

SEPARATIONS

Modeling and Optimization of an Emulsion Pertraction Process for Removal and Concentration of Cr(VI)

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This work reports the modeling and optimization of an emulsion pertraction process for the removal and concentration of Cr(VI) from aqueous effluents. The emulsion pertraction technology that combines the efficiency of emulsion liquid membranes with the advantages of using hollow-fiber modules as contactors has been applied to the removal of the Cr(VI) initially contained in aqueous effluents of defined composition together with its simultaneous concentration for reuse. A mathematical model that considered mass-transfer resistances in the aqueous feed film and in the membrane phase coupled to the kinetics of the back-extraction reaction described satisfactorily well the experimental results of Cr(VI) removal and concentration obtained after careful planning. Finally, the methodology leading to the determination of the optimal flow configuration that maximizes the effluent flowrate treated by the process is presented; a two-step process has been proposed, and its optimal operation has been found by solving a nonlinear programming problem. The present approach provides a useful strategy for future design of industrial-scale plants using this new technology for effluent treatment and pollutant recovery.

1. Introduction

Higher and higher demands are put onto new separation technologies due to environmental legislation and needs for cost reduction. To meet these ever increasing demands, there is a tendency to propose new processes that are technically effective and cost-effective. One of those technologies is the emulsion pertraction that combines the efficiency of emulsion liquid membranes with the advantages of using hollow-fiber modules.¹ In the emulsion pertraction process, the water phase is kept apart from the emulsion phase by a hydrophobic microporous membrane.^{2,3} The emulsion phase consists of an organic solvent with a dissolved extractant as continuous phase with aqueous droplets of strip liquid dispersed in it. The contact surface between the aqueous feed phase and the emulsion phase lies in the pores of the membrane. The metal to be removed from the wastewater stream is bounded by the extractant present in the pores of the membrane. At the other side of the membrane, in the shell side the extractant is regenerated by the back-extraction or stripping solution. The hydrophobic nature of the membrane keeps the wastewater and the stripping solution always separated.^{4–7}

Emulsion pertraction has been applied to the selective recovery of different heavy metals such as Zn, Hg, Fe, Pb, Cd, Cu, Cr, and Ni. The emulsion pertraction

process is especially suitable for selective removal of these metals from low concentration levels and their simultaneous concentration to a much higher level.^{8,9} Effluents coming from galvanic processes, nuclear industries, zinc-containing wastewaters from the rayon industry, etc. have been successfully treated by means of this technology. Other substances that can be economically treated by emulsion pertraction include chlorinated solvents (e.g., carbon tetrachloride, chloroform, etc.) PCBs, di- and trichlorobenzene, pesticides, and higher polycyclic hydrocarbons.¹⁰ Despite the promising results of the emulsion pertraction technology, only scarce applications have been developed at the industrial scale. TNO, a Dutch contract research organization, in cooperation with an engineering firm has developed the first installation for the treatment of water heavily polluted with an aromatic compound formed in one reactor. The plant has a capacity of 15 m³ h⁻¹, and it has recently been put into operation. In the pertraction installation, the organic compound is extracted from the wastewater using a feedstock for the reactor as extractant. In this way, not only is the water cleaned, but lost product is recycled back to the reactor.⁸

The case of study selected in this work deals with the recovery of Cr(VI) from polluted waters by means of the emulsion pertraction technology. After determination of the mathematical model and model parameters from correlation to experimental data, this paper presents the optimal operating variables by solving a nonlinear programming problem (NLP).

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Table 1. Hollow-Fiber Membrane Module Characteristics

characteristics of the modules	values
cartridge dimensions ($D \times L$), cm	6.65 \times 28.25
no. of fibers	10 200
effective surface area, m ²	1.4
effective length, m	0.15
cartridge material	epoxy
fiber potting material	stainless steel
cartridge material	Celgard X10 polypropylene
fiber type	240
inner diameter, μm	30
thickness, μm	0.05
porosity, %	30
tortuosity factor	2.6

Table 2. Physicochemical Characterization of Feed Waters

	values
chromate	2170–2692 mg/L
calcium	543 mg/L
sulfate	1735 mg/L
chlorides	1187 mg/L
silica	14 mg/L
aluminum	58 mg/L
TOC	52 mg/L
conductivity	7 mS/cm
pH	7.3

2. Experimental Section

The experimental analysis was carried out in an experimental setup provided with Liqui-Cel Extra-Flow 4- \times 28-in. membrane contactors of 1.4 m² purchased from Hoechst Celanese. Other characteristics are shown in Table 1.

Figure 1 presents a flow diagram of the experimental setup. Detailed description of the elements and of the operation procedure can be found elsewhere.¹¹

Physicochemical characterization of the feedwaters is given in Table 2, where it is shown that the initial concentration of Cr(VI) varied in the range from 6.5 to 8.3 mol m⁻³.

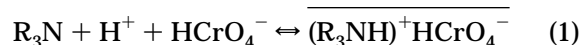
The emulsion was prepared by dispersing the aqueous sodium hydroxide solution (the back-extraction phase, 3000 mol m⁻³) in the organic phase at a volume ratio of 1:4. The organic solution was formed with 10% (v/v) of Alamine 336, a tertiary amine, 10% (v/v) of dodecanol (modifier of the extractant), and 5% (v/v) of Pluronic L31 (block copolymer of ethylene oxide and propylene oxide, added to enhance the phase separation of the aqueous stripping solution from the organic solution in the absence of agitation for the recovery of the stripping solution) in Isopar L (an isoparaffinic hydrocarbon solvent). Feedwaters were acidified, and the pH was maintained at a constant value of 1.5 by addition of sulfuric acid.

In the experimental work, the feed flowed in a single-pass mode, whereas the emulsion phase recycled itself. The feed solution was pumped through the lumen of the hollow fibers, while the emulsion phase ran counter-current through the shell of the module.

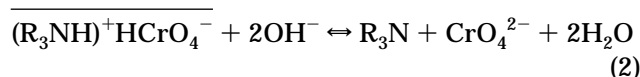
The concentration of Cr(VI) in the aqueous phase and in the stripping phase after emulsion breakage was measured in a spectroquant VEGA 400 spectrophotometer. Two different sets of consecutive experiments were carried: the first set was constituted of 8 experiments and the second set comprised 11 experiments. Feed and stripping phases were renewed each experimental run, whereas the organic phase was kept constant in the whole set of experiments. Figure 2 is a representative graph of the evolution of the chromium concentration values with time in the first set of experiments while the outlet feed concentration of chromium was kept below 0.00961 mol/m³.

3. Mathematical Modeling of the Chromium(VI) Pertraction

3.1. Chemistry of Solvent Extraction. Feed solutions containing chromium(VI) were acidified to pH 1.5; thus, the predominant species was HCrO_4^- , and the reaction with the selective extractant can be represented through the following equation:³



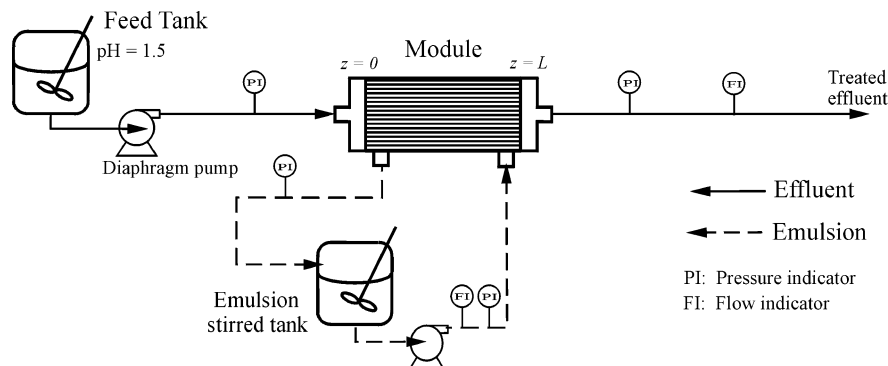
The back-extraction reaction with NaOH can be represented by



3.2. Mass Transfer in the Pertraction Process.

Figure 3 shows an enlarged view of the membrane with the aqueous phase in the lumen side and the continuous organic phase and dispersed droplets of the stripping solution (emulsion phase) in the shell side. The hydrophobic microporous membrane is wetted by the organic phase.

In the proposed model, the mass transfer of chromium from the feed to the stripping phase takes place in four steps: (i) diffusion in the feed-phase stagnant layer to the interface with the membrane; (ii) interfacial reaction of Cr(VI) with the extractant Alamine 336 to form the complex species (eq 1); (iii) diffusion within the supported liquid membrane; and (iv) chemical reaction at the interface of the stripping globules (eq 2). Thus, the main model hypotheses are the following: the extraction

**Figure 1.** Experimental setup.

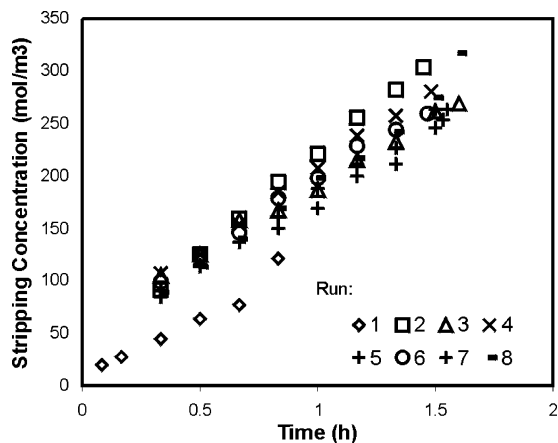


Figure 2. Experimental chromium concentrations in an experimental run. $F_e = 0.006\text{--}0.007\text{ m}^3\text{ h}^{-1}$, $F_m = 0.008\text{--}0.010\text{ m}^3\text{ h}^{-1}$, $C_e^{\text{in}} = 7\text{--}8\text{ mol m}^{-3}$, $C_o^{\text{f}} = 0\text{--}96\text{ mol m}^{-3}$.

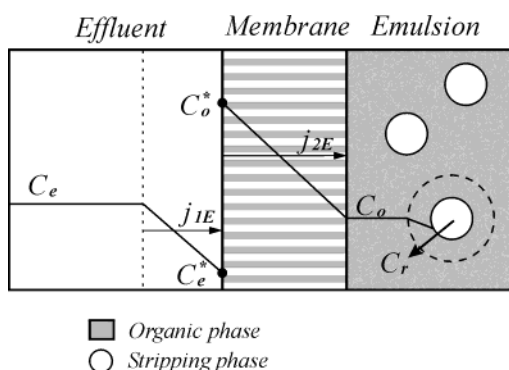


Figure 3. Enlarged view of the fiber with the feed aqueous phase in the lumen side and the emulsion phase in the shell side.

chemical reaction (eq 1) is considered fast enough to reach equilibrium instantaneously, and the chromium mass-transfer resistance in the stripping phase stagnant film is considered negligible.³ The diffusion of the other species is assumed to be faster than the correspondent to the chromium compounds.

Then, the mass-transfer flux through the feed-phase stagnant layer can be described according to Fick's equation,

$$j_1 = k_L(C_e - C_o^*) \quad (3)$$

and in the organic membrane,

$$j_2 = k_m(C_o^* - C_o) \quad (4)$$

where C_e is the chromium bulk concentration in the aqueous phase, C_o^* is the aqueous chromium concentration at the membrane interface, C_o^* is the organic chromium concentration at the membrane interface in equilibrium with C_o^* , and C_o is the chromium concentration in the organic phase, as shown in Figure 3. Interfacial equilibrium concentrations in the extraction side are related through the expression of the chemical equilibrium parameter,

$$K_{\text{eq}} = \frac{[(R_3NH)^+HCrO_4^-]^*}{[R_3N]^*[H^+]^*[HCrO_4^-]^*} \quad (5)$$

with the initial concentration of the extractant used in

the organic-phase solution, R_3N , equal to 212 mol m^{-3} . The asterisk indicates equilibrium concentrations.

Assuming pseudo-steady state, then:

$$j_1 = j_2 \quad (6)$$

At the interface of the stripping solution, the rates of formation and dissociation of CrO_4^{2-} (eq 2) are given by R_1 and R_{-1} :

$$R_1 = k_1OH^2C_o \quad (7)$$

$$R_{-1} = k_{-1}C_r \quad (8)$$

where C_r is the chromium concentration at the stripping phase.

Thus, the flux of chromium from the organic phase to the stripping phase through the dispersion bubbles interface is given by

$$j_3 = R_1 - R_{-1} = k_1\left(OH^2C_o - \frac{C_r}{K_r}\right) \quad (9)$$

K_r is the equilibrium parameter of the stripping chemical reaction. However, the OH^- concentration in the back-extraction phase, initially 3000 mol m^{-3} , decreased not only due to the reaction with the organic chromium complex species, but also due to the neutralization reaction with other competitive anions such as SO_4^{2-} present in the feedwaters and transported to the stripping phase by means of the organic extractant.³ In this work, the evolution of the OH^- concentration in the back-extraction phase with time has been considered as an empirical function of the chromium concentration in the same phase of the type

$$[OH] = 3000 - rC_r \quad (10)$$

where r is a coefficient that would take the value of 2 (stoichiometric coefficient of OH^- according to eq 2) if there were no competitive reactions between Alamine 336 and other anions different from chromate, but in the present case r can take a value higher than 2.

The value of the mass-transfer parameter k_L for fluids flowing through tubes in laminar flow may be calculated from the Lévêque equation:¹²

$$\left(\frac{k_L d}{D_a}\right) = 1.62 \left(\frac{d^2 u_{\text{tube}}}{D_a L}\right)^{1/3} \quad (11)$$

where d is the inside diameter of the hollow fiber, D_a the diffusivity of the chromic anion in the aqueous feed solution, u_{tube} the mean velocity of the aqueous feed solution, and L the module length. The value of D_a was reported by Ho³ as equal to $1.97 \times 10^{-9}\text{ m}^2\text{ s}^{-1}$, and the hollow-fiber membrane module characteristics are described in Table 1. For the experimental conditions given in this table, the value of the mass-transfer coefficient k_L was equal to $1.3 \times 10^{-5}\text{ m s}^{-1}$.

The membrane mass transport coefficient k_m may be calculated by using the following equation:

$$k_m = \frac{D_o \epsilon}{\tau l} \quad (12)$$

where D_o is the diffusivity of the chromic complex species in the organic phase supported in the mem-

brane, τ is the tortuosity of the membrane, ϵ the porosity, and l the membrane thickness; the values of these parameters are given in Table 1. The value of D_0 was reported by Ho³ as equal to $7.4 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. The final value of the mass-transfer coefficient in the membrane phase, k_m , was equal to $2.85 \times 10^{-7} \text{ m s}^{-1}$.

In eq 1, the proton concentration can be expressed according to Cr(VI) concentration in the aqueous phase in the equilibrium,

$$H_e^* = H_e - (C_e^{\text{in}} - C_e^*) \quad (13)$$

For a system operating at non-steady state, it is also necessary to describe the change of the solute concentration with time. For simplicity, the concentration of Cr(VI) in the aqueous and organic phases has been described by means of macroscopic mass balances of the permeating solute developed in a certain volume of the fiber at a time interval.⁵

Module mass balance:

Feed solution:

$$\frac{V_e^{\text{M}}}{L} \frac{dC_e}{dt} = -F_e \frac{dC_e}{dz} - \frac{A}{L} j_1, \quad t=0 \quad C_e = 0 \\ z=0 \quad C_e = C_e^{\text{in}} \quad (14)$$

Organic solution:

$$\frac{V_o^{\text{M}}}{L} \frac{dC_o}{dt} = F_o \frac{dC_o}{dz} + \frac{A}{L} j_1 - \frac{V_r^{\text{M}}}{L} A_v k_1 \left(\text{OH}^2 C_o - \frac{C_r}{K_r} \right), \\ t=0 \quad C_o = C_o^0 \\ z=L \quad C_o = C_o^{\text{T}} \quad (15)$$

Stripping solution:

$$\frac{V_r^{\text{M}}}{L} \frac{dC_r}{dt} = F_r \frac{dC_r}{dz} + \frac{V_r^{\text{M}}}{L} A_v k_1 \left(\text{OH}^2 C_o - \frac{C_r}{K_r} \right), \\ t=0 \quad C_r = C_r^0 \\ z=L \quad C_r = C_r^{\text{T}} \quad (16)$$

The term on the left-hand side of eqs 14–16 corresponds to the solute accumulation. The first term on the right-hand side represents the convective transport along the tube length, the second term in eqs 14 and 15 represents the transfer of solute from the aqueous feed phase to the organic phase, and finally the last term in eqs 15 and 16 shows the flux of Cr(VI) from the organic phase to the stripping phase contained in the emulsion globules, where A_v is the interfacial area of the stripping bubbles by volume of the stripping phase.

To give a complete description of the separation process, it is necessary to include the mass balances in the emulsion reservoirs as well as the interfacial equilibrium expression at the feed-membrane side.

Mass balance of the stripping solution in the stirred tank:

Stripping phase:

$$V_r^{\text{T}} \frac{dC_r^{\text{T}}}{dt} = F_r (C_{r,z=0} - C_r^{\text{T}}), \quad t=0 \quad C_r^{\text{T}} = C_r^0 \quad (17)$$

Organic phase:

$$V_o^{\text{T}} \frac{dC_o^{\text{T}}}{dt} = F_o (C_{o,z=0} - C_o^{\text{T}}), \quad t=0 \quad C_o^{\text{T}} = C_o^0 \quad (18)$$

In the experiments carried out, the stripping and organic phases that constitute the emulsion are mixed in a volume ratio of 1:4. Then,

$$F_m = F_o + F_r \quad (19)$$

$$\frac{F_o}{F_r} = 4 \quad (20)$$

$$V_m^{\text{T}} = V_o^{\text{T}} + V_r^{\text{T}} \quad (21)$$

$$\frac{V_o^{\text{T}}}{V_r^{\text{T}}} = 4 \quad (22)$$

where F_m is the emulsion flowrate and V_m^{T} the emulsion volume in the tank.

4. Parameter Estimation and Analysis

In the mathematical model proposed in the previous section, four parameters are unknown: the chemical equilibrium parameters K_{eq} and K_r of the extraction and of the stripping chemical reactions, respectively, the coefficient r defined in eq 10, and the product $A_v k_1$ of the interfacial area of the emulsion and the kinetic constant of the forward stripping reaction. The parameter estimation tool gEST of gPROMS¹³ was used. The system of differential and algebraic equations in the previous section and the experimental values for the stripping and output concentrations were loaded in a file. The least-squares technique was used to find the numerical values of the parameters that minimize the experimental and simulated values. The solution reported in Table 3 was found in 10 988 s and 36 iterations by using a 700-MHz Pentium III computer. The simulated and actual values of the experimental concentration are shown in Figure 4. The correlation coefficient r^2 was 0.97.

With regard to the numerical values found, it must be noticed that the stripping chemical equilibrium parameter K_r tends to infinity, implying that the chemical reaction given by eq 2 can be considered as irreversible. For that reason, the term C_r/K_r from eqs 15 and 16 can be neglected, simplifying the resulting equations.

5. Optimization of a Pertraction Plant

5.1. Problem Statement. In this work, it is intended to obtain the optimal operation point that maximizes the amount of chromium treated in an emulsion pertraction plant operating continuously that must reduce the concentration of Cr(VI) in the effluent to 0.00961 mol m⁻³ (0.5 ppm) and at the same time concentrate the metal above 384.615 mol m⁻³ (20 000 ppm) in another phase for further reuse.

For this purpose, a cascade-type plant with two membrane modules is proposed, as shown in Figure 5. The effluent enters the first module and leaves it with the imposed output concentration level. In the same module, the emulsion runs in countercurrent mode, and after leaving the module, the phases are separated. The organic phase is mixed with fresh back-extraction phase

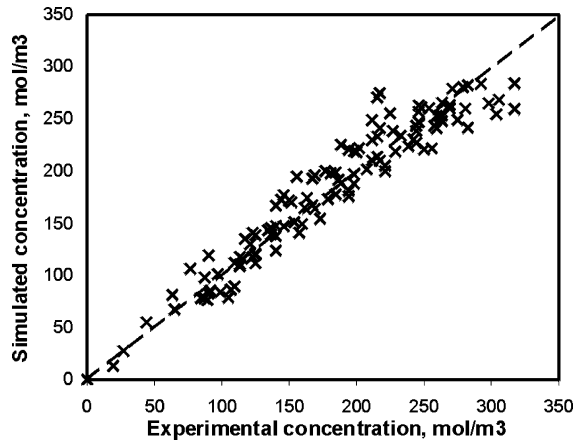


Figure 4. Simulated data with the obtained parameters vs experimental concentrations.

Table 3. Parameters Found Using gEST

K_{eq} , mol ⁻² m ⁻⁶	1.041
K_r , mol ⁻² m ⁻⁶	infinite
$A_r k_1$, m ⁶ mol ⁻² h ⁻¹	10.62
r (dimensionless)	6.101

and returns to the first module, while the aqueous phase is acidified to pH 1.5 and then goes to the second module.

In the second module, the aqueous phase transfers the metal to a second emulsion batch, and finally it is mixed with the effluent that enters the first membrane module. The second emulsion concentrates the chromium in the back-extraction aqueous phase, and after the phase separation at the output, the organic phase is mixed with fresh back-extraction solution and returned to the same module.

There are two reasons for proposing the previous configuration. The first is related to the desired chromium levels in the output streams. It is not possible to reach both concentration constraints without a cascade-type configuration in continuous operation. The second reason concerns the undesired presence of sulfate in the concentrated stream. According to Ho,³ the sulfate mass transfer for high Cr(VI) concentration in the aqueous phase is small. Then, in the plant devised, the sulfate is transferred to the stripping phase in the first module, but there is not significant mass transfer from the aqueous stream to the re-extraction in the second module, as the aqueous stream has a relatively high chromium concentration.

5.2. Mathematical Formulation. The model for the pertraction process has been explained in the previous section. A system of partial differential equations describes the behavior of the aqueous and emulsion phases, and ordinary differential equations describe the dynamic behavior of the tanks. There is also a set of algebraic equations for the chemical equilibrium expression and connections between the equipments.

As the plant to be optimized considers a process operating at steady state, then the variation of the phase concentrations with time is zero. For that reason, the mathematical model that describes the plant is a set of ordinary differential equations, as the phase concentrations depend only on the module axial position. In the tanks, the concentrations are constant. The differential-algebraic nonlinear optimization (DNLPO) problem P1 to be solved includes the ordinary dif-

ferential equations that represent the mass balances for the phases in the membrane module. The objective function to be maximized is the amount of metal processed, $F_e C^{in}$, where F_e is the effluent flowrate whose Cr(VI) concentration after dilution from wastewaters is C^{in} . The problem has the following form:

$$\begin{aligned} & \underset{\mathbf{v}}{\text{Max}} F_e C^{in} \\ \text{s.t.: } & h(\dot{\mathbf{x}}, \mathbf{x}, \mathbf{w}, \mathbf{v}) = 0 \\ & g(\dot{\mathbf{x}}, \mathbf{x}, \mathbf{w}, \mathbf{v}) \leq 0 \\ & I(\mathbf{x}(0), \mathbf{x}(L)) = 0 \\ & x^{LB} \leq \mathbf{x} \leq x^{UB} \\ & w^{LB} \leq \mathbf{w} \leq w^{UB} \\ & v^{LB} \leq \mathbf{v} \leq v^{UB} \\ & \mathbf{x} \in R^n \end{aligned} \quad (\text{P1})$$

where \mathbf{x} represents the set of differential distributed variables such as the aqueous, organic, and back-extraction concentration profiles along the modules, $\dot{\mathbf{x}}$ being the derivative of \mathbf{x} with respect to the module axial position z (with $z \in [0, L]$). The vector \mathbf{w} is the set of algebraic distributed variables, such as the interface concentration along the modules. The set of nondistributed optimization variables, such as the aqueous or emulsion flowrates in the network, is represented by \mathbf{v} . For all variables types, upper and lower bounds are imposed.

The mass balances, equilibrium, and interconnection relationships are represented by the set of differential and algebraic equalities h for the membrane modules, while the restrictions on the effluent output concentrations and the recovered metal concentration are represented by the inequalities g . The initial conditions for the differential equations are given by I .

The aim in the optimization problem is to maximize the objective function by selecting the optimum values for the optimization variables \mathbf{v} . To solve the optimization problem P1 in GAMS,¹⁴ a discretization of the differential equations is needed, as that optimization software admits only algebraic equations. The discretization methodology is detailed in the Appendix.

5.3. NLP Formulation. The following is the resulting NLP problem P2, derived from P1 after discretization of the differential equations by using the orthogonal collocation technique:

$$\begin{aligned} & \underset{\mathbf{v}}{\text{Max}} F_e C^{in} \\ \text{s.t.: } & h(\mathbf{x}, \mathbf{v}, \mathbf{w}) = 0 \\ & g(\mathbf{x}) \leq 0 \\ & x^{LB} \leq \mathbf{x} \leq x^{UB} \\ & w^{LB} \leq \mathbf{w} \leq w^{UB} \\ & v^{LB} \leq \mathbf{v} \leq v^{UB} \\ & \mathbf{x} \in R^n \end{aligned} \quad (\text{P2})$$

The equations included in P2 are described in the next subsections.

5.3.1. Material Balances for the Membrane Modules. After removal of the time derivatives and replace-

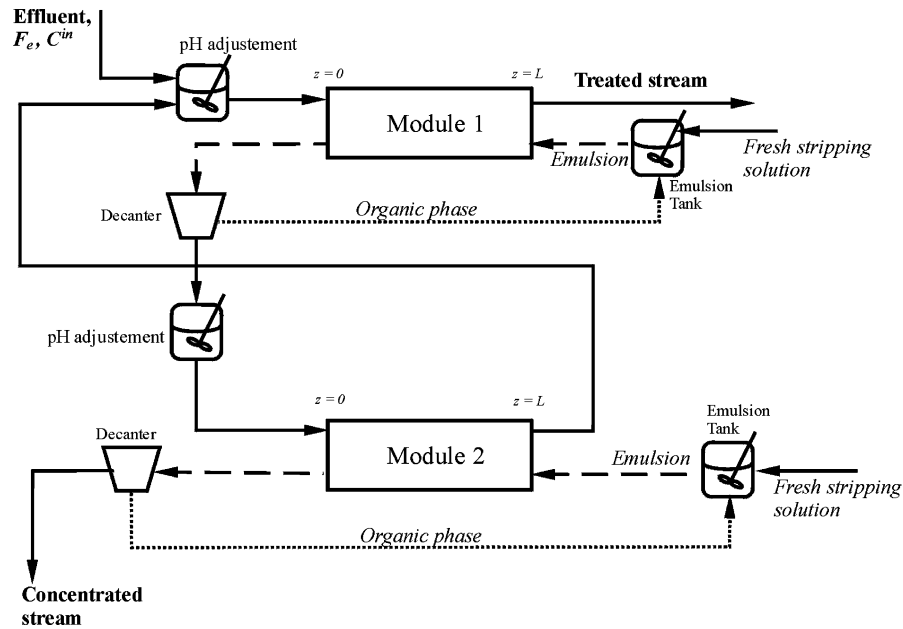


Figure 5. Proposed configuration for the pertraction plant.

ment of the differential mass balances given by eqs 14–16 by a set of algebraic equations applying orthogonal collocation (Appendix), the mass balances for the membrane module j are

Aqueous phase

$$\sum_{q=0}^{N+1} C_{e,q}^j \hat{\psi}_q(z_j) = -k_L(C_{e,i}^j - C_{e,i}^{j*}) \frac{A}{LF_e^j}, \quad i = 1, \dots, N+1; j = 1, 2 \quad (23)$$

$$C_{e,0}^j = C_e^{j,\text{in}} \quad (24)$$

Organic phase

$$\sum_{q=0}^{N+1} C_{o,q}^j \hat{\psi}_q(z_j) = -k_L(C_{e,i}^j - C_{e,i}^{j*}) \frac{A}{LF_o^j} + A_v k_1 (\text{OH}_i^j)^2 C_{o,i}^j \frac{V_r^M}{LF_o^j}, \quad i = 0, \dots, N; j = 1, 2 \quad (25)$$

$$C_{o,N+1}^j = C_{o,0}^j \quad (26)$$

Back-extraction phase

$$\sum_{q=0}^{N+1} C_{r,q}^j \hat{\psi}_q(z_j) = -A_v k_1 (\text{OH}_i^j)^2 C_{o,i}^j \frac{V_r^M}{LF_r^j}, \quad i = 0, \dots, N; j = 1, 2 \quad (27)$$

$$C_{r,N+1}^j = 0 \quad (28)$$

The organic and stripping flowrate that constitute the emulsion stream are related by

$$4F_r^j = F_o^j, \quad j = 1, 2 \quad (29)$$

5.3.2. Chemical Equilibrium and Other Relationships. Equations 5, 6, 10, and 13 are replaced by the

following set of equations:

$$K_{\text{eq}} C_{e,i}^{j*} H_{e,i}^{j*} (C_T - C_{o,i}^{j*}) = C_{o,i}^{j*} \quad (30)$$

$$k_L(C_{e,i}^j - C_{e,i}^{j*}) = k_m(C_{o,i}^{j*} - C_{o,i}^j) \quad (31)$$

$$\text{OH}_i^j = 3000 - rC_{r,i}^j \quad (32)$$

$$H_{e,i}^{j*} = H_e^{j,\text{in}} - (C_e^{\text{in}} - C_{e,i}^{j*}) \quad (33)$$

where $i = 0, \dots, N+1$ refers to the collocation points along the module axial position, and $j = 1, 2$ refers to the module number.

5.3.3. Material Balances for Mixers and Tanks.

The mass balance for any mixer or a tank of Figure 5 is given by

$$F_k^{\text{out}} = \sum_n F_{k,n}^{\text{in}}, \quad k = e, o, r \quad (34)$$

where k represents the organic, stripping, or organic phase, whose inlet streams are represented by $F_{k,n}^{\text{in}}$ and the output stream by F_k^{out} .

The chromium balance for the phases that constitute the emulsion is given by

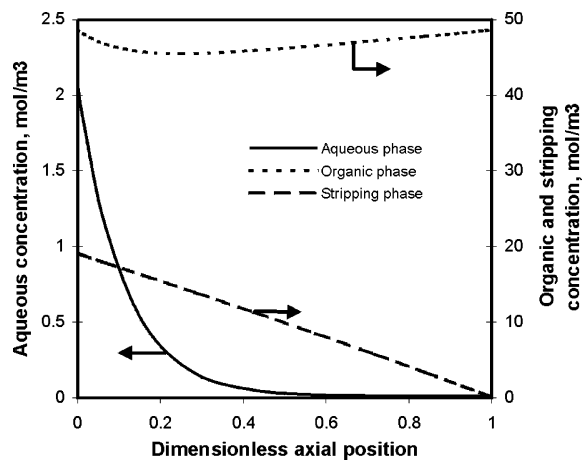
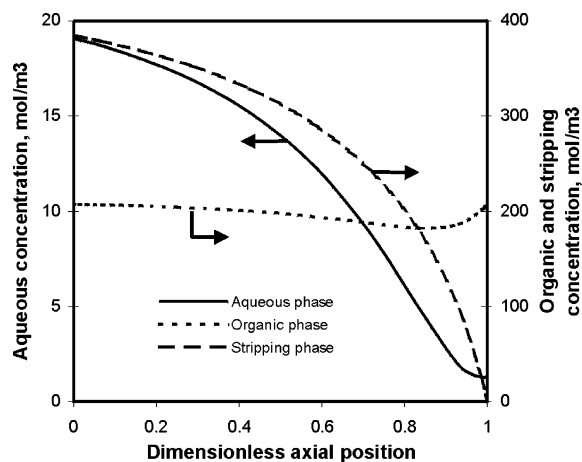
$$F_k^{\text{out}} C_k^{\text{out}} = \sum_n F_{k,n}^{\text{in}} C_{k,n}^{\text{in}}, \quad k = e, o, r \quad (35)$$

6. Optimization Results

This work considers a process that treats an effluent having Cr(VI), using two membrane modules of 19.3 m² each. The discretization for the differential equations was carried out using 10 collocation points in each membrane module, as it allows a good accuracy with a relatively small number of equations. The NLP problem P2 was formulated and solved with the optimization code GAMS¹⁴ using the NLP solver CONOPT2. As the model has several nonlinear equations, a given solution obtained might not be the global optimum. For that reason, several initial points were tried in order to

Table 4. Optimal Operating Conditions

	NLP solution	lower bound	upper bound
objective function: Cr(VI) treated (mol h ⁻¹)	0.311	0.005	1
optimization variables: effluent flowrate, F_e (m ³ h ⁻¹)	0.131	0.020	0.200
effluent input concentration, C_{in} (mol m ⁻³)	2.37	1.92	7.77
emulsion flowrate (module 1) (mol m ⁻³)	0.116	0.020	0.200
emulsion flowrate (module 2) (mol m ⁻³)	0.004	0.001	0.020
constraints: output stripping concentration (mol m ⁻³)	384.615	384.615	500
output aqueous concentration (mol m ⁻³)	0.00961	0.001	0.00961

**Figure 6.** Concentration profiles for module 1 at the optimal point.**Figure 7.** Concentration profiles for module 2 at the optimal point.

identify a local optimal. In each optimization run, the same result was found, thus allowing that solution to be considered as the global optimum. Depending on the initial point selected, the solution takes from 15 to 25 s and from 1200 to 1500 iterations on a 700-MHz Pentium III computer.

The solution is reported in Table 4. Both the treated effluent and the concentrated chromium solution for reuse are at their upper and lower bounds, respectively. 99.5% of the metal is removed from the wastewater and concentrated for reuse. The chromium concentration profiles along the membrane modules are shown in Figures 6 and 7. The stripping phase is then concentrated up to nearly 20 mol m⁻³ in the first module and then goes to the second one, where its relatively high chromium level allows the mass transfer to the stripping phase at 384.615 mol.m⁻³, as shown in Figure 7.

It can be seen in Figure 6 that almost all the metal is removed from the effluent in the first half of the module. As a consequence, in the second half of module 1, the effluent concentration remains constant. However, that fact does not imply that the second portion of the module is idle, but only that the mass transfer from the effluent to the organic phase is null. In all the module there is mass transfer from the organic phase to the stripping phase. That is the reason the stripping phase increases its concentration as it flows from $z = L$ to $z = 0$. The organic phase concentration decreases as it flows from $z = L$ to a given point located more or less in the middle of the membrane module. That happens as the mass transfer from the effluent to the organic phase is nearly zero, while the mass transfer from the organic phase to the stripping phase is not null. Mathematically, that occurs because the second term on the right-hand side of eq 25 dominates the first term, which is close to zero.

As the emulsion continues flowing from the middle of the module to $z = 0$, the mass transfer from the effluent to the organic phase increases and outnumbers the mass transfer from the organic phase to the stripping phase. In other words, the first term on the right-hand side of eq 25 compensates the second, which has an opposite sign.

As the organic phase is reused after being separated from the emulsion in a decanter, the organic concentrations at $z = 0$ and $z = L$ are the same.

The same happens in module 2, as its organic phase is also separated from the emulsion and reused.

7. Conclusions

The optimal operation of a pertraction process for hexavalent chromium removal from effluent and simultaneous concentration for reuse has been determined for the first time in this paper. This new technology seems to be a promising strategy to deal with effluents containing highly pollutant heavy metals, as it can extract them and also concentrate the chemical for further reuse.

A model has been proposed consisting of a set of partial differential equations that takes into account the mass transport through the feed and supported liquid membrane and two chemical reactions at the feed-membrane side and organic phase-stripping phase interface as main steps in the separation process. Careful experimental planning was carried out in order to determine model parameters after integration of the model equations with gEST¹³ and comparison of experimental and simulated results. A cascade-type plant containing two membrane modules operating in continuous mode was proposed. The differential equations describing the metal mass transfer along the membrane module were discretized to a set of algebraic equations using orthogonal collocation. The resulting mathemati-

cal model was implemented in GAMS and solved using CONOPT2.¹⁴

The results obtained in this work are considered a first step toward the exploitation of this new membrane technology at an industrial scale. Future work must be concerned with synthesis of a pertraction industrial plant, including the economical evaluation of the technology.

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Appendix: Discretization of the Differential Equations

The first step to obtain the optimal operation of the membrane plant is to discretize the differential equations that represent the mass balances in the modules. This implies a greater amount of variables and equations, in direct proportion to the quantity of discretization points chosen. Many techniques are available, such as finite differences and orthogonal collocation. The latter method was selected because it can reach the same accuracy as the finite differences method with considerably fewer discretization points along the axial position in the membrane modules. In other words, using the orthogonal collocation method, the size of the problem is smaller than utilizing the finite differences method, for the same precision in the results.

In this work, a collocation method was implemented in which the discretization points along the membrane length are the shifted roots of the Legendre polynomials.^{15–17} Then, given an ordinary differential equation (ODE),

$$\frac{dx}{dz} = F(x, v, z), \quad z \in [0, L] \quad (\text{A.1})$$

with the boundary condition

$$x(0) = x_0 \quad (\text{A.2})$$

It can be discretized by using polynomial Lagrange form:

$$x(z) = \sum_{i=0}^{N+1} x_i \varphi_i(z) \quad (\text{A.3})$$

where

$$\varphi_i(z) = \prod_{k=0, k \neq i}^{N+1} \frac{z - z_k}{z_i - z_k} \quad (\text{A.4})$$

Note that the Lagrange form polynomial has the desirable property that $x(z_i) = x_i$. Thus, $x(z)$ is an $(N + 1)$ th-degree polynomial, and the polynomial coefficients x_i represent physically meaningful quantities, such as concentrations along the axial position z_i , as is the case in this work. The latter is a useful fact in process simulation or optimization, because it is a direct way to initialize profiles or to give adequate bounds to the variables.

Substitution of eq A.3 into A.1 and discretization of the ODE using orthogonal collocation yields the following set of algebraic equations:

$$\begin{aligned} \sum_{q=0}^{N+1} x_q \dot{\varphi}_q(z_i) - F(x_i, v, z_i) &= 0, \quad i = 1, \dots, N+1 \\ x_i &= x_0, \quad i = 0 \end{aligned} \quad (\text{A.5})$$

The location of the points z_i ($i = 1, \dots, N$) corresponds to the shifted roots of an orthogonal Legendre polynomial of degree N . It must be noted that the parameters $\dot{\varphi}_q(z_i)$ can be calculated off-line, given the roots of the selected Legendre polynomial degree, because

$$\dot{\varphi}_q(z_i) = \frac{\partial \varphi_q(z_i)}{\partial z} = \begin{cases} \sum_{k=0, k \neq q}^{N+1} (z_q - z_k)^{-1} & (i = q) \\ \frac{\prod_{k=0, k \neq q, i}^{N+1} (z_i - z_k)}{\prod_{k=0, k \neq q}^{N+1} (z_q - z_k)} & (i \neq q) \end{cases} \quad (\text{A.6})$$

Finally, the ODE given by model equations A.1 are replaced by the algebraic set of eq A.5.

List of Symbols

φ = Lagrange polynomial
 A = effective surface area, m^2
 A_v = stripping phase specific area, $m^2 m^{-3}$
 C = solute concentration, $mol m^{-3}$
 C_T = total concentration of the extractant in the organic phase
 F = flowrate, $m^3 h^{-1}$
 j = chromium flux, $mol m^{-2} h^{-1}$
 K_{eq} = chemical equilibrium constant (extraction)
 K_r = chemical equilibrium constant (re-extraction)
 k_L = mass transfer coefficient for the aqueous phase, $m h^{-1}$
 k_m = membrane mass transfer coefficient, $m h^{-1}$
 k_1, k_{-1} = direct and reverse stripping chemical reaction coefficient, $m h^{-1}$
 L = fiber length, m
 N = Legendre polynomial degree
 R_1, R_{-1} = direct and reverse stripping chemical reaction at the bubbles interface, $mol h^{-1} m^{-2}$
 V = volume, m^3
 z = axial distance, m

Superscripts

* = equilibrium
in = input
j = module number
M = membrane module
out = output
T = tank
0 = initial concentration

Subscripts

e = effluent phase
i = collocation point
m = emulsion
o = organic phase
r = stripping phase

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