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Simulation of a hybrid process involving extraction into ionic liquid impregnated microparticles and microfiltration

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ABSTRACT

A new hybrid process involving the extraction of butyric acid (BA) into ionic liquid impregnated microparticles and the microfiltration (extraction-microfiltration, EMF) process has been proposed and its feasibility examined by simulation. Diafiltration of the regenerated suspension of the solvent impregnated resin (SIR) with water is important to decrease the amount of BA in the recycled regenerated suspension, BA concentration in the lean fermentation broth, consumption of chemicals and to increase the yield of the BA in concentrates. Improvement of these parameters is significant (decrease of chemicals' consumption and BA concentration in the lean fermentation broth by over 80% and increase of the BA yield from 56 to 91% for a three stage EMF process) for diafiltration with the volumetric flowrate of washing water being twice the volumetric flowrate of the diafiltered suspension. Above this ratio, the gain in the BA yield and consumption of chemicals is not high. At the same time, concentration factor of the product in the primary concentrate decreases. The introduction of more extraction/MF stages significantly increases the concentration factor and yield of BA due to its higher concentration and the equilibrium capacity of SIR particles in the suspension entering the regeneration up to three stages. However, with the increasing number of stages, the capital and operating costs of the separation increase as well. Applicability of the EMF process in cases requiring a higher yield of the solute is not high. The EMF process can be more competitive in separations with lower requirements on the yield of separated species and higher capacity of SIR at the output concentration of the solute, where only one extraction/MF stage is adequate.

Keywords: Extraction; Solvent impregnated resin; Butyric acid; Microfiltration; Hybrid process; Simulation

1. Introduction

Product inhibition is a typical problem of carboxylic acids fermentation production. Continual separation of the product from the fermentation broth allows achieving high substrate utilization at reasonable biosynthesis rates and prolonged utilization of biomass [1–4]. Fermentation of butyric acid (BA) by *Clostridium butyricum* and its in situ solvent extraction by tertiary amines on oleylalcohol and pure oleylalcohol were tested in papers [5,6].

Ionic liquids (ILs) are prospective solvents also for extractive separation of carboxylic acids [7–10]. Preferable hydrophobic ILs for these applications are usually surface active and sensitive to the formation of emulsions in dispersive contacting of organic/aqueous L/L systems [8]. Extractive separations with one or

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two immobilized L/L interfaces can solve this problem [4,11]. These processes can be realized in systems with immobilized L/L interface(s), e.g., with supports in the form of a microporous wall supporting the liquid membrane with two immobilized interfaces [4,12,13]. Alternative processes utilize systems with one immobilized L/L interface in membrane based solvent extraction [4,11] or in extraction into solvent impregnated resins (SIRs) [14–17].

Utilization of SIR for the extraction of substances is a widely studied topic, mostly for separation of metals [14]. The use of particles impregnated with ammonium IL and its solution in dodecane for the extraction of BA were studied by Blahušiak et al. [15,17]. A very interesting result of a kinetic study in this system was that the mass transfer rate is high and a 90% saturation of macroparticles with the mean diameter of 654 μm is achieved in less than 350 s. Compared to this, in case of classical ion-exchange resins is the adsorption time for organic acids by one order of magnitude higher, showing much slower kinetics, e.g., more than 1 h in the adsorption of formic acid in an anion-exchange resin [18], and more than 5 h in that of lipoic acid in a neutral polystyrene/divinylbenzene adsorbent [19] which is similar to the support used in SIR for the BA extraction in [17]. Slow kinetics was observed also in the adsorption of boric acid into a chelating adsorbent (particle size in the interval of 0.25–1.0 mm), where the time needed to achieve a 95% of the equilibrium saturation was more than 5 h [20]. Such adsorbents can be applied in column apparatus at low superficial velocity of the treated solution resulting in a relatively large amount of adsorbents needed for a given plant capacity. Another possibility is the use of adsorbent microparticles in a hybrid adsorption-microfiltration (AMF) process [21–24].

Stability of SIR impregnated with IL is promising. After five extraction/stripping cycles, performance of SIR was not changed [17]. A two phase system in the extraction into SIR with one immobilized L/L interface is schematically shown in Fig. 1.

Hybrid processes combining production and separation processes in an interactive way can provide synergistic improvement of reaction/separations processes. Moreover, also hybrid separations combining two separation processes can be advantageous. A hybrid process coupling fermentation and pertraction through liquid membrane is discussed in paper [25]. Results of a simulation of the hybrid adsorption-microfiltration (AMF) process application for the removal of boron from reverse osmosis permeate using microparticles of adsorbent are encouraging [23]. Based on this work, the possibility of combining BA extraction with SIR microparticles and separation of loaded suspension by microfiltration in a hybrid extraction-microfiltration (EMF) process for the separation of BA from the fermentation broth has been examined. This is a novel approach to the separation of carboxylic acids and can be an alternative to classical extraction based separation processes.

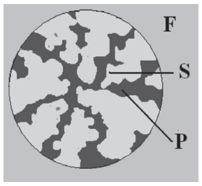


Fig. 1. Two phase system in the extraction into solvent impregnated resin (SIR) with one immobilized L/L interface. F – aqueous feed, P – polymer (resin), S – solvent phase.

The aim of this work was to simulate the EMF process and to estimate the influence of the main process parameters on its performance in BA separation from the fermentation broth. Based on the simulation, feasibility and applicability of the process were evaluated. The simulation was based on our own experimental data on the equilibrium and kinetics of BA extraction with SIR macroparticles impregnated with ammonium IL.

2. Hybrid EMF process

Flowsheet of a proposed hybrid process involving extraction into ionic liquid impregnated microparticles and microfiltration (EMF process) is shown in Fig. 2. Main idea of the proposed process is the combination

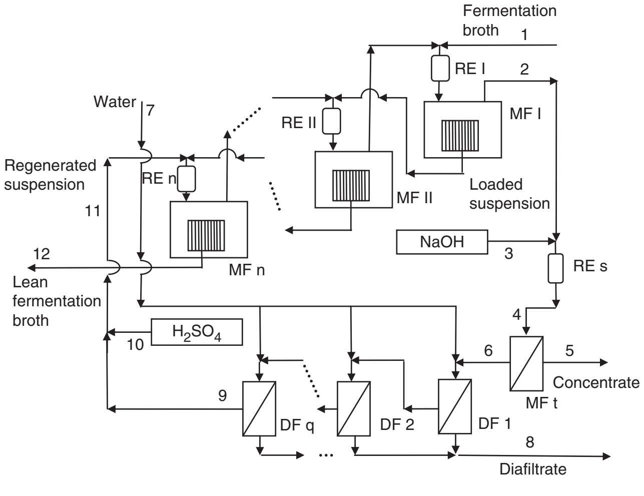


Fig. 2. Flowsheet of the EMF process with *n* extraction/MF stages and *q* diafiltration stages with an addition of water to each diafiltration stage. RE I to RE *n* – plug flow extractors, MF I to MF *n* microfiltration of the suspension from the respective extraction stage in submerged membrane modules, MF *t* – microfiltration of the preconcentrated loaded suspension in the tubular membrane module, DF 1 to DF *q* – diafiltration stages of the regenerated suspension.

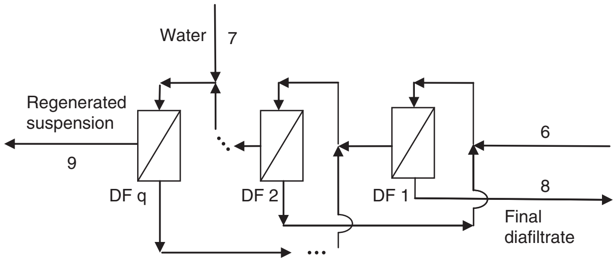


Fig. 3. Flowsheet of regenerated suspension diafiltration with counter-current flow of the diafiltrate through the diafiltration stages, DF 1 to DF *q* – diafiltration stages of the regenerated suspension.

of fast BA extraction kinetics with SIR microparticles, as shown in Fig. 3b, and the separation of microparticles from the fermentation broth by microfiltration (MF). The process can be divided in two parts: extraction and regeneration circuit of the SIR suspension. Stripping is achieved by pH swing by increasing pH of the preconcentrated suspension to about 10. A slight stoichiometric excess of alkali is required.

In the extraction part, more consecutive extraction stages can be considered in order to better utilize the capacity of the SIR microparticles due to higher equilibrium concentration of BA in the suspension entering the regeneration stage.

Fermentation broth (1) is mixed with the suspension leaving the second stage of extraction (when only one extraction stage is assumed, regenerated suspension (13) is mixed with the fermentation broth). The suspension then passes through a plug flow extractor of the first extraction stage RE *I*, where a defined approach to equilibrium is achieved by adjusting the adequate residence time using the retention volume of the extractor. Consequently, the suspension is concentrated by MF in submerged membrane modules, with the permeate entering the second stage of extraction and the concentrated suspension entering the regeneration stage (2). In the following extraction/MF stages, suspension from the previous stage and permeate from the following stage are mixed, and after the extraction and MF, the concentrated suspension enters the previous extraction stage and the permeate goes to the following extraction stage. Regenerated suspension (11) enters the last extraction stage; permeate from this extraction stage is the lean fermentation broth (12) and it is returned to the fermentation process.

In the regeneration part of the process, the suspension of loaded SIR microparticles (2) is mixed with the concentrated solution of NaOH (3) to adjust a pH value appropriate for effective stripping. After stripping in a plug flow retention volume, REs, the suspension (4) is further concentrated in a tubular membrane module. Permeate (5) is the concentrate of the product. The part of BA left in the concentrated suspension is removed by diafiltration with pure water. The diafiltration is done by several consecutive additions of equal water amounts, and microfiltration in tubular MF modules. Collected diafiltrates (8) form a second product stream with lower concentration of the product. Alternatively, a counter-current flow of the diafiltrate through the diafiltration stages can be considered, Fig. 3, aiming at higher concentration of BA salt in the second concentrate (8) and decreased consumption of diafiltration water at the cost of a larger surface area in tubular membrane modules needed and higher demand on energy for pumping. pH of the diafiltered suspension (9) is adjusted to a value appropriate for extraction by an addition of H_2SO_4 (10) and the regenerated suspension (11) enters the extraction part of the separation process. Lean fermentation broth is returned to the fermenter.

3. Simulation model

3.1. Mass balance equations

A simulation model of the process is based on mass balance equations at steady state conditions. Overall mass balance equations for volumetric flowrates of the fermentation broth and BA can be written as (numbering of streams according to Fig. 2)

$$\dot{V}_1 + \dot{V}_7 = \dot{V}_5 + \dot{V}_9 + \dot{V}_{12} \tag{1}$$

$$c_1\dot{V}_1 = c_5\dot{V}_5 + c_9\dot{V}_9 + c_{12}\dot{V}_{12} \tag{2}$$

Since all volumetric flowrates of suspensions were calculated according to the maximum mass concentration of SIR microparticles present, the following equation holds

$$\dot{V}_{s,\mathrm{I}} = \dot{V}_{s,\mathrm{II}} = \ldots = \dot{V}_{s,n} = \dot{V}_s = \frac{\dot{m}_{\mathrm{SIR}}}{\rho_{\mathrm{SIR,sub}}} \tag{3}$$

Volumetric flowrates of permeates for the I, II …*n*-1th extraction/MF stages are equal

$$\dot{V}_{p,\mathrm{I}} = \dot{V}_{p,\mathrm{II}} = \ldots = \dot{V}_{p,n-1} = \dot{V}_p = \dot{V} \tag{4}$$

Volumetric flowrate of permeates for the *n*-th extraction stage can be calculated according to the following equation:

$$\dot{V}_{12} = \dot{V}_{11} + \dot{V}_p - \dot{V}_{\mathrm{s}} \tag{5}$$

Mass balance equation for BA for the I-st extraction stage can be written as follows

$$\dot{V}_1 c_1 + \dot{V}_s c_{\mathrm{II}} + X_e q_m(c_{\mathrm{II}})\dot{m}_{\mathrm{SIR}} = X_e q_m(c_{\mathrm{I}})\dot{m}_{\mathrm{SIR}} + \dot{V}_{p,n} c_{\mathrm{I}} + \dot{V}_s c_{\mathrm{I}} \tag{6}$$

where X_e represents the assumed approach to the extraction equilibrium achieved in the retention volume RE and $q_m(c_n)$ is the equilibrium capacity of SIR at the BA concentration in the fermentation broth c_n. Mass balance equation of the n-th extraction stage follows

$$\begin{aligned}\dot{V}_{11} c_{11} + \dot{V}_p c_{n-1} + (1 - X_d) X_e q_m(c_{\mathrm{I}})\dot{m}_{\mathrm{SIR}} \\ = X_e q_m(c_n)\dot{m}_{\mathrm{SIR}} + \dot{V}_{p,n} c_n + \dot{V}_s c_n\end{aligned} \tag{7}$$

where X_d is the efficiency of stripping. Mass balance equations for BA in form of molar flowrates for the II, III, …, n–1th extraction stage can be written as

$$\begin{aligned}\dot{V}_p c_{i-1} + \dot{V}_s c_{i+1} + X_e q_m(c_{i+1})\dot{m}_{\mathrm{SIR}} \\ = \dot{V}_p c_i + \dot{V}_s c_i + X_e q_m(c_i)\dot{m}_{\mathrm{SIR}}\end{aligned} \tag{8}$$

If there is only one extraction/MF stage in the process, then

$$\dot{V}_s c_{\mathrm{II}} = \dot{V}_{11} c_{11} \tag{9}$$

$$X_e q_m(c_{\mathrm{II}})\dot{m}_{\mathrm{SIR}} = X_e (1 - X_d) q_m(c_{\mathrm{I}})\dot{m}_{\mathrm{SIR}} \tag{10}$$

For the suspension entering the regeneration stage it can be stated that

$$\dot{V}_2 = \dot{V}_s \tag{11}$$

$$c_2 = c_{\mathrm{I}} \tag{12}$$

and for the lean fermentation broth it can be written that

$$\dot{V}_{12} = \dot{V}_{p,n} \tag{13}$$

$$c_{12} = c_n \tag{14}$$

The amount of NaOH needed was calculated according to the total amount of BA present in the loaded suspension stream (in water solution and extracted in SIR microparticles) and for the neutralization of H_2SO_4 present in the fermentation broth after the pH adjusting for the extraction. The stoichiometric amount of the NaOH solution was calculated.

$$\dot{n}_{\mathrm{NaOH}} = \dot{V}_s c_n + X_e q_m(c_{\mathrm{I}})\dot{m}_{\mathrm{SIR}} + c_{\mathrm{H_2SO_4},n}\dot{V}_2 \tag{15}$$

Since the volumetric flowrate of added concentrated NaOH solution is relatively low and can be neglected, volumetric flowrate of stream (4) is equal to the volumetric flowrate of the loaded suspension from the first extraction/MF stage

$$\dot{V}_4 = \dot{V}_2 \tag{16}$$

Concentration of BA in the fermentation broth after the desorption can be expressed as follows

$$c_4 = \frac{X_d X_e q_m(c_{\mathrm{I}})\dot{m}_{\mathrm{SIR}} + \dot{V}_s c_n}{\dot{V}_4} \tag{17}$$

Volumetric flowrates of the suspensions from MF modules in the regeneration stages can be expressed in respect to the maximum concentration of SIR similarly to the calculation for the submerged modules

$$\dot{V}_5 = \dot{V}_{11} = \frac{\dot{m}_{\mathrm{SIR}}}{\rho_{\mathrm{SIR,tub}}} \tag{18}$$

Volumetric flowrate of stream (7) can be calculated from the volumetric flowrate of the diafiltered suspension (6) by defining the following ratio t as a process parameter

$$t = \frac{\dot{V}_7}{\dot{V}_6} \tag{19}$$

In the diafiltration of the regenerated suspension, several stages in series were assumed with additions of equal amounts of diafiltration water to each stage. For the residual concentration of the BA salt in diafiltered suspension (9), the following equation holds

$$c_9 = \left(\frac{q}{q+t}\right)^q c_6 \tag{20}$$

Alternatively, when counter-current diafiltration was assumed (minimum of two stages), the residual concentration of BA in the diafiltered suspension, c_9, can be calculated from the set of mass balance equations for each diafiltration stage

$$c_j = \frac{t}{t+1} c_{j+1} + \frac{c_{j-1}}{t+1} \tag{21}$$

where j is the respective diafiltration stage (ranging from 1 to q). Following equations were used for the first and the q-th diafiltration stage

$$c_j = \frac{t}{t+1}c_{j+1} + \frac{c_6}{t+1}, \; j = 1 \tag{22}$$

$$c_j = \frac{c_{j-1}}{t+1}, \; j = q \tag{23}$$

From the overall balance of the BA salt when $\dot{V}_9 = \dot{V}_6$, for the BA salt concentration in collective DF permeate, can be derived

$$c_8 = \frac{(c_6 - c_9)}{t} \tag{24}$$

Amount of mineral acid needed in the fermentation broth is calculated as a sum of the acid portion needed for the exchange of Na^+ cations in the BA salt for protons, the amount needed to neutralize NaOH not spend in the BA neutralization reaction due to incomplete desorption (in the base case, an addition of diafiltration water to each diafiltration stage was assumed in the calculations), and that needed to achieve the desired H_2SO_4 concentration in the regenerated suspension. pH of the regenerated suspension entering the *n*-th stage of extraction is equal to pH in extraction.

$$\dot{n}_{H_2SO_4} = \frac{1}{2}\dot{V}_{11}c_{11} + \frac{1}{2}\left(\frac{q}{q+t}\right)^q (1 - X_d)X_e q_m(c_I)\dot{m}_{SIR} + c_{H_2SO_4,n}\dot{V}_{11} \tag{25}$$

The H_2SO_4 concentration needed in the fermentation broth can be calculated from the pH needed to keep all BA in the undissociated form, pH_{extr}, equal approximately to 4 as follows:

$$c_{H_2SO_4,n} = \frac{1}{2}10^{-pH_{extr}} \tag{26}$$

Since the volumetric flowrate of added concentrated H_2SO_4 is relatively negligible, volumetric flowrates and concentrations of streams (11) and (9) are assumed to be equal

$$\dot{V}_{11} = \dot{V}_9 \tag{27}$$

$$c_{11} = c_9 \tag{28}$$

The concentration ratio of the primary or secondary product stream (5,8) as a process performance evaluation parameter is defined as

$$Z_i = \frac{c_i}{c_1} \tag{29}$$

The yield of BA in the process is defined as

$$\eta = \frac{c_5\dot{V}_5 + c_8\dot{V}_8}{c_1\dot{V}_1} \tag{30}$$

The set of Eqs. (1) to (30) was solved using the Matlab solver for non linear equations.

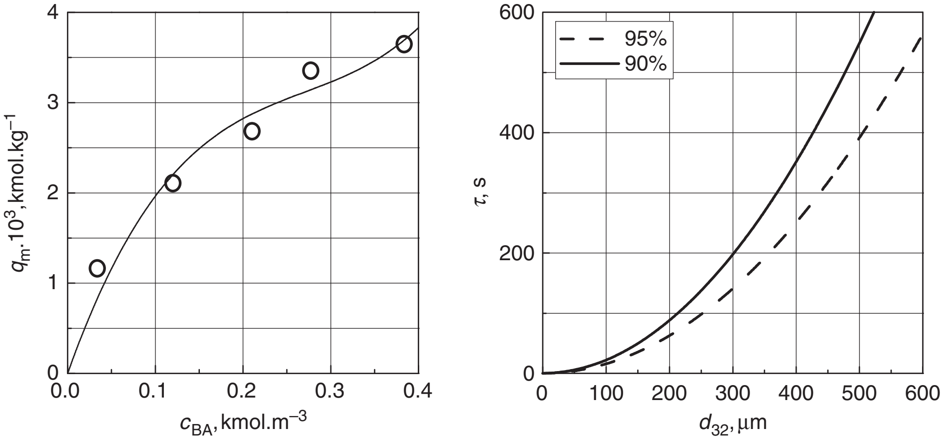
3.2. Input data into the simulation of the EMF process

The simulation was done for a unit of the capacity of 10 m^3/h of fermentation broth containing 0.11 kmol/m^3 of BA. This concentration is the same as that in the feed for the hybrid fermentation-pertraction process for BA fermentation with immobilized cells of *Clostridium tyrobutyricum* in paper [25]. Extraction properties of SIR are based on data presented in paper [17].

Concentration dependence of the equilibrium capacity of the solvent impregnated resin was obtained by a correlation of the experimental data from SIR/L equilibrium measurements with SIR macroparticles impregnated with pure IL trialkylmethylammonium bis(2,4,4-trimethylpentyl)phosphinate, TAMA-BTMPP [17], shown in Fig. 4a. Results of the correlation on the following polynomial equation are presented in a Table 1.

$$q_m(c) = a_1c + a_2c^2 + a_3c^3 \tag{31}$$

Since the extraction kinetics is favorable, Fig. 4b, it is possible to achieve a 90% approach to the extraction equilibrium with particles of 100 μm in the diameter within 16 s. To achieve this residence time at the flowrate of the fermentation broth in the extraction stages of 10 m^3/h, the volume of the extractors with plug flow retention volume needed is only 45 l and a prolonged pipe can be used. Higher concentrations of SIR microparticles of 200 kg/m^3 in submerged MF modules and of 300 kg/m^3 in tubular modules were assumed according to the adsorption/MF process [23]. The assumed diameter of the SIR microparticles of 100 μm is much larger than that of the adsorbent microparticles in MF experiments, where it was only 4.7 μm [27,28]. Performance data for MF of SIR microparticle suspensions should be estimated to evaluate the membrane area needed in the submerged and tubular membrane modules and to give precise information on possible concentrations of microparticles in the concentrated suspension streams. In the first approximation, membrane surface areas needed in submerged and tubular MF modules were not calculated in this paper. In simulation, diafiltration with an addition of water to each diafiltration stage was assumed. All fixed and assumed values of parameters for the simulation are summarized in Table 2.



a) b)

Fig. 4. Experimental (markers) and correlated (lines) BA concentration dependence of the SIR equilibrium capacity containing IL TAMA-BTMPP (a), and times needed for the 90% and 95% approach to the SIR extraction equilibrium as a function of the SIR particles' diameter (lines are calculated with the value of $D_{ef} = 2.68 \cdot 10^{-11}$ m^{2}s^{-1} obtained from experimental SIR extraction data correlation according to the Urano model [26]) (b) based on experimental data in paper [17].

Table 1
Coefficients of the correlation in Eq. (31)

Parameter	Value
a_1, m^3·kg^{-1}	0.0273
a_2, kmol^{-1}·m^6·kg^{-1}	−0.0878
a_3, kmol^{-2}·m^9·kg^{-1}	0.1084
R^2, -	0.9487

Table 2
Fixed and assumed values of parameters used in the simulation, if not otherwise stated

Parameter	Value
c_1, kmol/m^3	0.11
$\dot{V}_1$, m^3/h	10
*t, -	2
$\rho_{SIR, SUB}$, kg/m^3	200
$\rho_{SIR, TUB}$, kg/m^3	300
$\dot{m}_{SIR}$, kg/s	0.3
n, -	3
q, -	3
X_d, -	0.9
X_e, -	0.9

*diafiltration with an addition of diafiltration water to each diafiltration stage was assumed in the simulation, if not otherwise stated.

4. Results and discussion

Results of the simulation are shown in Figs. 5–8 and Tables 3, 4. Specific consumption of chemicals for BA separation by the EMF process is strongly dependent on the introduction of diafiltration, Fig. 5a. As shown, the introduction of diafiltration into a process with three extraction/MF stages with the volumetric flowrate of water equal to that of the diafiltered suspension reduces the amount of H_2SO_4 needed by 78% and with the volumetric flowrate of water two times higher than that of the diafiltered suspension by 88% compared to the process without diafiltration. Further increase of the volumetric flowrate of washing water results in lower gain in the H_2SO_4 consumption at the cost of a higher dilution of BA in the diafiltrate as the second product stream. The concentration of SIR particles in the suspensions leaving MF modules has significant impact on the consumption of H_2SO_4. With the increasing suspension concentration in the submerged membrane module and decreasing suspension concentration in the tubular membrane module, specific consumption of H_2SO_4 increases, Fig. 5b. This is caused by the fact that the suspension concentration difference between the submerged and tubular modules determines the amount of BA which can be recovered in the concentrate (5). Similar trends were observed for the dependences of NaOH consumption for BA stripping from SIR with a higher molar amount of NaOH needed.

The yield of BA in the concentrate and diafiltrate and the BA concentration in the lean fermentation broth are greatly influenced by the introduction of diafiltration and the number of extraction/MF stages, as shown in

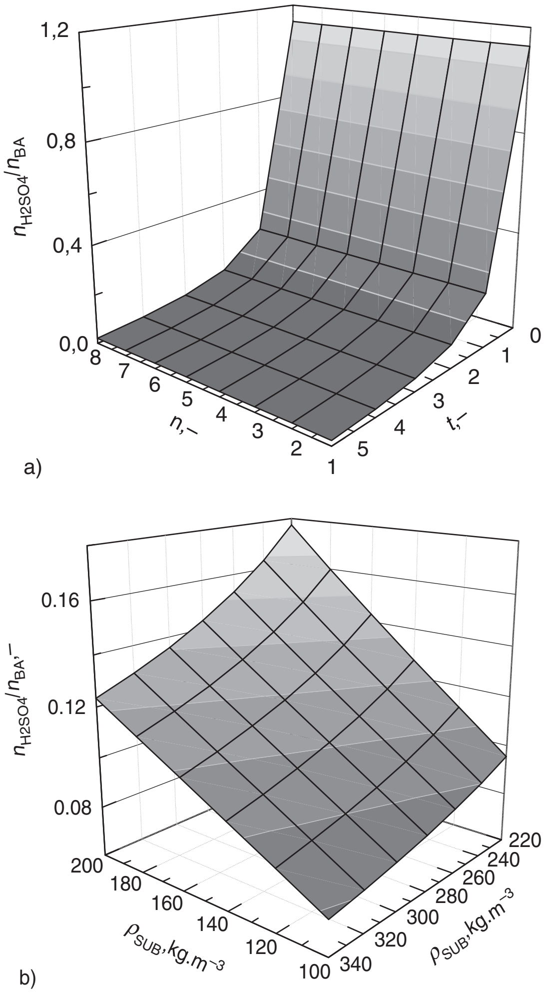


Fig. 5. Consumption of sulfuric acid per one mole of BA separated in the EMF process as a function of the number of extraction/MF stages and the ratio of the volumetric flowrates of diafiltration water and diafiltered suspension, *t*, (a); and as a function of the concentration of SIR particles in the suspension from submerged modules ρ_{sub}, and from tubular membrane modules, ρ_{tub}, (b). Fixed values of parameters are presented in Table 2.

Fig. 6. Introduction of diafiltration increases the BA yield, with more significant increase at lower volumetric flowrates of washing water up to two times that of the diafiltered suspension. At the same time, BA concentration in the lean fermentation broth significantly decreases. A higher volumetric flowrate has not such a great impact on the improvement of these parameters. It is advantageous to introduce diafiltration in more stages. The yield and concentration of BA in the lean fermentation broth are improved by 3–4% when three diafiltration stages with an addition of diafiltration water to each stage are introduced instead of one. A further increase of the number of diafiltration stages does not improve these parameters significantly. At the same time, the BA concentration factor in the main concentrate (5) decreases by 4%. This positive effect on the yield and lean fermentation broth concentration is caused by the improved efficiency of the excess BA removal from the regenerated suspension, resulting in lower concentration of BA in the regenerated suspension, c_9, as shown in Table 3. Furthermore, when counter-current diafiltration in three stages is introduced, the volumetric flowrate of the diafiltration water can be reduced by 45% ($t = 1.1$) and the concentration of the BA salt in the second concentrate, diafiltrate (8), increases by 78% compared to

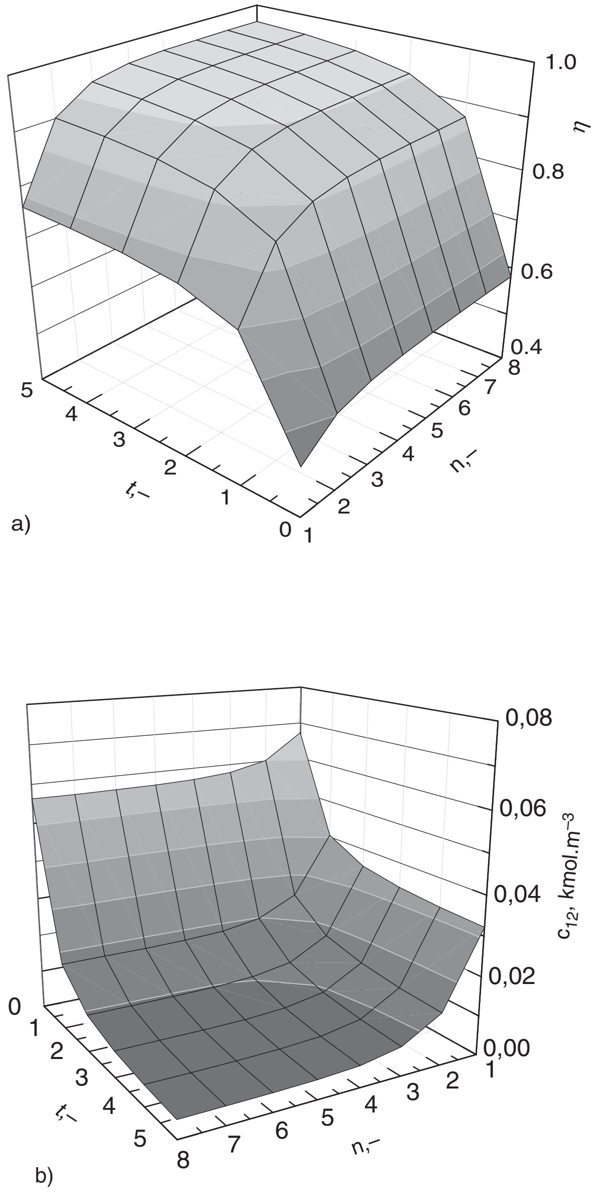


Fig. 6. Yield of BA in the EMF process (a) and concentration of BA in the lean fermentation broth, c_{12}, (b) as a function of the number of extraction/MF stages, *n*, and the ratio of the volumetric flowrates of diafiltration water and diafiltered suspension, *t*. Fixed values of parameters are presented in Table 2.

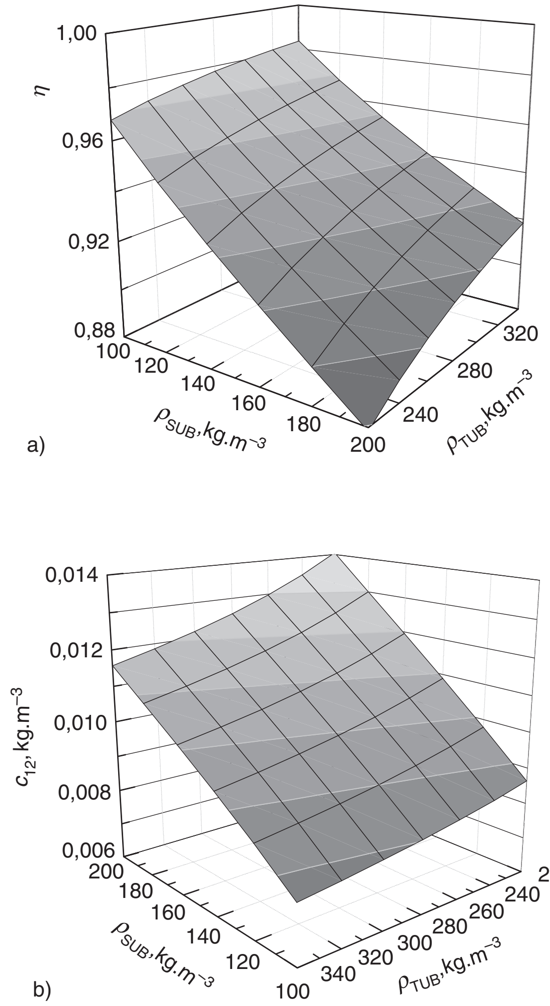


Fig. 7. Yield of BA in the EMF process (a) and concentration of BA in the lean fermentation broth (b) as a function of the concentration of SIR particles in the suspension concentrated by submerged and tubular membrane modules. Fixed values of parameters are presented in Table 2.

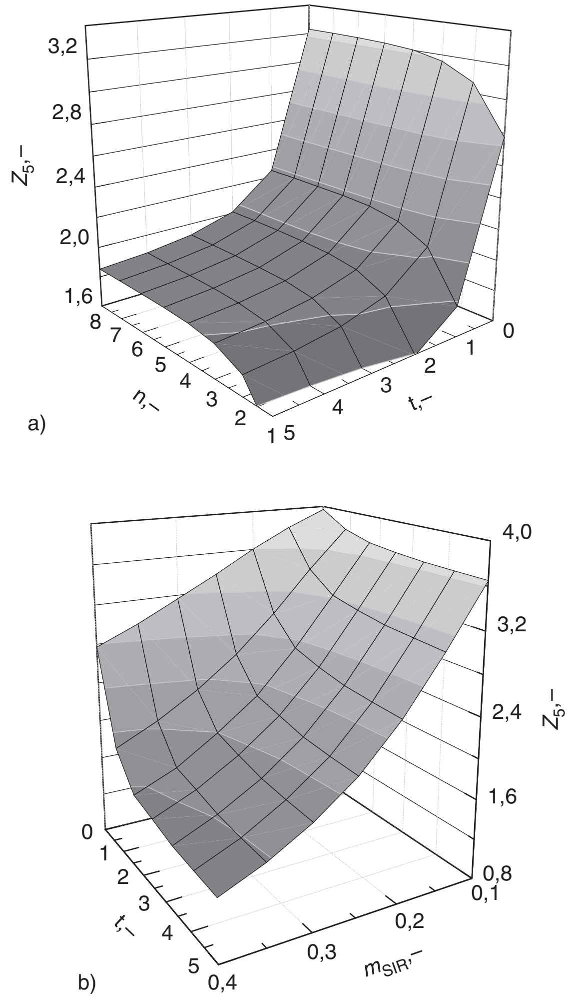


Fig. 8. Concentration ratio of BA in the primary concentrate (5) to the concentration in the processed fermentation broth as a function of the number of extraction/MF stages and the ratio of the volumetric flowrate of diafiltration water to that of diafiltered suspension, *t*, (a) and as a function of the mass flowrate of SIR particles in the regenerated suspension circulation loop and the ratio of the volumetric flowrates of diafiltration water to diafiltered suspension. Fixed values of parameters are presented in Table 2.

the diafiltration with step addition of fresh water to diafiltration stages while achieving the same removal of the BA salt from the diafiltered suspension, Table 3. In both DF variants, the same BA concentration in the lean broth was kept. At the same time, the demands on the membrane area and pumping energy increased by 35% due to higher volumetric flowrate of the permeate in counter-current diafiltration.

The number of extraction/MF stages has a similar influence on these parameters. Increasing the number of extraction/MF stages increases the yield and decreases the BA concentration in the lean fermentation broth, with the relative change being significant up to three extraction/MF stages, especially when higher volumetric flowrates of diafiltration water are used. Yield of BA in concentrates and BA concentration in the lean fermentation broth can be further improved by increasing the suspension concentration leaving the tubular membrane module. This is done at the cost of a lower concentration ratio in the concentrate, Fig. 7.

The ratio of BA concentration in the primary concentrate and in the fermentation broth, *Z*, is important for lowering the demand to process this stream to the final product, free BA. The introduction of diafiltration decreases this ratio rapidly, especially for the process with only one extraction/MF stage, Fig. 8a, where the ratio decreases by 55% and 70% for the introduction of diafiltration with the same and twice the amount of

Table 3
Selected parameters for the EMF process with various number of diafiltration stages, *q*. Two variants of diafiltration are compared with the same BA salt concentration in the diafiltered suspension, c_9. Fixed values of other parameters are presented in Table 2

Parameter	$q = 1$	$q = 2$	$q = 3$	$q = 6$
Addition of diafiltration water to each diafiltration stage, $t = 2$				
η, -	0.88	0.90	0.91	0.92
c_{12}, kmol/m^3	0. 016	0.013	0.012	0.011
Z_5, -	2.09	2.00	1.97	1.93
c_9, kmol/m^3	0.077	0.055	0.047	0.036
Z_8, -	0.698	0.751	0.771	0.793
Counter-current diafiltration				
t, -	2	1.3	1.1	0.92
Z_8, -	0.698	1.146	1.404	1.741

Table 4
Selected parameters for the EMF process with 1, 2, 3 and 6 extraction/MF stages. Fixed values of parameters are presented in Table 2

Parameter	n=1	n=2	n=3	n=6
η, -	0.74	0.87	0.91	0.93
c_{14}, kmol/m^3	0.035	0.017	0.012	0.096
Z_5, -	1.59	1.87	1.97	2.0
$n_{\mathrm{H2SO4}}/n_{\mathrm{BA}}$, -	0.095	0.095	0.095	0.095
$n_{\mathrm{NaOH}}/n_{\mathrm{BA}}$, -	1.27	0.76	0.55	0.48

water compared to the volumetric flowrate of diafiltered suspension, respectively. At the same time, the ratio decreases with the amount of SIR particles in the circulation loop, with the decrease being more significant when diafiltration is introduced, Fig. 8b. A comparison of the selected calculation results for EMF processes with various number of extraction/MF stages is shown in Table 4.

Based on these results, a process with three extraction/MF stages is needed to achieve a reasonable BA yield of 90% at a reasonable concentration ratio. On the other hand, higher number of extraction/MF stages increases the investment costs for the submerged membrane modules and the pumping costs proportionally, making the EMF process less competitive. It was shown that even the introduction of SIR microparticles with reasonably better extraction capacity does not decrease the number of extraction/MF stages needed in the process of BA recovery from the fermentation broth [29]. This suggests that the EMF process is not suitable for the removal of BA from real fermentation broths. Fast extraction kinetics also supports the utilization of larger SIR particles (100–200 µm) in a column with a fixed bed.

On the contrary, simulation of a similar adsorption/microfiltration process for the removal of boron from RO permeate of a seawater desalination plant using a microparticulate adsorbent showed much more promising results [23]. In this paper, microparticles were used for the removal of boron as a xenobiotic microcomponent (1.2 mg/l) in water treatment, which resulted in the recirculation of a relatively low flowrate of suspension and a low consumption of chemicals at a relatively high concentration factor compared to an adsorption in column [30].

In general, according to the simulation in this work and in paper it appears that the one stage process combining the adsorption or extraction of separated species into microparticles with the separation of loaded suspension by microfiltration and continual regeneration of this suspension by a pH swing in the circulation loop are more favorable for the separation of microcomponents, where a certain level of the solute concentration in the purified stream is the goal and the ratio of the initial and final concentrations of solute is not high (e.g., yield is not high) [23]. In case of boron removal, this ratio was equal to 3 (0.4 mg/l of boron in the outlet of the purified water), while for BA extraction from the fermentation broth it is equal to 10 to achieve a reasonable yield of 90%. Furthermore, the concentration dependence of the equilibrium capacity of microparticles and the amount of separated species needed to achieve the desired concentration in raffinate is also important. Lower values of the capacity at low BA concentrations in the raffinate result in more extraction (sorption)/MF stages needed to achieve higher yields and concentration ratios at a reasonable mass flow of the suspension in the circulation loop. Thus, microparticles with steep equilibrium capacity dependences on the solute concentration in the region of low concentrations are preferable in these systems. For example, for boron removal in a batch system, less than 0.1 kg of adsorbent is needed to treat 1 m^3 of the feed and to achieve the final desired concentration with the yield of 67%; whereas in BA extraction, 340 kg of SIR microparticles are needed to achieve a 90% yield in the separation. This leads to the recirculation ratio of the regenerated suspension of 0.0027 and 0.36 (based on the feed flowrate) in AMF and EMF processes, respectively.

5. Conclusions

Based on our own experimental data on the extraction into SIR, a simulation of the hybrid process involving extraction into ionic liquid impregnated microparticles and microfiltration (EMF process) was done.

The simulation has shown that diafiltration of the suspension with fresh water is important to significantly decrease the amount of BA in the recycled regenerated suspension, BA concentration in the lean fermentation broth and the consumption of chemicals, and to increase the yield of BA in concentrates. Improvement of the parameters is significant for the diafiltration with fresh water of the volumetric flowrate being twice that of the diafiltered suspension for three stage diafiltration with an addition of water to each stage. For counter-current diafiltration, the volumetric flowrate of fresh water can be reduced by 45% and the concentration of BA in the second concentrate (diafiltrate) substantially increased by 78%. A further increase of the diafiltration water flowrate has no more significant impact on the BA yield and the consumption of chemicals. On the other hand, it decreases the concentration factor of the product in the primary and secondary concentrate.

Introduction of more extraction/MF stages significantly increases the concentration factor and yield of BA due to higher concentration of BA and equilibrium capacity of SIR particles in the suspension entering the regeneration process. The increase is significant up to three stages, where a reasonable yield of BA equal to 91% is achieved. On the other hand, an increase of the number of extraction/MF stages proportionally increases the capital and operating costs for the membrane area needed in MF and also the energy for pumping increases proportionally to the number of stages.

Thus, fixed bed of SIR particles with good extraction kinetics is probably a more suitable alternative to the EMF process due to the high expenses coupled with three extraction and microfiltration stages in the EMF process. Contrary to this, a similar process combining adsorption on a microparticulate adsorbent and microfiltration of loaded suspension for the removal of low concentration boron has been found competitive to column operation.

Applicability of the EMF process when higher yield of the solute is required is not high. Steep equilibrium capacity dependence on the solute concentration is needed to decrease the number of extraction (sorption)/MF stages and the flowrate of the recycled suspension. The EMF process can be more competitive in separations with lower demand on the yield of separated species and higher capacity of SIR at the output solute concentration, where only one extraction/MF stage can be adequate. There is a challenge to develop SIRs with higher capacity at lower concentrations which not necessarily need to have higher maximum capacity.

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Symbols

c — concentration of BA or its salt, kmol/m^3
$c_{H_2SO_4,n}$ — desired concentration of H_2SO_4 in extraction, kmol/m^3
D_{ef} — effective diffusion coefficient of BA complexes in SIR, m^2/s
$\dot{m}_{SIR}$ — mass flowrate of SIR microparticles in recirculation loop, kg/h
n — number of extraction/MF stages
$\dot{n}_{H_2SO_4}$ — molar flow of H_2SO_4 in suspension regeneration, Eq. (25), kmol/h
$\dot{n}_{NaOH}$ — molar flow of NaOH in suspension regeneration, Eq. (15), kmol/h
pH_{extr} — desired pH in the regenerated suspension for extraction, -
q — number of diafiltration stages, -
q_m — capacity of SIR microparticles, kmol/kg
$q_m(c)$ — capacity of SIR microparticles at BA concentration c, kmol/kg
t — ratio of the volumetric flowrate of the fresh diafiltration water to the volumetric flowrate of the diafiltered suspension defined by Eq. (19), -
$\dot{V}$ — volumetric flowrate of the aqueous phase in suspension, m^3/h
X_e — approach to the extraction equilibrium, -
X_d — efficiency of stripping, -
Z_i — concentration factor of solute in the *i*-th stream, Eq. (29), -
η — yield of BA in EMF process, Eq. (30), -
$\rho_{SIR,\,sub}$ — relative mass concentration of SIR microparticles (mass per unit of aqueous phase volume) in suspension leaving submerged membrane modules, kg/m^3
$\rho_{SIR,\,tub}$ — relative mass concentration of SIR microparticles (mass per unit of aqueous phase volume) in suspension leaving submerged membrane modules, kg/m^3

Lower indices

1, 2, ...12 — number of the stream as shown in Fig. 2
I, II,.....n — number of the extraction/MF stage, Fig. 2
p — concerning permeate from MF/extraction step stage
s — concerning suspension leaving MF/extraction stage

Abbreviations

BA — butyric acid
DF — diafiltration
EMF — extraction-microfiltration

MF t — microfiltration in tubular membrane module
MF — microfiltration in submerged membrane module
RE — retention volume

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