

Minimum Membrane Area of a Pertraction Process for Cr(VI) Removal and Recovery

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Abstract

A pertraction membrane plant is designed for the treatment of wastewater containing hexavalent chromium and its recovery for industrial reuse. Pertraction is a new technology that combines the efficiency of emulsion liquid membranes with the advantages of using hollow fiber membrane modules. It can selectively remove low concentrated metals from process streams and reach high concentrations of the recovered stream required for industrial reuse of pollutants. The total membrane area required is minimised, complying with effluent disposal regulations and concentrations levels required for reusing Cr(VI). The algebraic and differential equation system modelling the mass transfer along the membrane modules for the continuous plant operation are presented. The differential equations are discretised using orthogonal collocation on finite elements in order to generate a nonlinear programming problem. The estimation of the minimum membrane cost allows the evaluation of its industrial application.

Keywords: pertraction, chromium recovery, wastewater, membranes.

1. Introduction

The increasing public concern about the environment is the driving force for stricter regulations worldwide, in particular those related to the industrial activities. It also introduces the need of recycling as much as possible the Earth non-renewable resources. Pertraction is a new membrane technology that can meet these ever-growing demands, allowing the treatment of industrial effluents or wastewaters and simultaneously recovering the pollutants for further industrial reuse. In particular, this technology had been first applied to, but it is not limited to, heavy metals dissolved in aqueous industrial wastewaters. Effluents coming from galvanic processes, nuclear industries, zinc-containing wastewaters from the rayon industry, etc. have been successfully treated by means of this technology (Klaasen et Jansen, 1996, Ho, 2001). Nonmetallic compounds that can be processed includes chlorinated solvents (e.g., carbon

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tetrachloride, chloroform, etc.), PCBs, di- and trichlorobenzene, pesticides, and higher polycyclic hydrocarbons (Klaasen et al., 1994, Klaasen and Jansen, 2001).

In a pertraction process that treats an aqueous effluent, the later is pumped along the lumen side of a hollow fiber membrane module. An emulsion consisting of an organic phase in which a third aqueous stripping phase is dispersed flows by the shellside. A chemical dissolved in the organic phase extracts the pollutant from the effluent as they reacts at the membrane interface. A second reaction takes place at the bubbles interface, releasing the compound of interest to the discontinued phase in which the contaminant is concentrated. After leaving the membrane modules, the emulsion is broken to recover the stripping phase as the organic phase is recycled to the module emulsified with a fresh aqueous stripping phase.

The removal and recovery of hexavalent chromium is studied in this work. Cr(VI) is one of the most toxic elements to be discharged into the environment, thus tight legal restrictions apply for its release into inland waters. In a previous work (Ortiz et al., 2003), the mathematical model for this specific application was proposed, and the numerical values of the parameters related to chemical equilibrium constants and mass transfer coefficients were estimated by using the experimental data obtained in a laboratory scale set-up. For the continuous operation mode, the mathematical model consists of a set of differential equations for the mass balance along the membrane modules plus algebraic equations for the chemical equilibrium and mass transfer relationships.

The main objective of this work is to calculate the minimum total area required to treat a given wastewater while inequality constraints related to maximum Cr(VI) concentration for disposal and minimum Cr(VI) concentration of the recovered product are met. This technology fulfils both separation objectives although high membrane areas are required. The differential equations are discretised by using orthogonal collocation on finite elements along the modules length. The resulting nonlinear programming problem is solved using GAMS, and the main results are shown and discussed.

2. Configuration of the Pertraction Membrane Plant

The proposed configuration for the membrane plant is shown in Figure 1. The emulsion is prepared by dispersing an aqueous sodium hydroxide solution of an initial concentration of 3000 mol.m^{-3} in the organic phase at a volume ratio of 1:4. The organic solution consists of Isopar L in which the extractant Alamine 336 is dissolved, together with emulsion modifiers, as it was detailed in Ortiz et al. (2003). The aqueous phase from which the chromium is removed is acidified to $\text{pH}=1.5$.

The effluent or wastewater to be processed runs by the lumen of the membrane fibers in Module 1, and it leaves the plant after transferring the pollutant content to the emulsion that runs in countercurrent by the shell side. The emulsion leaving Sector 1 is broken in a decanter. The resulting organic phase returns to the same sector, after mixing it with fresh stripping phase with no Cr(VI) content. The pH of the aqueous stripping phase recovered in the decanter is adjusted before entering into Sector 2, where its chromium content is partially transferred to a second emulsion. After leaving Sector 2, this aqueous stream is mixed with the effluent that feeds Sector 1. As it happens in the other sector, the emulsion is broken after leaving the module. The

organic phase forms a new emulsion by adding a fresh stripping aqueous phase and it is recycled to the same module. As it can be seen, the organic phases are totally recycled in the plant.

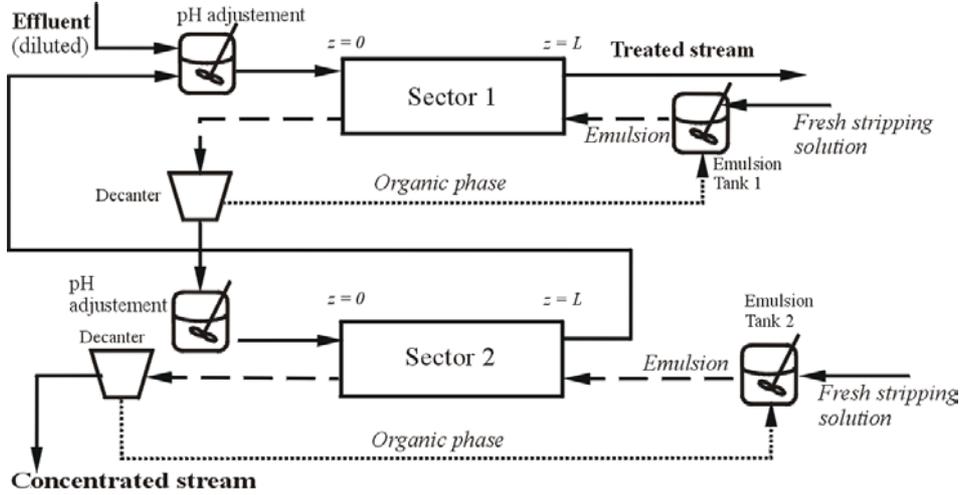


Figure 1. Configuration of the Pertraction Plant.

The concentration levels in each phase are higher in the second module than in the first. The cascade-type configuration presented is necessary to achieve the desired concentration levels at both the effluent output and concentrated stream (Ortiz et al., 2003). Another reason is concerned with the undesired presence of sulphate in the concentrated stream. According to Ho et al. (2001), the sulphate mass transfer for high Cr(VI) concentration in the aqueous phase is small. Then, in the plant devised, the sulphate 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.

3. Mathematical Model for the Pertraction Process

The mass transfer from an aqueous phase containing the pollutant to a stripping phase dispersed in an organic phase is schematised in Figure 2. The hydrophobic membrane wetted by the organic phase separates the aqueous phase and the emulsion.

It is assumed that the Cr(VI) mass transfer takes place in four steps: (i) diffusion in the feed-phase stagnant layer to the membrane interface, j_1 ; (ii) interfacial reaction of Cr(VI) with the extractant Alamine 336; (iii) diffusion within the supporting membrane, j_2 ; and (iv) chemical reaction at the stripping bubbles interface.

The chromium mass flux through the aqueous phase stagnant layer (j_1) and through the membrane (j_2), are respectively given by:

$$j_1 = k_L(C_e - C_e^*) \quad (1)$$

$$j_2 = k_m(C_o^* - C_o) \quad (2)$$

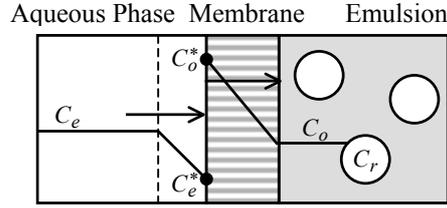
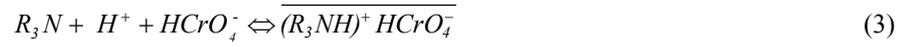


Figure 2. Enlarged view of the fiber with the feed aqueous phase in the lumen side and the emulsion phase in the shell side.

Where C_e and C_o represent the Cr(VI) bulk concentrations of the aqueous and organic phases respectively and the super index (*) indicates the equilibrium concentrations at the membrane interface. In steady state, both mass fluxes have the same value.

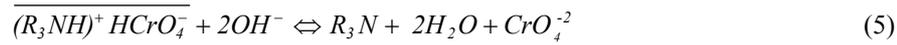
The chemical reaction at the membrane interface and its chemical equilibrium constant relationship are given by:



$$K_{eq} = \frac{[\overline{(R_3NH)^+ HCrO_4^-}]}{[R_3N][H^+][HCrO_4^-]} \quad (4)$$

Where $HCrO_4^-$ is the predominant form of Cr(VI) at pH=1.5, R_3N represents the extractant Alamine 336 and $\overline{(R_3NH)^+ HCrO_4^-}$ indicates the complex formed between them that is soluble in the organic phase.

A second chemical reaction takes place in the emulsion phase at the interface between the organic and the stripping phases:



As it was found in Ortiz et al. (2003), the chromium mass flux j_3 from the organic solution from the organic phase to the stripping phase through the bubbles interface is given by:

$$j_3 = k[OH^-]^2 C_o \quad (6)$$

Then, the Cr(VI) mass balances in each membrane module j are represented by the equations 7, 8 and 9 for the aqueous, organic and stripping phases respectively:

$$F_e^j \frac{dC_e^j}{dz} = -\frac{A^j}{L^j} j_1^j \quad , \quad z=0 \quad C_e^j = C_e^{in,j} \quad (7)$$

$$-F_o^j \frac{dC_o^j}{dz} = \frac{A^j}{L^j} j_1^j - \frac{V_r^{M,j} A_v}{L^j} j_3^j \quad , \quad z=L^j \quad C_o^j = C_o^{in,j} \quad (8)$$

$$-F_r^j \frac{dC_r^j}{dz} = \frac{V_r^{M,j} A_v}{L^j} j_3^j, \quad z = L^j \quad C_r^j = C_r^{in,j} \quad (9)$$

Where A_v indicates the interfacial area of the stripping bubbles by volume of the stripping phase, $V_r^{M,j}$ is the stripping phase volume contained in the Sector j , and A^j and L^j are the effective membrane area and length of Sector j .

4. Optimal Design of the Pertraction Plant

The pertraction model presented in the previous section consists of a set of algebraic and differential equations. The optimisation problem for the selection of the membrane areas was performed with GAMS (Brooke et al, 1998). The differential equations 7 to 9 were discretised into algebraic equations using orthogonal collocation on finite elements along the modules length in equations. The resulting optimisation problem has the following form:

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

Where AT is the total membrane area in the process, \mathbf{h} represents the model equations associated to mass balances, chemical equilibrium and mass transfer relationships and equipment connectivities; \mathbf{g} includes inequalities related to maximum chromium concentration for the treated effluent and minimum Cr(VI) concentration for reuse. The vector \mathbf{v} includes the following optimisation variables: membrane areas and emulsion stream flowrates that are needed sectors 1 and 2, while the other state variables are included in the vector \mathbf{x} . Upper and lower bounds were set for all types of the variables. In this work the design of a plant for the treatment of $2.5 \text{ m}^3\text{h}^{-1}$ of wastewaters with a Cr(VI) input concentration of 7.7 mol.m^{-3} is reported. The wastewater maximum chromium level for final disposal into the environment is $0.00961 \text{ mol.m}^{-3}$ according with environmental regulations. The stream containing the Cr(VI) recovered must be concentrated at less to $384.615 \text{ mol.m}^{-3}$.

Five finites elements were used for the membrane sectors along the axial position, and in each finite element a second-order Lagrange polynomial with roots corresponding to the shifted roots of a Legendre polynomial approximates the concentration profiles. The main results summarised in Table 1 were obtained using CONOPT2 as a solver in GAMS, and the computer time required was 2.4 seconds and 355 iterations.

Both concentration constraints are active at the optimal solution. As the Cr(VI) level is higher in Sector 2, their flowrates are smaller. It can be noticed that at the optimal point, the effluent is diluted from 7.7 to 4.076 mol.m^{-3} , and as the diluted effluent is mixed with the aqueous stream from Sector 1 the aqueous inlet concentration for Sector 1 is 2.99 mol.m^{-3} . Although in principle a high chromium concentration would favour

the mass transfer to the organic phase, it also caused a depletion in the H^+ level at the end of the sector as the Cr(VI) reacts, thus resulting in a less favourable tendency to form the complex with Aliquat that is soluble in the organic phase. This trade-off justifies the need of dilution in the wastewater treated in the case studied.

Table 1. Optimisation results.

Variables	Optimal Point	Lower Bound	Upper Bound
Objective Function:			
Total membrane area m^2	2415.3		
Optimisation variables:			
Area Sector 1, m^2	1177.3		
Area Sector 2, m^2	1238.0		
Diluted concentration, $mol.m^{-3}$	4.076	1	7.700
Emulsion flowrate Sector 1, m^3h^{-1}	10	1	10
Emulsion flowrate Sector 2, m^3h^{-1}	0.251	0.1	1
Constraints:			
Treated concentration, $mol.m^{-3}$	0.00961	0.001	0.00961
Recovered concentration, $mol.m^{-3}$	384.615	384.615	500

5. Conclusions

A successful strategy for the design of pertraction plants using a rigorous modelling of the membrane processes has been presented. The two separation objectives related to maximum Cr(VI) composition in the stream for final disposal and minimum Cr(VI) concentration of the product for industrial reuse are achieved with the pertraction process although high membrane areas are required. This work is an important step that provides the membrane cost of this new technology to evaluate the feasibility of its industrial application stand alone or in hybrid technologies.

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