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Recycled liquid membranes use for oxalic acid recovery. Mathematical model and functional optimization.

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Abstract

A column unit designated for extraction/back extraction using a recycled dispersed liquid membrane was modelled and simulated. Oxalic acid was used as a transported species within this work. Experimental results regarding formation and rising flow of the organic drops (dispersed liquid membrane) lead to the conclusion that the axial dispersion should be taken into account, completing our previous published model for this column (Dinculescu and Lavric, 2005). The mathematical model was solved using the orthogonal collocation technique that allows the PDE transformation into an ODE system with respect to time, its integration being done using a self-adaptive Runge-Kutta type method. Its validation was done using our own batch experimental data; the optimal model parameters (the specific mass transfer coefficients and the dispersion group for both extraction and back-extraction zones), ensuring the agreement with the experiment, were found by means of a modified genetic algorithm technique.

Keywords: liquid membranes, liquid-liquid extraction, orthogonal collocation, membrane column modelling, parameter identification, genetic algorithm.

1. Introduction

The possibility of carboxylic acids recovery from aqueous streams such as fermentation broths and wastewaters using liquid membranes is proved to be a

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valuable technique that increases the concentration of the transported species in the receiver phase. Liquid-liquid equilibrium involved in the extraction of carboxylic acids with non-polar extractants is characterized by small partition coefficients; the extraction is inefficient especially when applied to dilute acid solutions. To overcome this, polar solvents characterized by higher distribution ratios are needed, despite their drawback of mixing with water in really significant proportions [1]. The liquid membrane transport is modelled using one of the following approaches: ordinary permeation, facilitated transport (type-II is the most studied case) and molecular pumping [2-4]. Few works present a complete mathematical model including both processes implied by a liquid membrane: the extraction and the back extraction [5-7], the majority considering only the classical liquid-liquid extraction columns or batch agitated liquid-liquid extractors [8-10].

The mathematical model of an innovative single column, designed for extraction and back extraction cascade, was presented in [4]. The column, divided by a sieve plate, allows a solute extraction with an organic solvent dispersed as ascending drops, from the aqueous continuous phase in the inferior half of the device. In the superior half, an inverse process leads to a back extraction from the same organic, also dispersed as ascending drops, to the aqueous phase. The mathematical model is based upon a simplified circulation model for both liquid phases. It includes the dynamic mass balance equations for the transported species, considering that at the liquid-liquid interface thermodynamic equilibrium governs and there are also mass transfer resistances. Thus, it encapsulates information related to the operating time and process parameters, unfolding the dynamic behaviour of the extraction - back extraction column [4].

2. The mathematical model

2.1. Main hypothesis

The physical model resulted from the abstraction of this column and the simplifying assumptions under which the mathematical model was built were presented in [4] together with the reference variables used to render it dimensionless. Although the mathematical model predicted reasonably well the experimental data, there was room for development, relaxing some of the constraints imposed to the dispersed membrane circulation. In order to take into account the coalescence – dispersion phenomena between the ascending drops, the plug flow associated with the organic drops ascending movement has to be improved considering also the axial dispersion.

2.2. Mathematical model development

Under these relaxed simplifying assumptions, the mathematical model's dimensionless equations, derived from mass balances for the carried species, are:

extraction zone – organic phase:

$$\frac{\partial \Gamma_{o,ex}}{\partial \tau} + \frac{1}{\alpha} \cdot \frac{\partial \Gamma_{o,ex}}{\partial \zeta_{ex}} - Dg_{ex} \cdot \frac{\partial^2 \Gamma_{o,ex}}{\partial \zeta_{ex}^2} = \left(\frac{\Gamma_{A,ex}}{K_{eq}} - \Gamma_{o,ex} \right) \cdot K_{o,ex} \tag{1}$$

– aqueous phase:

$$\frac{d\Gamma_{A,ex}}{d\tau} = -\left(\frac{\Gamma_{A,ex}}{K_{eq}} - \Gamma_{o,ex} \right) \cdot K_{ex,a} \cdot \left(\frac{\delta_{ex}}{1-\delta_{ex}^2} + \frac{1}{s_{ex}} \right) \tag{2}$$

under sieve zone:

$$\frac{d\Gamma_{o,ex-bk}}{d\tau} = \frac{\Gamma_{o,ex} - \Gamma_{o,ex-bk}}{\beta} + \left(\frac{H_{A,ex}}{K_{eq}} - \Gamma_{o,ex-bk} \right) \cdot K_{o,ex-bk} \tag{3}$$

back-extraction zone – organic phase:

$$\frac{\partial \Gamma_{o,bk}}{\partial \tau} + \frac{1}{\gamma} \cdot \frac{\partial \Gamma_{o,bk}}{\partial \zeta_{bk}} - Dg_{bk} \cdot \frac{\partial^2 \Gamma_{bk}}{\partial \zeta_{bk}^2} = \left(\Gamma_{A,bk} - K_{eq} \cdot \Gamma_{o,bk} \right) \cdot K_{o,bk} \tag{4}$$

– aqueous phase:

$$\frac{d\Gamma_{A,bk}}{d\tau} = \left(K_{eq} \cdot \Gamma_{o,bk} - \Gamma_{A,bk} \right) \cdot K_{bk,a} \cdot \left(\frac{\delta_{bk}}{1-\delta_{bk}^2} + \frac{1}{s_{bk}} \right) \tag{5}$$

top of the column:

$$\frac{d\Gamma_{o,f}}{d\tau} = \frac{\Gamma_{o,bk} - \Gamma_{o,f}}{\delta_{bk}} - \left(\Gamma_{a,bk} - K_{eq} \cdot \Gamma_{o,f} \right) \cdot K_{o,f} \tag{6}$$

buffer vessel:

$$\frac{d\Gamma_{bv}^{o}}{d\tau} = \frac{1}{\phi} \cdot \left(\Gamma_{in,bv}^{o} - \Gamma_{bv}^{o} \right) - \frac{\psi}{\phi} \cdot \Gamma_{in,bv}^{o} \tag{7}$$

The dimensionless initial and boundary conditions are:

$$\tau = 0, \forall \zeta : \quad \Gamma_{A,ex} = 1 \text{ and } \Gamma_{o,ex} = \Gamma_{o,ex-bk} = \Gamma_{o,bk} = \Gamma_{A,bk} = \Gamma_{o,f} = 0$$

$$\tau > 0, \zeta = 0 : \left| \begin{array}{l} \Gamma_{o,f} = \Gamma_{o,ex} - Dg_{ex} \dfrac{\partial \Gamma_{o,ex}}{\partial \zeta_{ex}} \\ \Gamma_{o,ex-bk} = \Gamma_{o,bk} - Dg_{bk} \dfrac{\partial \Gamma_{o,bk}}{\partial \zeta_{bk}} \end{array} \right. ; \zeta = 1 \quad \left| \begin{array}{l} \dfrac{\partial \Gamma_{o,ex}}{\partial \zeta_{ex}} = 0 \\ \dfrac{\partial \Gamma_{o,bk}}{\partial \zeta_{bk}} = 0 \end{array} \right. \tag{8}$$

The axial dispersion is observed through the dispersion groups for the extraction and back-extraction zones $Dg_{ex} = D_{L,ex} / u_{ex} H_{ex}$ and $Dg_{bk} = D_{L,bk} / u_{bk} H_{bk}$ respectively. All other notations used in Eqs. (1)÷(8) are fully documented in [4].

The method used for solving the hybrid system of partially and ordinary differential equations (1)÷(8) was to transform it into an ODE system, by orthogonal collocation, then integrate it with a suitable self-adjustable RK-type method.

3. Results and discussions

The model validation was done using some proprietary experimental data for the extraction of the oxalic acid with a recycled membrane of cyclohexane [11], to identify the model's parameters: the partial mass transfer coefficients $k_{o,ex}$, $k_{A,ex}$, $k_{o,re}$, $k_{A,re}$ and the dispersion groups Dg_{ex}, Dg_{bk} for the extraction and back-extraction zones. To eliminate the doubts related to the computation of the interfacial areas between the rising droplets and the stagnant liquid phase, we used $k_{o,ex}A_{ex}$, $k_{A,ex}A_{ex}$, $k_{o,bk}A_{bk}$ and $k_{A,bk}A_{bk}$, the specific partial mass transfer coefficients as parameters to be identified. The partition coefficient for the system oxalic acid/cyclohexane was experimentally found to be 0.31, at the working temperature [11]. All other parameters were computed using the experimental set-up or the operating conditions. The objective function was the usual sum of the squared residuals model-experiment, which had been minimized. Since it could be multimodal, we used an improved variant of Genetic Algorithm (GA) as optimization tool, to avoid entrapment in local minima. Each adjustable parameter was directly encoded into a gene, so the chromosome had six genes. Each chromosome defines an individual from the population. Initially, a population pool is created, having a convenient number of individuals. The restrictions are coped with naturally, simply eliminating those individuals outside the feasible domain as given in literature [1-3,6-11]. Then, the mathematical model is solved for each individual (i.e. the six parameters). After that, the individuals are interbreed according to their frequency of selection, using one-point crossover method, and then mutation is applied to randomly selected individuals producing a new generation.

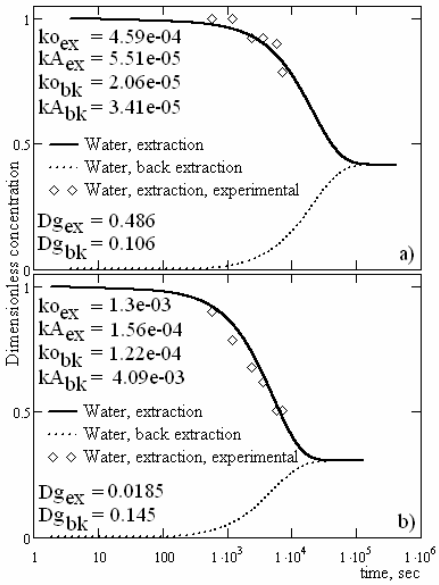

Fig. 1 The results of the identification of model's parameters (where appropriate, the units are in SI). a) membrane flow 0.4 cm^3/s; b) membrane flow 0.8 cm^3/s

The comparison model-experiment is presented in Fig. 1. The oxalic acid concentration profile in the back extraction zone is also presented, although no experimental data are available for it. The analysis of Fig. 1 shows that, due to the transport of the oxalic acid from the extraction to the back-extraction zones,

its concentration profiles reach an equilibrium value, which decreases with the flow rate of the organic liquid membrane. The thermodynamic equilibrium in the column is expected to happen when the concentration of the transported species reaches the same value in both extraction and back-extraction zones. This assumption takes into consideration that the two sections of the column have equal volumes of water and disregard the volume of the organic carrier. But, due to the oxalic acid entrapped into the liquid membrane (corresponding to its equilibrium concentration, eventually), which is drawn from the extraction zone, the thermodynamic equilibrium of the oxalic acid concentration between the extraction and the back-extraction zones changes a little bite, as can be seen from Fig.1, at the end of the process. The influence of the carrier could be disregarded only if the organic responsible for the liquid membrane would be saturated with the carried species from the beginning of the transport process.

As expected, the time needed to reach equilibrium decreases as the carrier flow rate increases (Fig. 1 a and b). This fact, experimentally proved by the growth of the droplets number into both zones of the column, can be explained, on one hand, by the growth of the interfacial area, and in another, by the increase in the mass transfer coefficients, due to the improved hydrodynamics (see the values in Fig. 1). The turning point towards the asymptote of the concentration profiles near the end of the process suggests that there could be some critical concentration in the back-extraction zone beyond which any attempt to increase it would be uneconomical, due to the mass transfer limitations near thermodynamic equilibrium. As can be seen from Fig. 1, there is a good match between the experimental profiles of the oxalic acid in the extraction zone and the ones predicted by the mathematical model. As expected, the dispersion group is an order of magnitude higher for the lower carrier flow rate in the extraction zone, and is approximately the same in the back-extraction zone. When the flow rate is higher, the drops are formed quicker, at the bottom of the column, so they preserve their individuality better from the beginning. At lower flow rates, probability of coalescence – breakage phenomena at drops

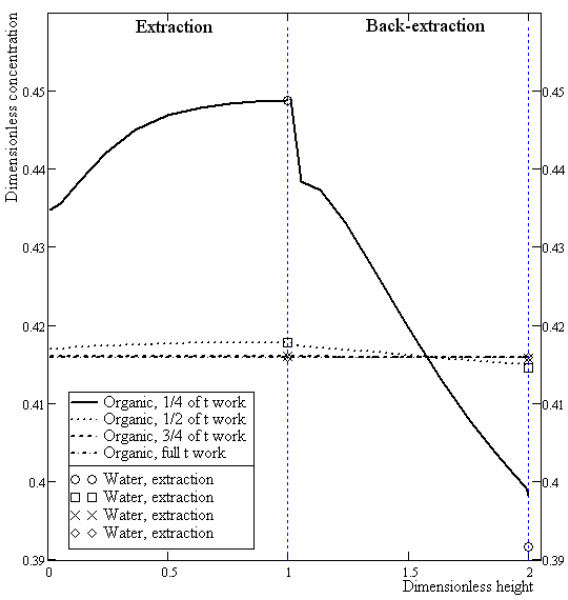

Fig. 2 The column profiles of the oxalic acid for the membrane flow rate of 0.4 cm^3/s

formation increases, thus the larger value for the dispersion group.
The oxalic acid profiles along the column are presented in Fig. 2, for the lower value of the carrier flow rate. After a quarter of the working time, the carrier has still a large potential of transportation, given by the differences in concentrations between input and output of the extraction and back-extraction zone, and also between the carrier and water. This difference diminishes considerably after half of the working time, which means that the column is close to equilibrium. Beyond this, the equilibrium is reached as witnessed by the flat profiles of the oxalic acid and the lack of difference in concentrations between the zones.

4. Conclusions

In this paper the axial dispersion model for a new extraction-back extraction process which develops in a single column is proposed. The mathematical model was solved using the orthogonal collocation method. An improved GA was used to match the computed and experimental concentration profiles. To eliminate the difficulties associated with the computation of the correct values for the interfacial area between the rising droplets and the stagnant liquid phase, the adjustable parameters were the specific partial mass transfer coefficients: $k_{o,ex}A_{ex}$, $k_{A,ex}A_{ex}$, $k_{o,re}A_{re}$, $k_{A,re}A_{re}$. The values resulted after regression, using some proprietary experimental data, are in the range given in literature; for the dispersion group there are no available correlations to compare with, but the values are in agreement with what would be expected. The proposed model describes with sufficient accuracy the process that runs into the experimental device. The model permits to emphasize the interdependency of several time scales, whose predominance determines the characteristics of the column operating regime. The main benefit of this new mathematical model its potential use in the designing phase of the extraction back-extraction processes.

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