separated into a permeate stream (whose flowrate, pressure and composition are denoted by $F^P_q$, $P^P_q$ and $x^P_q$, respectively) and a reject stream (whose flowrate, pressure and composition are designated by $F^r_q$, $P^r_q$ and $x^r_q$, respectively). The permeate as well as the reject streams leaving the ROMB are fed to the SDB.

Figure 1 schematically demonstrates the proposed state-space representation for the mass-exchange/reverse-osmosis hybrid system. Such a representation provides a powerful tool for embedding all potential configurations of interest.

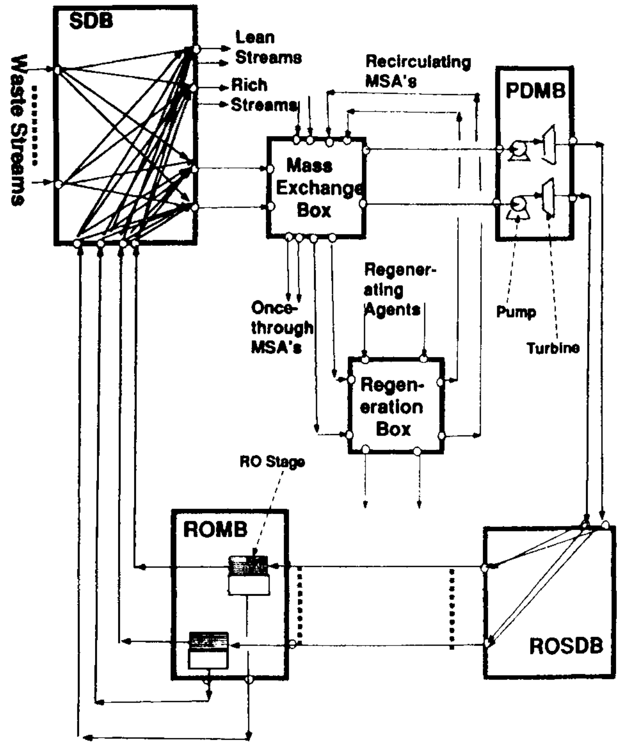


*FIGURE 1. State-space representation of the hybrid network.*



Hence, one can systematically formulate the design task as an optimization problem. This formulation is given in Appendix I. Having developed the theoretical representation of the problem, it is now appropriate to demonstrate the applicability of the proposed procedure via a case study on the dephenolization of an aqueous waste.

## EXAMPLE: DEPHENOLIZATION OF AN AQUEOUS WASTE FROM AN OIL-RECYCLING PLANT

One of the major environmental problems associated with lube-oil recycling plants is the removal of phenol from an aqueous waste stream. Several potential

TABLE 1. GEOMETRICAL DATA OF THE RO MODULES EMPLOYED IN EXAMPLE PROBLEM

| Module Property | B-9 (Dephenolization Example) |
|---|---|
| Fiber length, l, m | 0.750 |
| Fiber seal length, $l_s$, m | 0.075 |
| Outer radius of fiber, $r_o$, m | $42 \times 10^{-6}$ |
| Inner radius of fiber, $r_i$, m | $21 \times 10^{-6}$ |
| Membrane area, $S_m$, $m^2$ | 180.00 |

TABLE 2. INPUT DATA FOR THE DEPHENOLIZATION EXAMPLE

| | |
|---|---|
| Feed flowrate (phenol-free), $F_1^w$, kg/s | 131.42 |
| Feed composition, $x^w_1$ | $4.00 \times 10^{-3}$ |
| Minimum acceptable product (permeate) flowrate, $F_1^{l,min}$, kg/s | 131.42 |
| Maximum allowable product (permeate) composition, $x^c_1$ | $0.04 \times 10^{-3}$ |
| Maximum flowrate per module, kg/s | 0.460 |
| Minimum flowrate per module, kg/s | 0.210 |
| Maximum feed pressure, $N/m^2$ | $28.58 \times 10^5$ |
| Pressure drop per module, $N/m^2$ | $0.405 \times 10^{-5}$ |
| Pure-water permeability, A, $\frac{kg}{S.N}$ | $1.2 \times 10^{-10}$ |
| Solute transport parameter, $K_1$, $\frac{kg}{m^2.S}$ | $2.43 \times 10^{-4}$ |

technologies may be used to affect this separation task. Solvent extraction using lube oil as an extractant is one option. Oil is a process MSA ($S_1$) which can selectively remove phenol from wastewater. Besides the purification of the waste streams, the transfer of phenol to the oil is a beneficiary process for the oil stream itself. Phenol tends to act as oxidation inhibitors and serves to improve color stability and reduce sediment formation during the storage of oil. Another potential MSA is activated carbon (external MSA, $S_2$). After leaving the primary transfer MEN, the spent activated carbon ought to be regenerated so that it may be recycled back to the MEN. This is achieved by contacting it with caustic soda, which strips the adsorbed phenol by solvating it and then reacting with it to form sodium phenolate.



Another dephenolization process that can be potentially used in conjunction with the foregoing mass-exchange operations is reverse osmosis. The use of DuPont B-9 RO modules is considered (see Table 1 for geometrical properties of modules). The following module modeling equations can be used (13):

$$F_q^P / N_q^S = A S_m \, (\Delta P_q - \pi_q) \gamma \tag{5}$$

where

$$\gamma = \frac{\eta}{1 = 16 \; A \; \mu \; r_o \; U_s \; \eta / r_i^4} \tag{6}$$

and

$$\eta = \frac{\tanh \; [(16 \; A \; \mu \; r_o / r_i^2)^{1/2} \; (l / r_i)]}{[(16 \; A \; \mu \; r_o / r_i^2)^{1/2} \; (l / r_i)]} \tag{7}$$

Also

$$x_{q,m}^P = \frac{K_m x_{q,m}}{A (\Delta P_q - \pi_q) \gamma} \tag{8}$$

The necessary input data for this case study are summarized in Table 2. The economic data employed in design are given in Appendix II. Basic equilibrium and transport data are summarized in Appendix III.

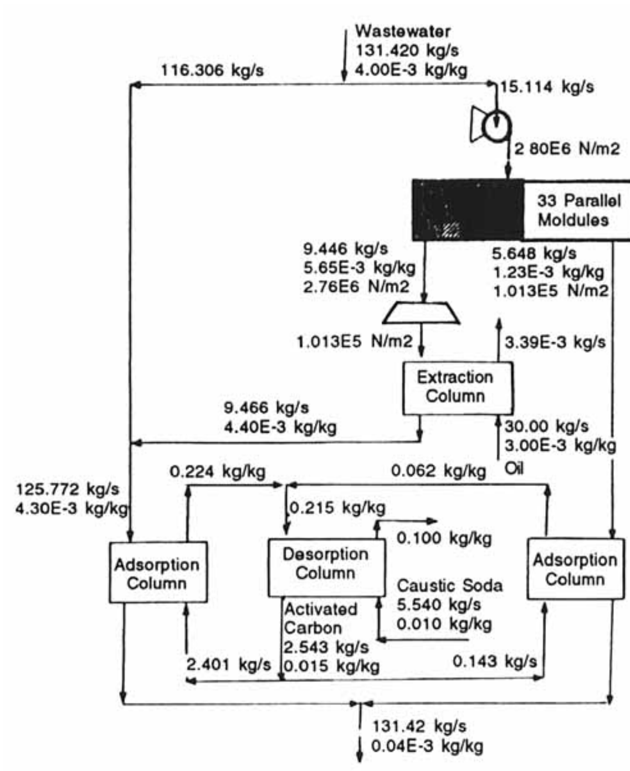


*FIGURE 2. Optimal dephenolization hybrid system.*

Using the proposed synthesis procedure, the problem is formulated as a mixed-integer nonlinear program "MINLP". This MINLP is solved using the software GINO (14),(15). This package is based upon the "generalized reduced gradient method". The optimization program was executed on a Sun Sparcstation II. Computing time is 549 CPU seconds. The solution of this program is shown in Fig. (2). It features one extraction column, one adsorption column, one regeneration unit, one pump, two RO stages (33 modules) and an energy-recovery turbine. The total annualized cost of this network is $6,811,948 per year. It is worth pointing out that the devised procedure provides a useful tool for performing sensitivity analysis for design. The influence of varying several economic and environmental factors can be readily examined. For instance, when the cost of membranes per unit area is doubled, the optimal solution will not include RO. The total annualized cost of this MEN is $7,094,526. In a similar fashion, the effect of changing mental specifications on the network cost can be assessed. These useful properties of the procedure can, therefore, provide the designer with a systematic technique for developing cost-effective designs of membrane-hybrid systems and assessing the sensitivity of these systems over a wide range of economic and environmental data.



## CONCLUSIONS

A systematic procedure for synthesizing waste-reduction mass-exchange/ membrane hybrid processes has been introduced. First, a structural representation was devised to account for all potential configurations of interest. The problem was then formulated as an MINLP whose solution provides a waste-reduction hybrid system that features minimum total annualized cost. A case study on dephenolizing an aqueous waste was presented to elucidate the applicability of the proposed procedure.

## APPENDIX I

## MATHEMATICAL DESCRIPTION

In this appendix, the task of synthesizing a hybrid mass-exchange/reverse-osmosis system is formulated as an optimization program whose objective is to minimize the sum of the annualized fixed cost (for all RO units, pumps and energy-recovery devices) and the operating cost (cost of power necessary for pumping less the value of power generated by turbines, cost of membrane replacement, cost of MSA's and cost of regenerating agents). Depending upon the types of RO units, pumps and turbines, one can derive an explicit expression for the objective function in terms of the various flowrates, pressures and concentrations throughout the system as well as a number of binary integer variables that indicate the existence or absence of RO modules, pumps and turbines. As demonstrated by El-Halwagi and Manousiouthakis (2) the identification of a solution featuring minimum cost of MSA's and regenerating agents does not commit the designer to any particular network configuration. Nonetheless, by solving a mixed-integer linear program one can generate a mass-exchange/regeneration network that features minimum annualized fixed cost subject to the obtained minimum cost of MSA's and regenerants. In addition to the objective function, a number of constraints should be included. These constraints account for the various environmental and technical aspects of the problem as follows:



Material balances for the inlet junctions of the SDB:

$$F_i^w = \sum_{n=1}^{N_o+2N_w} F_{i,n}^w \qquad i=1,2,\ldots,N_w$$

$$F_q^p = \sum_{n=1}^{N_o+2N_w} F_{q,n}^p \qquad q=1,2,\ldots,N_{RO}$$

$$F_q^r = \sum_{n=1}^{N_o+2N_w} F_{q,n}^r \qquad q=1,2,\ldots,N_{RO}$$

Material balances for the outlet junctions of the SBD:

$$F_n = \sum_{i=1}^{N_w} F_{i,n}^w + \sum_{q=1}^{N_{RO}} F_{q,n}^p + \sum_{q=1}^{N_{RO}} F_{q,n}^r \qquad n=1,2,\ldots$$

$$F_n X_n = \sum_{i=1}^{N_w} F_{i,n}^w X_i^w + \sum_{q=1}^{N_{RO}} F_{q,n}^p X_q^p + \sum_{q=1}^{N_{RO}} F_{q,n}^r X_q^r$$

where, according to the nomenclature used in the network representation

$$F_i^1 = F_{N_o} + i \qquad i=1,2,\ldots,N_w$$

$$x_i^1 = X_{N_o} + i \qquad i=1,2,\ldots,N_w$$

$$x_i = X_{N_o} + N_w + i \qquad i=1,2,\ldots,N_w$$

Product-demand constraints:

$$F_i^1 \geq F_i^{1,\min} \qquad i=1,2,\ldots,N_w$$

Environmental constraints:

$$X_i^1 \leq X_i^e \qquad i=1,2,\ldots,N_w$$

Since only streams with equal pressures can be mixed together, the following constraints are necessary:

$$(P_n - P_i)\,F_{i,n}^w = O \qquad \begin{array}{l} i=1,2,\ldots,N_w \\ n=1,2,\ldots,N_o+2N_w \end{array}$$

$$(P_n - P_q^P)\,F_{q,n}^P = O \qquad \begin{array}{l} q=1,2,\ldots,N_{RO} \\ n=1,2,\ldots,N_o+2N_w \end{array}$$

and

$$P_n - P_q^r F_{q,n}^r = O \qquad \begin{array}{l} q=1,2,\ldots,N_{RO} \\ n=1,2,\ldots,N_o+2N_w \end{array}$$

<u>**Material balances for the mass-exchange and the regeneration boxes**</u>

In searching for the minimum cost of MSA's and regenerants, one can exploit the powerful concept of mass-exchange pinch points. A detailed discussion of the following constraints can be found (2).

$$\sum_{n=1}^{N_o} F_n(x_n^s - x_n) - \sum_{j=1}^{N_s} L_j(u_j^t - u_j^t) = O \qquad \begin{array}{l} j\epsilon S \\ n=1, \end{array}$$

$$\sum_{n=1}^{N_o} F_n\{\lambda_{n,pp}^t(x^{pp} - x_n) - \lambda_{n,pp}^t(x^{pp} - x_n^s)\}$$

$$- \sum_{j\in S} \{\eta^{s}_{j,pp}(u^{pp}_{j} - u^{s}_{j}) - \eta^{t}_{j,pp}(u^{pp}_{j} - u^{t}_{j})\} \leq O \qquad \forall\ pp \in \overline{P}$$

$$\sum_{j\in SR} L_j(u^{t}_{j} - u^{s}_{j}) - \sum_{k\in H} M_k(z^{t}_{k} - z^{s}_{k}) = O$$

$$O \leq M_k \leq M^{c}_{k} \qquad k\in H$$

$$(2\lambda^{t}_{n,pp}-1)(y^{pp}-y^{t}_{n}) \geq O \qquad n=1,2,\ldots,N_o$$

$$(2\lambda^{t}_{n,pp}-1)(y^{pp}-y^{s}_{n}) \geq O \qquad n=1,2,\ldots,N_o$$

$$(2\eta^{s}_{j,pp}-1)(x^{pp}_{j}-x^{t}_{j}) \geq O \qquad j\in S, pp\in\overline{P}$$

$$(2\eta^{s}_{j,pp}-1)(x^{j^{pp}}-x^{s}_{j}) \geq O \qquad j\in S, pp\in\overline{P}$$

$$(2\psi^{s}_{j,qq}-1)(x^{qq}-x^{s}_{j}) \geq O \qquad j\in SR, qq\in Q$$

$$(2\psi^{t}_{j,qq}-1)(x^{qq}-x^{t}_{j}) \geq O \qquad j\in SR, qq\in Q$$

$$(2\phi^{s}_{k,qq}-1)(z^{qq}_{k}-z^{s}_{k}) \geq O \qquad k\in H, qq\in Q$$

$$(2\phi^{t}_{k,qq}-1)(z^{qq}_{k}-z^{t}_{k}) \geq O \qquad k\in H, qq\in Q$$

$$\lambda^{s}_{n,pp}=O,1 \qquad n\in R$$

$$\lambda^{t}_{i,pp}=O,1 \qquad n\in R$$

$$\eta^{s}_{j,pp}=O,1 \qquad j\in S$$

$$\eta^{t}_{j,pp}=O,1 \qquad j\in S$$

$$\psi^{s}_{j,qq}=O,1 \qquad j\in SR$$

$$\psi^{t}_{j,qq}=O,1 \qquad j\in SR$$

$$\phi^{s}_{k,qq}=O,1 \qquad k\in H$$

$$\phi^{t}_{k,qq}=O,1 \qquad k\in H$$

## Constraints for the PDMB

Since a pump will only raise the pressure of a stream while a turbine can only reduce the pressure of a stream, the following constraints are necessary:

$$P_n^i - P_n \geq O \qquad n=1,2,\ldots,N_o$$

and

$$P_n^i - P_n^o \geq O \qquad n=1,2,\ldots N_o$$

Now, let us employ the binary integer variables $B_n$ and $T_n$ to account for the existence of the nth booster pump and turbine, respectively. When the nth pump (turbine) exists, $B_n$ ($T_n$) assumes the value of one, whereas if it is absent, the binary variable becomes zero. Therefore, the following constraints identifying the values of the binary variables are necessary:

$$U*B_n \geq P_n^i - P_n \geq L*B_n \qquad n=1,2,\ldots,N_o$$

where U and L are arbitrary large and small numbers, respectively. The foregoing constraint forces $B_n$ to become one if $P_n^i$ is larger than $P_n$ (i.e. the stream entering the nth junction of the PDMB is pressurized), otherwise it becomes zero. A similar constraint can be written for the turbines:

$$U*T_n \geq P_n^i - P_n^o \geq L*T_n \qquad n=1,2,\ldots,N_o$$

Since, it is illogical to pressurize a stream and immediately depressurize it, the following constraint is needed:

$$B_n + T_n \leq 1 \qquad n=1,2,\ldots,N_o$$

## Constraints for the ROSDB

Material balances for the inlet junctions of the ROSDB:

$$F_n = \sum_{1=1}^{N_{RO}} F_{n,q} \qquad N=1,2,\ldots,n_o$$

Material balances for the outlet junctions of the ROSDB:

$$F_q^f = \sum_{n=1}^{N_o} F_{n,q} \qquad q=1,2,\ldots,N_{RO}$$

$$F_q^f x_q^f = \sum_{n=s}^{N_o} F_{n,q} x_n^t \qquad q=1,2,\ldots N_{RO}$$

Isobaric mixing of streams:

$$(P_q^f - P_n^o) F_{n,q} = O \qquad q=1,2,\ldots,N_{RO} \quad n=1,2,\ldots,N_o$$

**Constraints for the ROMB**

**Stage-design equations:**

It is essential to have a set of equations relating the flowrates and composition of the reject and the permeate leaving a stage to the flowrate, pressure and concentration of the stream entering that stage as well as the pressures of the permeate and the reject leaving that stage. In general, these equations can be expressed as:

$$F_q^p = \Phi_1(F_q^f, x_q^f, P_q^f, P_q^r, P_q^p, N_q^s) \qquad q=1,2,\ldots,N_{RO}$$

$$F_q^r = \Phi_2(F_q^f, X_q^f, P_q^f, P_q^r, P_q^p, N_q^s) \qquad q=1,2,\ldots,N_{RO}$$

$$X_q^p = \Phi_3(F_q^f, X_q^f, P_q^f, P_q^r, P_q^p, N_q^s) \qquad q=1,2,\ldots,N_{RO}$$

and

$$X_q^r = \Phi_4(F_q^f, X_q^f, P_q^f, P_q^r, P_q^p, N_q^s) \qquad q=1,2,\ldots,N_{RO}$$

where $\phi_1$, $\phi_2$, $\phi_3$ and $\phi_4$ are the functional relations constituting the model equations for a single RO stage.

## Operational Constraints

Typically, manufacturers of RO modules recommend operating ranges for pressure, flowrate and concentration. These can be expressed as:

$$F^{\min} \leq F_q^f / N_q^S \leq F^{\max} \qquad q=1,2,\ldots,N_{RO}$$

$$P_q^f \leq P^{\max} \qquad q=1,2,\ldots N_{RO}$$

The following constraint will be employed to identify the existence or absence of a certain RO unit:

$$U*R_q \geq F_q^P \geq L*R_q \qquad q=1,2,\ldots,N_{RO}$$

where $R_q$ is a binary integer variable that assumes the value of one when the qth RO stage exists and vanishes when this stage is absent.

The above mathematical formulation is a mixed-integer nonlinear optimization program "MINLP". Its solution requires the identification of the optimal values of continuous as well as discrete variables. The solution of this MINLP identifies the network configuration, stream distribution and operating conditions.

## APPENDIX II

## SUMMARY OF COST DATA

Throughout this paper the following economic data are employed:

Annualized fixed cost of pumps (\$/yr) = 0.0157 [flowrate through pump (kg/s)* pressure difference across pump (N/m$^2$)]$^{0.79}$ (II.1)

Annualized fixed cost of turbines (\$/yr) = 0.4182 [flowrate through turbine (kg/s)* pressure difference across turbine (N/m$^2$)]$^{0.47}$ (II.2)

Cost (value) of electric power = 0.06 \$/KWR (II.3)

Mechanical efficiency of pumps (or turbines) = 65% (II.4)

Annualized cost of RO modules for the dephenolization example (including annualized installed cost, membrane replacements, labor and maintenance) = $1140 \frac{\$}{\text{module.yr}}$ (II.5)

Annualized fixed cost of stage-wise contactors = $600\ N^{0.74}$ \$/year where N is the number of contacting stages (II.6)

Annualized fixed cost of a moving-bed adsorption columns = $1{,}900\ H^{0.74}$ \$/year where H is the height of the column (II.7)

Cost of activated carbon makeup (assuming the annual loss of 5% of recirculating adsorbent) = 0.077 \$/kg of recirculating activated carbon (II.8)

Cost of recirculating caustic soda (including regeneration) = 0.001 \$/kg of recirculating caustic soda (II.9)



## APPENDIX III

## EQUILIBRIUM AND TRANSPORT DATA

Several linear (or linearized) equilibrium relations were used. In all these expressions, y and x denote the mass fractions of phenol in the phenol-rich and phenol-lean phases, respectively. All mixtures were assumed to be ideal. The equilibrium data are given by

$$y = 1.53x \qquad \text{(III.1)}$$

for phenol extraction in light gas oil (16)

$$y = 0.018x \qquad \text{(III.2)}$$

for phenol adsorption on activated carbon (17) linearized over the operating composition range, and

$$y = 1.429x \qquad \text{(III.3)}$$

for phenol desorption from activated carbon using caustic soda (17).

The mass-transfer coefficient for any liquid-activated carbon system was estimated via the following correlation (18):

$$k = (u/f)\ Sc^{-2/3}\ [0.765\ Re^{-0.82} + 0.365\ Re^{-0.386}] \qquad \text{(III.4)}$$

where u is the superficial liquid velocity, f is the bed porosity, Sc and Re are the Schmidt and Reynolds numbers, respectively.

## NOMENCLATURE

A pure-water permeability, $\frac{kg}{S.N}$.

$F_i^c$ flowrate of concentrated rich (retenate) stream i leaving the RON, kg/s.

$F_i^l$ flowrate of lean (product) stream i leaving the RON, kg/s.

$F_i^{l,min}$ minimum allowable flowrate of lean (product) stream i leaving the RON, kg/s.

$F^{max}$ maximum flowrate per module (as recommended by manufacturer), kg/s.

$F^{min}$ minimum flowrate per module (as recommended by manufacturer), kg/s.

$F_i^w$ flowrate of waste feed stream i entering the RON, kg/s.

$F^w_{i,n}$ flowrate of substream connecting inlet junction i and outlet junction j in the SDB, kg/s.

$F_n$ flowrate of stream leaving the PDSDB via outlet junction n, kg/s.

$F_{n,q}$ flowrate of substream connecting inlet junction n with outlet junction q in the ROSDB, kg/s.

$F_q^f$ flowrate of stream leaving the ROSDB through outlet junction q and entering the qth RO stage in the ROMB, kg/s.

$F_q^P$ flowrate of the permeate leaving the qth RO stage in the ROMB, kg/s.

$F^P_{q,n}$ flowrate of substream connecting the qth inlet junction of a permeate stream with the nth outlet junction in the SDB, kg/s.

$F_q^r$ flowrate of the reject leaving the qth RO stage in the ROMB, kg/s.

$F^r_{q,n}$ flowrate of substream connecting the qth inlet junction of a reject stream with the nth outlet junction in the SDB, kg/s.

H set of regeneration agents.

i an index for the waste feed streams or their corresponding inlet junctions to be SDB.

j index for lean streams.

JI set of inlet junctions to the ROSDB.

JO set of outlet junctions from the ROSDB.

J1 set of inlet junctions of the waste feed streams to the PDSDB.

J2 set of inlet junctions of the permeate streams to the PDSDB.

J3 set of inlet junctions of the reject streams to the PDSDB.

J4 set of outlet junctions from the PDSDB.

k index for regenerating agents.

$K_m$ transport parameter of solute m, m/s.

l fiber length, m.

$l_s$ fiber seal length, m.

L an arbitrary small number.

$L_j$ mass flowrate of lean stream j, kg/s.

$L_j^c$ upper bound on mass flowrate of lean stream j, kg/s.

$M_k$ flowrate of regenerating agent k, kg/s.

$M_k^c$ upper bound on flowrate of regenerating agent k, kg/s.

n an index for the pumps/turbines in the PDMB or their corresponding outlet junctions from the SDB and inlet junctions to the mass-exchange box.

$N_H$ number of regenerating agents.

$N_o$ number of pumps/turbines in the PDMB or their corresponding outlet junctions from the SDB and the inlet junctions to the mass-exchange box.

$N_q^S$ number of parallel RO modules in the qth stage of the ROMB.

$N_{RO}$ number of RO units in the ROMB or their corresponding outlet ROSDB junctions, inlet ROMB junctions, outlet ROMB permeate junctions, outlet ROMB reject junctions, inlet SDB permeate junctions or inlet PDSDB reject junctions.

$N_s$ number of lean-streams.

$N_{SO}$ number of once-through lean streams.

$N_{SR}$ number of regenerable lean streams.

$N_w$ number of waste feed streams or their corresponding inlet SDB junctions, outlet PDSDB lean (product) junctions or outlet SDB rich (retenate) junctions.

$\Delta P_q$ pressure difference across the membrane of any module in the qth stage in the ROMB.

PP index for pinch-point candidates in primary transfer MEN.

$P_i^c$ pressure of concentrated rich (retenate) stream i leaving the system, $N/m^2$.

$P_i^w$ pressure of waste feed stream i entering the system, $N/m^2$.

$P_n$ pressure of stream leaving the SDB via outlet junction n, $N/m^2$.

$P_q^f$ pressure of stream leaving the ROSDB through outlet junction q and entering the qth RO unit in the ROMB, $N/m^2$.

$P^{max}$ maximum allowable pressure for RO units (as recommended by module manufacturer), $N/m^2$.

$P_q^P$ pressure of the permeate leaving the qth RO unit in the ROMB, $N/m^2$.

$\bar{P}^r_q$ pressure of the reject leaving the qth RO stage in the ROMB, $N/m^2$.

$\bar{P}$ set of pinch-point candidates in primary transfer MEN.

q an index for the RO stages in the ROMB or their corresponding outlet ROSDB junctions, inlet ROMB junctions, outlet ROMB permeate junctions, outlet ROMB reject junctions, inlet SDB permeate junctions or inlet SDB reject junctions.

qq index for pinch-point candidates in regeneration MEN.

Q set of pinch-point candidates in regeneration MEN.

$r_i$ inner radius of the hollow fiber, m.

$r_o$ outer radius of the hollow fiber, m.

$R_q$ binary integer variable that corresponds the qth RO stage in the ROMB.

S set of hazardous species.

$S_m$ membrane area per module, $m^2$.

$T_n$ a binary integer variable to indicate the existence or absence of the nth turbine in the PDMB.

$u_j$ mass fraction of the key component in lean stream j.

$u_j^s$ supply mass fraction of key component in lean stream j.

$u_j^t$ target mass fraction of key component in lean stream j.

U an arbitrary large number.

W set of waste feed streams.

$x^c{}_i$ mass fraction of key component in concentrated rich (retenate) stream i leaving the system.

$x^e{}_i$ maximum allowable mass fraction of key species in lean (product) stream i leaving the system, as imposed by environmental-protection regulations.

$x^l{}_i$ mass fraction of key component in lean (product) stream i leaving the system.

$x^w{}_i$ mass fraction of undesirable key species in waste feed stream entering the system.

$X^w{}_i$ set of inlet composition of waste feed stream i.

$x_n$ mass fraction of key compound in the stream that is leaving the SDB via outlet junction n.

$x^f{}_q$ mass fraction of key component in the stream that is leaving the ROSDB through outlet junction q and entering the qth RO stage in the ROMB.

$x^p_q$ mass fraction of key component in the permeate leaving the qth RO stage in the ROMB.

$x_q$ average mass fraction of key species in the high-pressure side of any module in the qth stage in the ROMB.

$x^r_q$ mass fraction of key species in the reject leaving the qth RO stage in the ROMB.

$x^s_n$ mass fraction of key species in nth waste stream entering mass-exchange box.

$x_n^t$ mass fraction of key species in nth waste stream leaving mass-exchange box.

$z_k$ mass fraction of key component in regenerating agent k.

$z_k^s$ supply mass fraction of key component in regenerating agent k.

$z_k^t$ target mass fraction of key component in regenerating agent k.



## Greek Letters

$\gamma$ defined by Eq. (6).

$\lambda^s_{n,pp}$ binary integer variable.

$\lambda^t_{n,pp}$ binary integer variable.

$\eta$ defined by Eq. (7).

$\eta^s_{n,pp}$ binary integer variable.

$\eta^t_{n,pp}$ binary integer variable.

$\phi^s_{k,qq}$ binary integer variable.

$\phi^t_{k,qq}$ binary integer variable.

$\mu$ viscosity, $\frac{kg}{m.s.}$

$\pi_q$ average osmotic pressure on the high-pressure side of the qth RO stage in the ROMB, $N/m^2$.

**Subscripts**

pp pinch point candidate in primary transfer MEN.

qq pinch point candidate in regeneration MEN.

s supply.

t target.

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