

Treatment of phenol-containing aqueous solutions by membrane-based solvent extraction in coupled ultrafiltration modules

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Abstract

Extractive treatment of phenol-containing aqueous streams by two coupled hollow fiber modules (for simultaneous extraction and stripping) is experimentally and theoretically studied. The effects of hydrodynamic conditions (linear velocities of all three liquids) and concentrations (initial phenol concentrations) are explored and an optimal combination of these process parameters is found for maximisation of the phenol fluxes in both modules. The extraction/stripping performance of the coupled HF modules was compared when using different organic solvent (alcohols and alkanes). Analysis of the mass-transfer resistances of the different liquid layers in both modules is presented based on mathematical model and experimental data from equilibrium measurements and kinetic experiments. It is found that an important part of the overall resistance is located in the aqueous phase's boundary layers. A substantial improvement of the stripping yield is reached by using a series of stripping modules.

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1. Introduction

Membrane-aided liquid–liquid extraction (ME) is regarded as a promising innovative extraction method which is based on the incorporation of microporous membranes in the extraction systems. The membrane separates the aqueous and organic bulk solutions and supports the interface between them. By maintaining an appropriate pressure difference on both sides of the membrane, stable dispersion-free extraction conditions can be easily created. This new approach to design dispersion free mass transfer processes in liquid–liquid systems offers some important advantages in comparison to the classical dispersive extraction: no separation problems because there is no need for agitation, no fear of back mixing, flexibility in equipment configuration and relatively easy scale-up because of the modular design. The main disadvantage, the additional resistance of the membrane itself, which lowers the mass transfer rate, is successfully compensated by using membrane contactors, which contain plenty of fine hollow fibers, with large surface area per unit apparatus volume.

For the above mentioned reasons, many researchers investigate intensively various applications of the hollow fiber membrane contactors (HFMC) for development of separation processes in liquid–liquid systems. Most of the studies have been devoted to the removal of organic acids from aqueous solutions to examine the practical application of ME to downstream processing (lactic acid [1–4]; citric acid [5]; valeric acid [6]). Dispersion free extraction utilizing microporous HFMC has been demonstrated to be an advantageous method for extraction of pharmaceutical products such as penicillin G [7–9], cephalosporin-C and cephalixin [10]. Other experiments have been focused on removal and separation of metal ions (Cu [11,12]; Cu and Ni [13]; Cr [14]; Cu and Mo [15]) from their aqueous solutions.

Although hollow fiber liquid–liquid contactors have been extensively studied during the past years, they have seldom been used for extractive treatment of aqueous streams containing toxic organic compounds [16]. Some liquid membrane techniques using hollow fibers like “hollow-fibres in tube pertraction” [17–20] and “supported liquid membrane” (one module in which the hollow fibers are impregnated with the organic solution, feed and stripping liquids are circulated on the opposite sides of the fibers) [21–25] have been applied for removal of phenol from aqueous solution.

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Nomenclature

List of symbols

C	concentration (g/m ³)
d	hollow fiber's diameter (m)
D	diffusion coefficient (m ² /s)
E	extraction degree (%)
J	phenol flux (g/m ² s)
k	individual mass transfer coefficient (m/s)
k_m	$(k_m = 2\pi D_e / (\ln(r_{out}/r_i)) = 2\pi\epsilon D / (\tau \ln(r_{out}/r_i))$ membrane mass transfer coefficient (m/s)
K	overall mass transfer coefficient (m/s)
m	distribution coefficient (–)
N	hollow fiber numbers (–)
Q	flow rate (m ³ /s)
r	hollow fiber's radius (m)
R	resistance (–)
R	stripping degree (%)
t	time (s)
v	linear velocity (m/s)
V	volume (m ³)
z	length coordinate (m)
ϵ	membrane porosity (–)
τ	tortuosity factor (–)

Superscripts

0	initial value
in	value at the entrance of HF-module
*	equilibrium value

Subscripts

aq(A)	aqueous
e	effective
EXTR (E)	extraction
i	inner
M	membrane
org (s)	organic
out	outer
ph	phenol
R	stripping solution
S	organic solvent
STR (R)	stripping

Unfortunately, because the stability of the liquid membrane technique is a continual problem, the industrial application of the above mentioned methods is a scarcity.

The aim of this work is to study the performance of an extraction equipment consisting of two coupled HFMC (one—for extraction and the other—for stripping) for simultaneous removing of toxic phenol from wastewater streams and concentrating it in acceptor-solutions which can be re-used. Our experience in the field of ME proved that the coupled HFMC-configuration ensures the most stable membrane-aided extraction/stripping process and, therefore,

it has the greatest potential of an industrial application [8,9,26,27].

2. Experimental

2.1. Chemicals and analytical methods

The following chemicals were used to perform the experiments: phenol (LOBA Chemie, Fischamend, Austria) and two kinds of organic solvents: alcohols (octanol and decanol, Fluka) and *n*-paraffines (C₁₀–C₁₃-fraction, Neftochim, Bulgaria). The pH-values of the aqueous solutions were adjusted using aqueous solutions of HCl (Valerus, Bulgaria) or NaOH (HIMSNAB, Dimitrovgrad, Bulgaria).

The phenol concentration in the aqueous solutions (feed and stripping) was determined spectrophotometrically at a wavelength of 280 nm (UV-vis spectrophotometer, Germany), whereas the concentration in the organic phase was calculated by the material balance of the two phase system.

2.2. Hollow fiber modules

Hollow fiber modules (with fibers made of polysulfone) produced for ultrafiltration were used in this study, but for another purpose—immobilisation of interface in ME and membrane stripping (MS). The modules were kindly supplied by the Chinese Academy of Sciences (Institute of Chemical Physics, Dalian, China). The relevant characteristics of each unit are given in Table 1.

2.3. Equilibrium measurements

Equilibrium experiments were performed by intensive mixing of equal volumes (20 ml) of both phases, organic and aqueous, using separatory funnels and a shaking device (at 20 °C). As equilibrium in the phenol distribution between both phases was attained, the heavier aqueous phase was separated and analysed to determine the residual phenol concentration in this solution. The distribution coefficient “*m*” (ratio of the phenol concentration in the organic phase to that in the aqueous one), which characterises the power of a given organic solvent to extract phenol from aqueous solutions, was then calculated:

$$m = \frac{C_{ph(org)} V_{org}}{C_{ph(aq)} V_{aq}}, \quad (1)$$

where $C_{ph(org)}$ was recalculated from the balance equation:

$$V_{org} C_{ph(org)} = V_{aq} (C_{ph(aq)}^0 - C_{ph(aq)}) \quad (2)$$

In this study, two kinds of organic solvents, alkanes (a fraction *n*-paraffins), which are practically insoluble in water, as well as classical solvents like alcohols (octanol and decanol), are selected as organic solvents and the corresponding phenol distribution coefficients were determined and compared.

Table 1
Hollow fiber membrane modules used

Module number	N_{HF}	Hollow fiber diameter (mm)		Catridge diameter (mm)		Effective fiber length (mm)	Effective internal surface area (cm ²)
		Internal	Outer	Internal	Outer		
1	300	0.74	1.03	28	31	160	1115.3
2	35	0.74	1.03	10	13	130	105.7
3	20	0.74	1.03	8	11	210	97.6

2.4. Kinetic experiments using coupled HFM contactors

As mentioned above, the kinetic studies were carried out using an experimental set-up consisting of two coupled hollow fiber modules (one for extraction and the second for stripping) with continuous recirculation of the organic solvent between both modules. In all the experiments, the aqueous phases were pumped in a closed loop through the lumen side of the hollow fibers whereas the organic solvent was circulated through the shell side. Since the organic phase preferentially wetted the membrane walls (hydrophobic pores), the aqueous phases were maintained at a pressure higher than that of the organic phase to avoid the undesirable mixing of both solutions.

In some experiments, not only one stripping module but series of them were installed to improve the efficiency of the second mass transfer step—the back extraction of phenol from the loaded organic solvent into the regenerating aqueous NaOH-solution.

To look at the possibility of practical application of the ME method, the effects of flow rates and initial phenol concentration on the extraction/stripping efficiency were explored. The flow rates of all the three phases were widely varied to receive experimental data characterising the behaviour of the systems at different hydrodynamic conditions and to found out the optimal combination of them.

At regular time intervals, samples from the aqueous phases (feed and stripping) were taken out and their phenol concentration was analysed. A material balance of the three-phase system was used for calculation of the phenol concentration in the organic solvent.

3. Permeation model of phenol

The mathematical model proposed is based on the Fick's first law and the following main assumptions:

1. The system is at steady-state conditions.
2. The phenol concentration change with time in both modules can be neglected in comparison to the concentration change due to the axial convection transport.
3. Following permeation steps of the phenol molecules in the second module were supposed: diffusion through the organic phase (first, from the bulk phase through the organic layer; second, through the membrane pores

which are filled by the same solution); then, from the organic–aqueous interface to a reaction plane (irreversible reaction phenol–NaOH) in the stripping aqueous layer [28].

The concentration profiles of the phenol (molecular state) around the fibers in both modules are shown in Fig. 1.

3.1. Mathematical description of the processes in the extraction module

At any axial location in one HF of the extraction module, the phenol flux per unit fiber length is a function of the following elementary transfer steps:

1. Diffusion rate of the phenol molecules through the feed aqueous layer:

$$J_1 = k_A \pi d_i (C_A - C_A^*) \quad (3)$$

2. Equilibrium distribution at the feed–membrane interface (the membrane is wetted better by the organic solution) expressed by the phenol distribution coefficient m_1 :

$$m_1 = \frac{C_{M1}^*}{C_A^*} = \left(\frac{C_{S1}}{C_A} \right)_{eq} \quad (4)$$

3. Diffusion rate through the organic solution in the membrane pores:

$$J_2 = k_{M1} \pi d_m (C_{M1}^* - C_{M1}) \quad (5)$$

4. Diffusion rate through the organic layer:

$$J_3 = k_{S1} \pi d_{out} (C_{M1} - C_{S1}) \quad (6)$$

5. At pseudo steady state conditions, all the fluxes are equal, i.e.:

$$J_{EXTR} = J_1 = J_2 = J_3 \quad (7)$$

By combining Eqs. (3)–(7), the following equation is obtained describing the phenol flux through one HF in the extraction module:

$$J_{EXTR} = K_E \pi d_i \left(C_A - \frac{C_{S1}}{m_1} \right) \quad (8)$$

$$\text{where } \frac{1}{K_E} = \frac{1}{k_A} + \frac{d_i}{d_m k_{M1} m_1} + \frac{d_i}{d_{out} k_{S1} m_1} \quad (9)$$

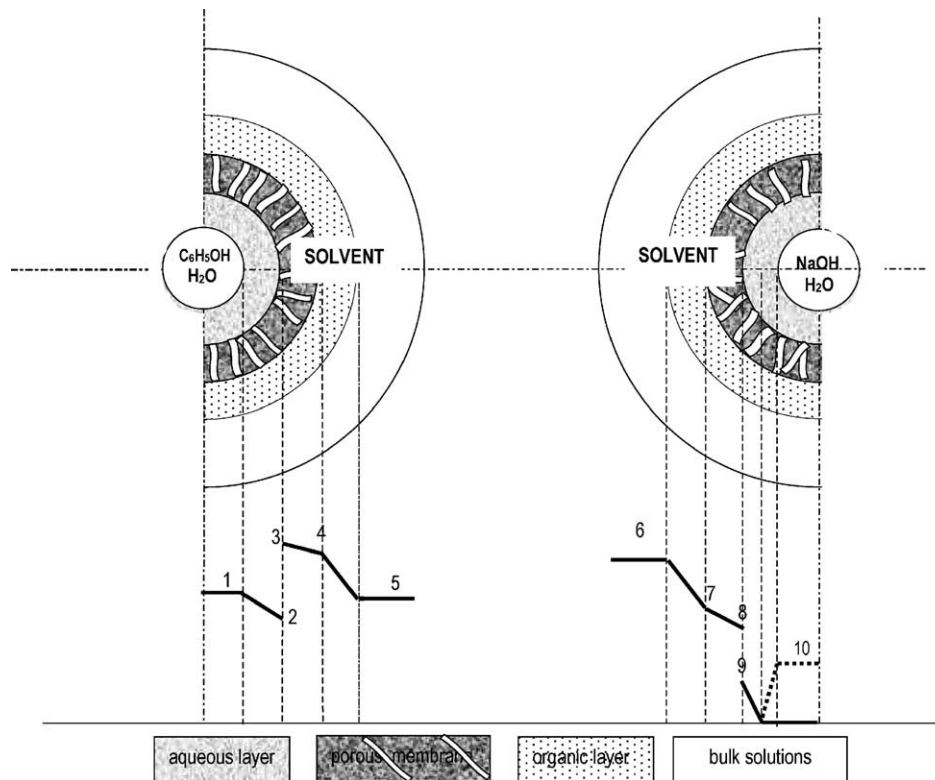


Fig. 1. Concentration profiles of phenol (undissociated) in both HF-modules (case $m > 1$). *Extraction module*: (1) C_A (phenol concentration in the bulk feed aqueous phase), (2) C_A^* (equilibrium phenol concentration at the feed layer–membrane interface), (3) C_{M1}^* (equilibrium phenol concentration at the membrane–feed interface), (4) C_{M1} (phenol concentration at membrane–organic solvent layer interface), (5) C_{S1} (phenol concentration in the bulk organic solvent phase). *Stripping module*: (6) C_{S2} (phenol concentration in the bulk organic solvent phase), (7) C_{M2} (phenol concentration at organic solvent layer–membrane interface), (8) C_{M2}^* (phenol concentration at the membrane–aqueous layer interface), (9) C_{M2}^{**} (equilibrium phenol concentration at the aqueous layer–membrane interface), (10) C_{NaOH} (sodium hydroxide concentration in the bulk stripping aqueous solution).

Further, the differential phenol balance over the section dz of the extraction module containing N_1 hollow fibers may be formulated as follows:

$$-Q_A \frac{dC_A}{dz} = K_E \pi d_i N_1 \left(C_A - \frac{C_{S1}}{m_1} \right) \quad (10)$$

$$\text{for } z = 0 \quad C_A = C_A^{\text{in}} \quad (11)$$

And the balance equation of the phenol concentration in the organic solution S1 is given by:

$$C_{S1} = C_{S1}^{\text{in}} + \frac{Q_A}{Q_S} (C_A^{\text{in}} - C_A) \quad (12)$$

3.2. Mathematical description of the processes in the stripping module

1. Rate of phenol transfer through the organic layer outside the membrane wall:

$$J_4 = k_{S2} \pi d_{\text{out}} (C_{S2} - C_{M2}) \quad (13)$$

2. Diffusion through the pores of the membrane wall wetted by the organic solvent:

$$J_5 = k_{M2} \pi d_M (C_{M2} - C_{M2}^*) \quad (14)$$

3. Equilibrium phenol distribution at the membrane–aqueous (stripping) interface:

$$m_2 = \frac{C_{M2}^*}{C_{M2}^{**}} = \left(\frac{C_{S2}}{C_R} \right)_{\text{eq}} \quad (15)$$

4. Rate of phenol transfer from the interface to the reaction plane in the stripping aqueous layer, where an instantaneous irreversible chemical reaction takes place ($C_6H_5OH + NaOH \Rightarrow C_6H_5ONa + H_2O$):

$$J_6 = \pi d_i k_R C_{M2}^{**} \quad (16)$$

5. Pseudo steady state holds thus, we obtain:

$$J_{\text{STRIP}} = J_4 = J_5 = J_6 \quad (17)$$

By combining Eqs. (13)–(17), the following expression describing the phenol flux in one HF of the stripping module is obtained:

$$J_{\text{STRIP}} = K_S \pi d_{\text{out}} C_{S2} \quad (18)$$

$$\text{where } \frac{1}{K_S} = \frac{1}{k_{S2}} + \frac{d_{\text{out}}}{d_m k_{M2}} + \frac{d_{\text{out}} m_2}{d_i k_R} \quad (19)$$

For the differential material balance (section dz) in the stripping module with N_2 hollow fibers, we have:

$$-Q_S \frac{dC_{S2}}{dz} = K_S \pi d_{out} N_2 C_{S2} \quad (20)$$

The phenolate concentration in the receiving solution R could be obtained by the following balance equation:

$$C_R = C_R^{in} + \frac{Q_S}{Q_R} (C_{S2}^{in} - C_{S2}) \quad (21)$$

Differential mass balances for the three tanks containing aqueous phenol solution (A), organic solvent (S) and regenerating aqueous solution (R) were expressed by the following equations:

$$-V_A \frac{dC_A^{in}}{dt} = Q_A (C_A^{in} - C_A^{out}) \quad (22)$$

$$V_S \frac{dC_S^{in}}{dt} = Q_S (C_S^{out} - C_S^{in}) \quad (23)$$

$$V_R \frac{dC_R^{in}}{dt} = Q_R (C_R^{out} - C_R^{in}) \quad (24)$$

$$\text{for } t = 0 \quad C_A^{in} = C_A^0; \quad C_S^{in} = 0; \quad C_R^{in} = 0 \quad (25)$$

4. Experimental results and discussion

4.1. Equilibrium phenol distribution

For the three organic solvents used, phenol distribution coefficients “ m ” were determined at different pH-values and phenol concentrations in the aqueous phase. Fig. 2 shows

the pH-dependence of the phenol distributions coefficients m using the solvents n -paraffins, octanol and decanol. It is seen that there is a broad pH-range (from 2 to nearly 9) in which m remains practically constant in all the three cases. At higher pH-values, however, m drops strongly because of dissociation of the phenol molecules at these alkaline conditions. Moreover, the influence of the chemical composition of the organic solvent (polar or nonpolar) on “ m ” is quite apparent.

In Fig. 3, the three extraction isotherms are illustrated. It is obvious that at the three solvents used, there is a linear increase in the phenol concentration in the organic phase with the equilibrium concentration in the aqueous phase. Then, it can be concluded that the distribution coefficients are constant in the phenol concentration range studied, which can be considered as an infinite dilution range.

The corresponding m -values resulting from the slopes of the lines obtained by linear regression of the data, are also presented in the figure. These values were used later in the mathematical analysis of the HFMC performance.

4.2. Kinetics of phenol extraction/stripping using coupled HFMCs

4.2.1. Effect of hydrodynamic conditions

Kinetic experiments were carried out to study the effect of the linear velocities of all the three liquids in the ranges shown in Table 2. For this purpose the flow rate of one of the phases was changed while the rates of the other two phases were maintained constant. The phenol concentration

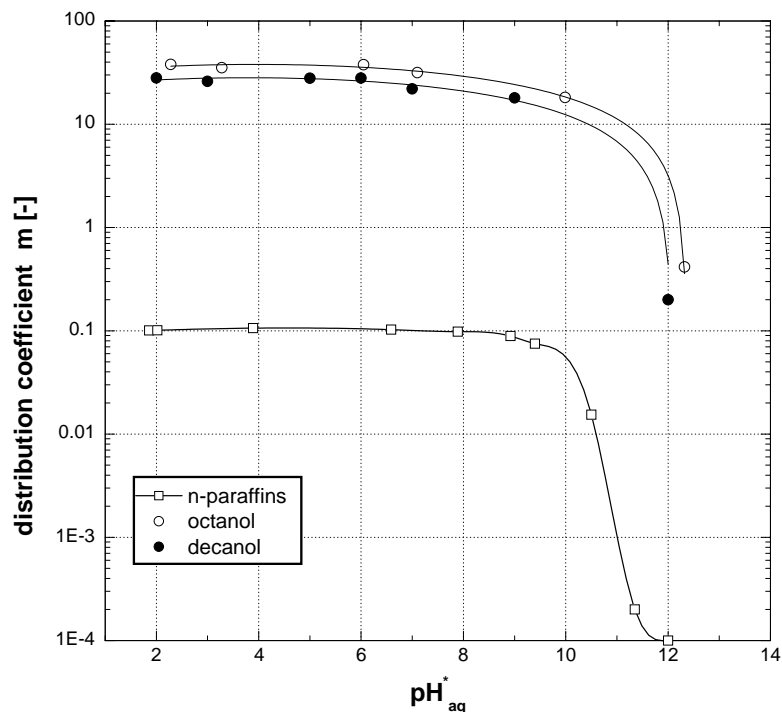


Fig. 2. Distribution coefficient of phenol (molecular state) as a function of aqueous phase pH-value at different organic solvents.

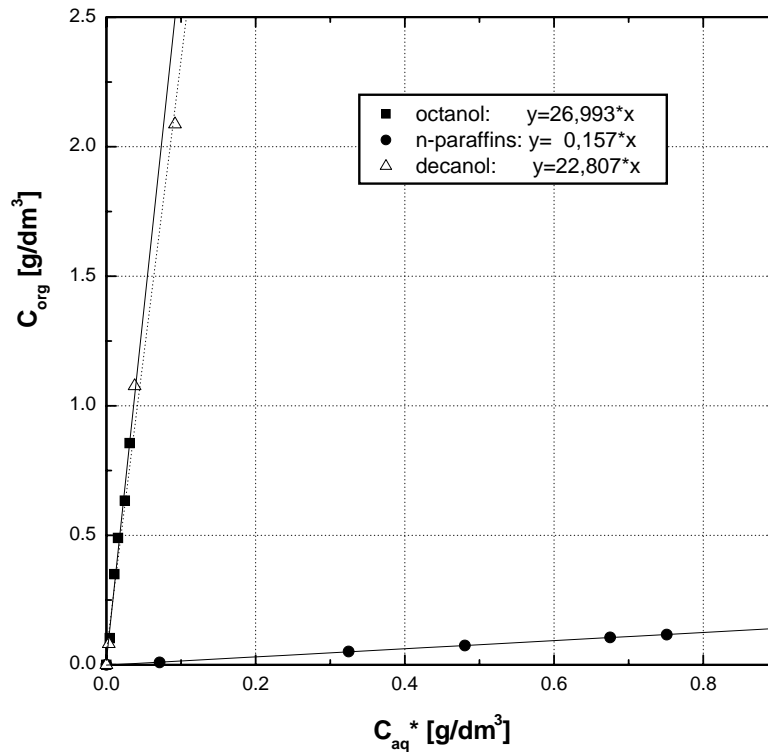


Fig. 3. Extraction isotherms of phenol at different organic solvents (pH = 6.0).

profiles in the liquid phases were presented as dependence of the dimensionless phenol and/or phenolate concentration $C_{A/R}^t/C_A^0$ versus time. The corresponding mass transfer coefficients k were evaluated by simultaneously solving the system of differential equations given above (see the mathematical model) and fitting the calculated concentration values $C_{A/R}^t/C_A^0$ to the experimental one. Furthermore, the corresponding mass transfer resistances were also calculated and compared.

The effect of the hydrodynamic conditions in each phase on the mass transfer coefficients was illustrated as the individual (k_A , $k_{S1,2}$, k_r) and overall mass transfer coefficients (K_{EXTR} , K_{STR}) were plotted against the mean linear velocities of the three phases (Figs. 4–6). The coefficient K_{EXTR} (module 1) is water phase based, whereas K_{STRIP}

(module 2) is related to the organic solution in the second module.

The K -analysis given below refers to the system phenol/*n*-paraffins (extraction: module 1/stripping: module 2). As shown in Fig. 4a, as the aqueous feed velocity V_A increases from 0.007 to 0.035 m/s, the individual coefficient k_A increases about three times. As a result, the overall coefficient K_{EXTR} also increases and becomes a value which is higher than that one of the coefficient K_{STRIP} in the stripping module. In Fig. 4b, the changes of all mass transfer resistances with V_A are shown. It can be seen, that the extraction process is controlled by the aqueous phase mass transfer ($R_A > R_{M1} > R_{S1}$). Moreover, in the range of $V_A > 0.015$ m/s, the extraction resistance becomes lower than the stripping one.

Table 2
Experimental conditions

	m ³ /s					
Q_A	$1,008 \times 10^{-6}$	$1,833 \times 10^{-6}$	$2,800 \times 10^{-6}$	$3,583 \times 10^{-6}$	$4,417 \times 10^{-6}$	
Q_S	$2,500 \times 10^{-6}$	$2,500 \times 10^{-6}$	$2,500 \times 10^{-6}$	$2,500 \times 10^{-6}$	$2,500 \times 10^{-6}$	
Q_R	$9,500 \times 10^{-7}$	$9,500 \times 10^{-7}$	$9,500 \times 10^{-7}$	$9,500 \times 10^{-7}$	$9,500 \times 10^{-7}$	
Q_A	$1,833 \times 10^{-6}$	$1,833 \times 10^{-6}$	$1,833 \times 10^{-6}$	$1,833 \times 10^{-6}$	$1,833 \times 10^{-6}$	$1,833 \times 10^{-6}$
Q_S	$0,458 \times 10^{-6}$	$1,183 \times 10^{-6}$	$1,875 \times 10^{-6}$	$2,500 \times 10^{-6}$	$3,142 \times 10^{-6}$	$3,833 \times 10^{-6}$
Q_R	$9,500 \times 10^{-7}$	$9,500 \times 10^{-7}$	$9,500 \times 10^{-7}$	$9,500 \times 10^{-7}$	$9,500 \times 10^{-7}$	$9,500 \times 10^{-7}$
Q_A	$4,417 \times 10^{-6}$	$4,417 \times 10^{-6}$	$4,417 \times 10^{-6}$	$4,417 \times 10^{-6}$	$4,417 \times 10^{-6}$	
Q_S	$2,500 \times 10^{-6}$	$2,500 \times 10^{-6}$	$2,500 \times 10^{-6}$	$2,500 \times 10^{-6}$	$2,500 \times 10^{-6}$	
Q_R	$6,667 \times 10^{-7}$	$9,500 \times 10^{-7}$	$1,417 \times 10^{-6}$	$1,833 \times 10^{-6}$	$2,667 \times 10^{-6}$	

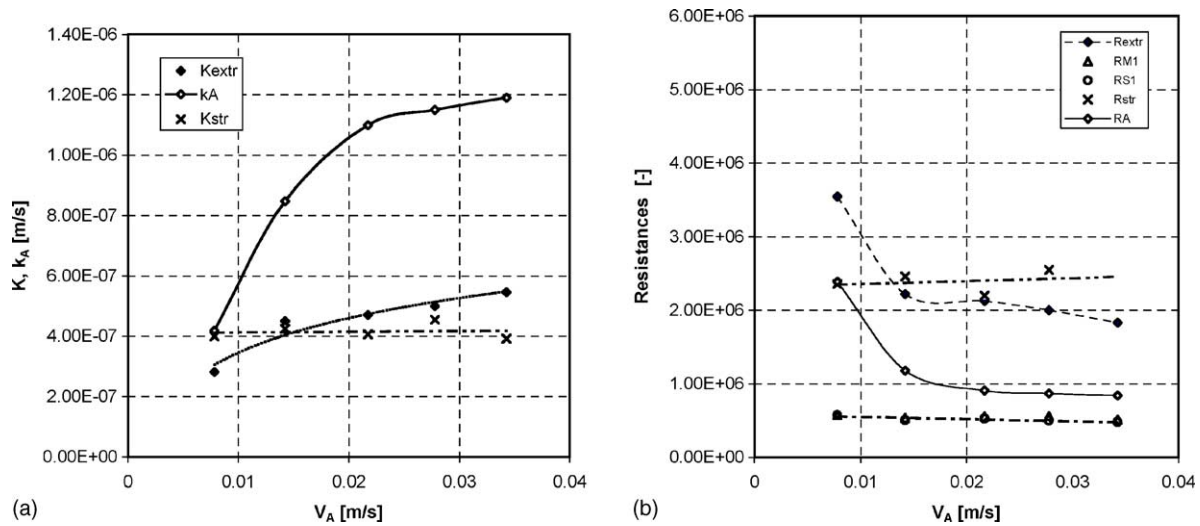


Fig. 4. Influence of aqueous feed phase linear velocity on: (a) mass transfer coefficients; (b) mass transfer resistances. Experimental conditions: $C_A^0 = 0.1 \text{ g/dm}^3$; $Q_r = 3.42 \text{ dm}^3/\text{h}$; $Q_s = 9.0 \text{ dm}^3/\text{h}$; $V_A = V_r = 0.150 \text{ dm}^3$; $V_s = 0.45 \text{ dm}^3$.

Similar experiments were conducted by raising the flow rate of the stripping aqueous phase while keeping other conditions constant (module 2). The experimental data show that an increase in the velocity V_r from 0.05 to 0.17 m/s leads to a two-fold rise in the values of k_r and, respectively, K_{STR} (see Fig. 5a and b). The observation that the stripping rate increases with aqueous stripping phase velocity is perhaps sufficient to conclude that at the given experimental conditions the stripping rate is controlled also by the aqueous stripping phase resistance. From Fig. 6a and b, virtually no dependence can be seen of the k_s mass transfer coefficients on the organic flow rate although the organic phase velocities were varied by factor more than an order of magnitude (for example, from 0.001 to 0.01 m/s in module 1).

At the experimental conditions studied, the resistances in the organic solution (in organic boundary layers and in membrane pores) are lower than these in the aqueous layers (see Fig. 4b and Fig. 5b).

The results on the effects of aqueous and organic phase flow rates are important from technology point of view. Operation at high aqueous phase flow rates should be advantageous.

4.2.2. Effect of phenol initial concentration

An important parameter affecting the membrane-aided extraction/stripping process appears to be the initial phenol concentration. The experimental data shown in this part of the paper refer also to the system phenol/*n*-paraffins. The

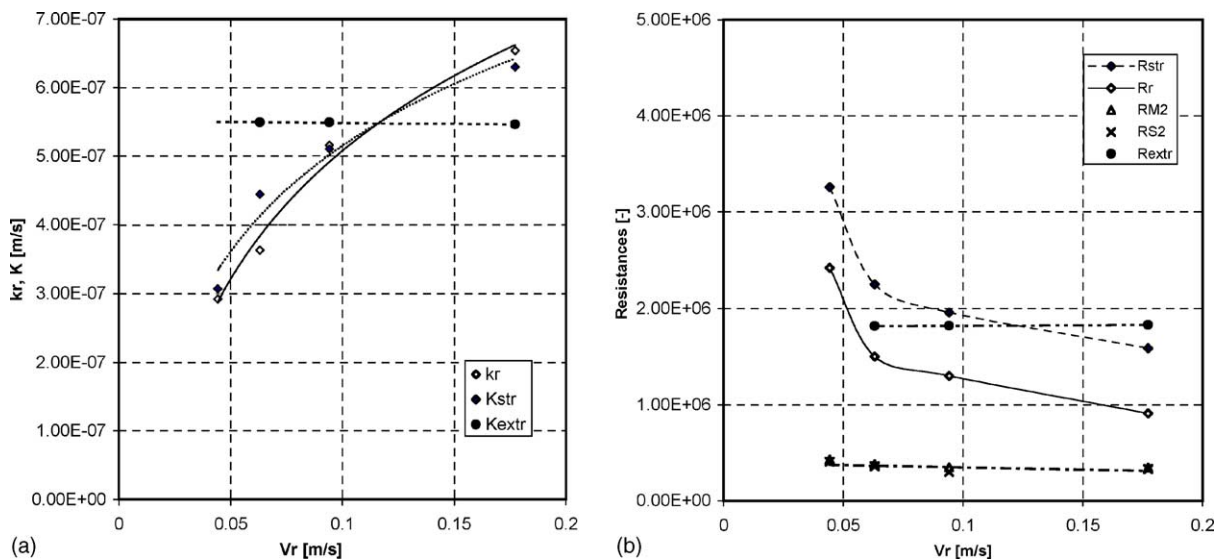


Fig. 5. Influence of aqueous stripping phase linear velocity on: (a) mass transfer coefficients; (b) mass transfer resistances. Experimental conditions: $C_A^0 = 0.1 \text{ g/dm}^3$; $Q_A = 15.9 \text{ dm}^3/\text{h}$; $Q_S = 9.0 \text{ dm}^3/\text{h}$; $V_A = V_r = 0.150 \text{ dm}^3$; $V_s = 0.45 \text{ dm}^3$.

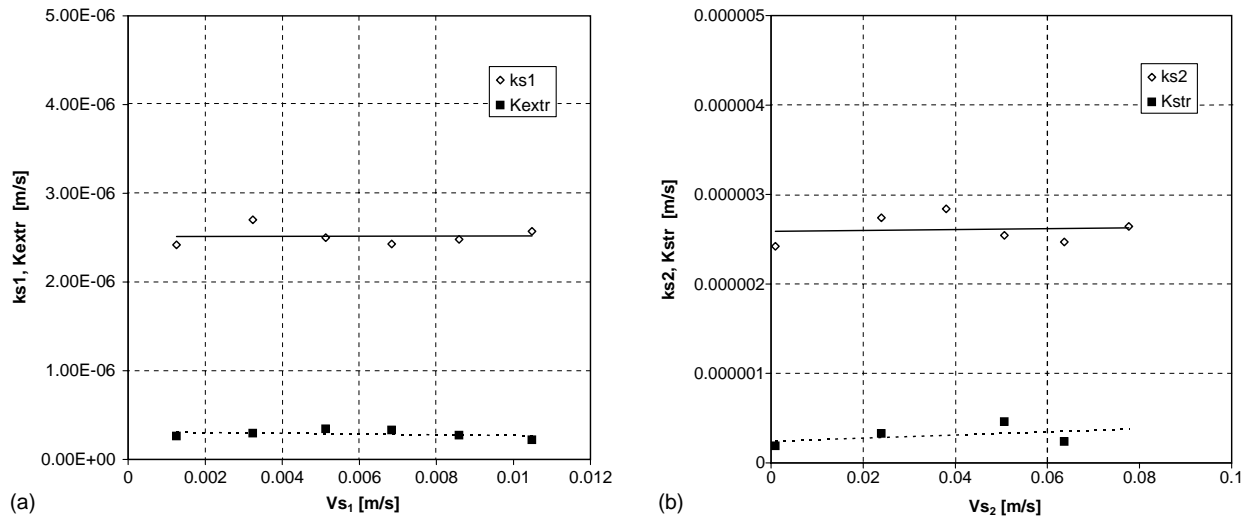


Fig. 6. Influence of organic phase linear velocity on: (a) mass transfer coefficients; (b) mass transfer resistances. Experimental conditions: $C_A^0 = 0.1 \text{ g/dm}^3$; $Q_A = 6.6 \text{ dm}^3/\text{h}$; $Q_r = 3.42 \text{ dm}^3/\text{h}$; $V_A = V_r = 0.150 \text{ dm}^3$; $V_s = 0.45 \text{ dm}^3$.

phenol concentration in the source aqueous solution was varied from 0.2 to 2.1 g/dm^3 .

In Fig. 7a, kinetic profiles of extraction and stripping degrees (respectively, E and R) at different initial phenol concentrations are demonstrated. It could be seen that at lower phenol concentrations, both E and R values are higher. It means that the method is more effective in treatment of very diluted phenol containing solutions. In Fig. 7b, the $E(R)$ end-values, which are reached at experimental time 300 min, are given as a function of the initial phenol concentration. It can be seen that E and R decrease with higher phenol concentration but there is a difference in the shape of both experimental curves: the extraction degree E decreases linearly, whereas R falls asymptotically.

4.2.3. Improvement of stripping efficiency

The experimental results shown in Fig. 8 illustrate one possibility for improvement of the stripping efficiency. In this case, instead of only one stripping module, a series of HF-modules are used (one module 2 and three modules 3). The data represented here refer to a system containing octanol as an organic solvent.

When using several modules for the second step, the contact time between the loaded organic solution and the stripping NaOH-reagent increases. In this way, a substantial improvement of the stripping efficiency could be reached. Moreover, it can be also seen that the stripping process influences back the first, extraction step: the higher the stripping degree of phenol (i.e., the more effective the regeneration of

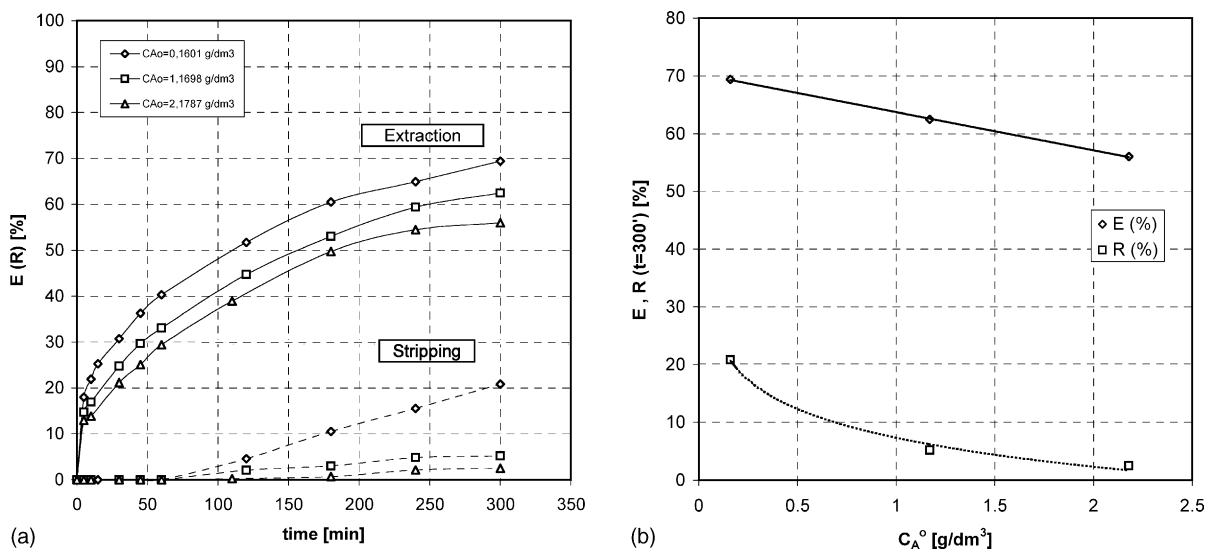


Fig. 7. Influence of initial phenol concentration on extraction/reextraction degrees: (a) time plots extraction/reextraction degrees at $t = 300$ as a function of the initial phenol concentration. Experimental conditions: $Q_A = 15.9 \text{ dm}^3/\text{h}$; $Q_r = 7.0 \text{ dm}^3/\text{h}$; $Q_s = 9.0 \text{ dm}^3/\text{h}$; $V_A = V_r = 0.150 \text{ dm}^3$; $V_s = 0.45 \text{ dm}^3$.

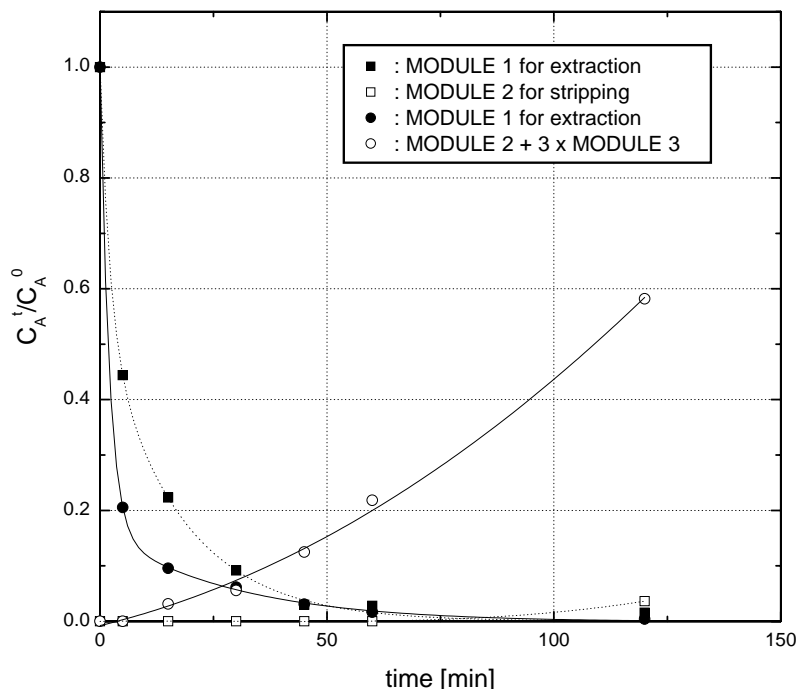


Fig. 8. Membrane extraction/stripping of phenol using series of stripping modules: kinetics concentration profiles in feed and stripping aqueous solutions. Experimental conditions: $C_A^0 = 0.1 \text{ g/dm}^3$; $Q_A = 5.0 \text{ dm}^3/\text{h}$; $Q_T = 5.0 \text{ dm}^3/\text{h}$; $V_A = V_T = 0.150 \text{ dm}^3$; $V_S = 0.350 \text{ dm}^3$.

the circulating organic solvent), the faster the first step—the extraction.

4.2.4. ME of phenol using different organic solvents

In Fig. 9, the kinetic curves (extraction: module 1 and stripping: module 2) for the three organic solvents

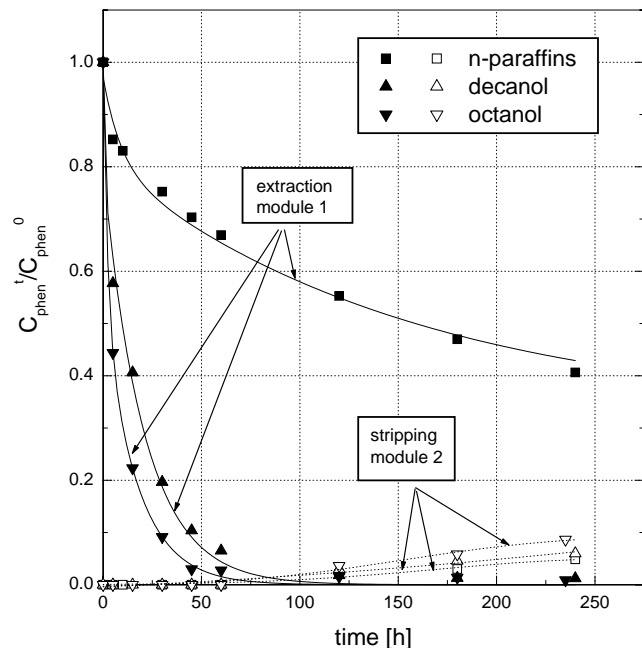


Fig. 9. Membrane extraction/stripping of phenol using different organic solvents: kinetics concentration profiles in feed and stripping aqueous solutions. Experimental conditions: $Q_A = 15.9 \text{ dm}^3/\text{h}$; $Q_T = 7.0 \text{ dm}^3/\text{h}$; $Q_S = 9.0 \text{ dm}^3/\text{h}$; $V_A = V_T = 0.150 \text{ dm}^3$; $V_S = 0.45 \text{ dm}^3$.

(*n*-paraffins, decanol and octanol) are shown. Under otherwise identical conditions of phase flow rates, aqueous phase pH-values and initial phenol concentrations, the dimensionless extraction concentration is substantially lower (i.e. extraction degree is higher) when using polar organic solvents (alcohols) apparently due to the larger values of the phenol distribution coefficients. The stripping degree, however, remains practically almost unaffected by the physical characteristics of organic solvents.

5. Conclusions

The features of the membrane-aided extraction/stripping method using two coupled hollow fiber modules for treatment of aqueous phenol-containing streams are studied.

The overall mass transfer coefficients K_{EXTR} and K_{STR} are found to be a function of the linear velocities of the aqueous streams which flow in the lumen side of hollow fibers in both HF-modules. These coefficients are nearly independent on the organic solution flow rate in the shell side of the modules and the membrane resistance.

The performance of the membrane-aided process in the stripping stage was substantially improved by using a series of stripping modules to increase the stripping contact time.

It is proved that the method is appropriate for treatment of diluted phenol-containing aqueous streams because higher extraction and stripping degrees are achieved at lower phenol concentrations.

References

- [1] L. Giorno, P. Spicka, E. Drioli, Downstream processing of lactic acid by membrane-based solvent extraction, *Sep. Sci. Technol.* 31 (16) (1996) 2159–2169.
- [2] Y. Tong, M. Hirata, H. Takanashi, T. Hano, Back extraction of lactic acid with microporous hollow fiber membrane, *J. Membr. Sci.* 157 (1999) 189–198.
- [3] Y. Tong, M. Hirata, H. Takanashi, T. Hano, Extraction of lactic acid from fermentation broth with microporous hollow fiber membranes, *J. Membr. Sci.* 143 (1998) 81–91.
- [4] I.M. Coelho, P. Silvestre, R.M. Viegas, J.P.S.G. Crespo, M.J.T. Carrondo, Membrane-based solvent extraction and stripping of lactate in hollow-fibre contactors, *J. Membr. Sci.* 134 (1997) 19–32.
- [5] R.S. Juang, J.D. Chen, H.C. Huan, Dispersion-free membrane extraction: case studies of metal ion and organic acid extraction, *J. Membr. Sci.* 165 (2000) 59–73.
- [6] R.M.C. Viegas, M. Rodriguez, S. Luque, J.R. Alvarez, I.M. Coelho, J.P.S.G. Crespo, Mass transfer correlations in membrane extraction: analysis of Wilson-plot methodology, *J. Membr. Sci.* 145 (1998) 129–142.
- [7] C. Yang, E.L. Cussler, Reactive extraction of Penicillin G in hollow-fiber and hollow-fiber fabric modules, *Biotechnol. Bioeng.* 69 (1) (2000) 66–73.
- [8] Z. Lazarova, B. Syska, K. Schuegerl, Application of large-scale hollow fiber membrane contactors for simultaneous extractive removal and stripping of Penicillin G, *J. Membr. Sci.* 202 (2002) 151–164.
- [9] D. Rindfleisch, B. Syska, Z. Lazarova, K. Schuegerl, Integrated membrane extraction, enzyme conversion and electro dialysis for the synthesis of ampicillin from Penicillin G, *Process Biochem.* 32 (1997) 605.
- [10] G.C. Sahoo, S. Borthakur, N.N. Dutta, N.N. Dass, Reactive extraction of cephalosporin antibiotics in hollow fiber membrane, *Bioprocess Eng.* 20 (1999) 117–125.
- [11] S.H. Lin, R.S. Juang, Mass-transfer in hollow-fiber modules for extraction and back-extraction of copper(II) with LIX64N carriers, *J. Membr. Sci.* 188 (2001) 251–262.
- [12] S.H. Lin, R.S. Juang, Kinetic modeling of simultaneous recovery of metallic cations and anions with a mixture of extractants in hollow-fiber modules, *Ind. Res. Chem. Res.* 41 (2002) 853–861.
- [13] C. Yang, E.L. Cussler, Reaction dependent extraction of copper and nickel using hollow fibers, *J. Membr. Sci.* 166 (2000) 229–238.
- [14] A.I. Alonso, B. Galan, M. Gonzalez, I. Ortiz, Experimental and theoretical analysis of a nondispersive solvent extraction pilot plant for the removal of Cr(VI) from a galvanic process wastewaters, *Ind. Eng. Chem. Res.* 38 (1999) 1666–1675.
- [15] F. Valenzuela, H. Aravena, C. Basualto, J. Sapag, C. Tapia, Separation of Cu(II) and Mo(VI) from mine waters using two microporous membrane extraction systems, *Sep. Sci. Technol.* 35 (9) (2000) 1409–1421.
- [16] M.J. Gonzalez-Munoz, S. Luque, J.R. Alvarez, J. Coca, Recovery of phenol from aqueous solutions using hollow fibre contactors, *J. Membr. Sci.* 213 (2003) 181–193.
- [17] S. Schlosser, I. Rothova, H. Frianova, Hollow-fibre pertractor with bulk liquid membrane, *J. Membr. Sci.* 80 (1993) 99–106.
- [18] W. Cichy, S. Schlosser, J. Szymanowski, Transport of phenol through bulk liquid membranes. in: M. Cox, M. Hidalgo, M. Valiente (Eds.), *Solvent Extraction for the 21st Century*, Soc. Chem. Ind., London, 2001, pp. 1065–1070.
- [19] W. Cichy, S. Schlosser, J. Szymanowski, Recovery of phenol with Cyanex 923 in membrane extraction-stripping systems, *Solv. Extract. Ion Exch.* 19 (5) (2001) 905–923.
- [20] S. Schlosser, E. Sabolova, Three-phase contactor with distributed U-shaped bundles of hollow-fibers for pertraction, *J. Membr. Sci.* 210 (2002) 331–347.
- [21] A. Nanoti, S.K. Ganguly, A.N. Foswami, B.S. Rawat, Removal of phenols from wastewater using liquid membranes in a microporous hollow-fiber membrane extractor, *Ind. Eng. Chem. Res.* 36 (1997) 4369–4373.
- [22] A.M. Urriaga, M.I. Ortiz, E. Salazar, J.A. Irabien, Supported liquid membranes for the separation/concentration of phenol. 1. Viability and mass-transfer evaluation, *Ind. Eng. Chem. Res.* 31 (1992) 877–886.
- [23] A.M. Urriaga, M.I. Ortiz, E. Salazar, J. Airabien, Supported liquid membranes for the separation/concentration of phenol. 2. Mass transfer evaluation according to fundamental equations, *Ind. Eng. Chem. Res.* 31 (1992) 1745–1753.
- [24] S.W. Peretti, C.J. Tompkins, J.L. Goodall, A.S. Michaels, Extraction of 4-nitrophenol from 1-octanol into aqueous solution in a hollow fiber liquid contactors, *J. Membr. Sci.* 195 (2001) 193–202.
- [25] C.J. Tompkins, S.W. Peretti, A.S. Michaels, Removal of *p*-nitrophenol from aqueous solution by membrane supported solvent extraction, *J. Membr. Sci.* 75 (1992) 277–292.
- [26] Z. Lazarova, Y. Zhang, M. Jin, X.-J. Chai, Hollow fiber solvent extraction of gold from alkaline cyanide solution, *Chem. Eng. Proc.* 33 (1994) 33–37.
- [27] Z. Lazarova, S. Boyadzhieva, Hollow fiber membrane system for removal of aniline from water, in: *Proceedings of the Eighth International Summer School of Chemical Engineering*, 1998, Sozopol, Bulgaria.
- [28] R. Basu, R. Prasad, K. Sirkar, Nondispersive membrane solventback extraction of phenol, *AIChE J.* 36 (1990) 450.