

Extraction of Citric Acid by Liquid Surfactant Membranes: Bench Experiments in Single and Multistage Operation

C. Konzen, E. M. R. Araújo, J. C. Balarini, T. L. S. Miranda, and A. Salum* doi: 10.15255/CABEQ.2013.1789

Departamento de Engenharia Química, Universidade Federal de Minas Gerais, Av. Presidente Antônio Carlos, 6627/Escola de Engenharia, Bloco II, 5º andar CEP: 31.270–901 – Belo Horizonte – Minas Gerais – Brazil

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The extraction of citric acid by liquid surfactant membranes (LSM) was performed using W/O/W emulsions, composed of sodium acetate aqueous solutions (inner phase), mixtures of Alamine 336 and ECA 4360 dissolved in Exxsol D240/280 (membrane phase), and citric acid aqueous solutions (feed phase). Two factorial designs (2^{5-1} and 2^3) were used to define suitable operating conditions, in a single stage, producing citric acid solutions at 0.25 g mL^{-1} from aqueous feed solutions at 0.10 g mL^{-1} . The parameters investigated and the best operating conditions obtained were pH of the feed phase ($pH = 1.5$), surfactant ($w_s = 2 \%$) and carrier concentrations in the membrane phase ($w_c = 20 \%$), stirring speed ($v = 145 \text{ rpm}$), and permeation time ($t = 10 \text{ minutes}$) and the response variables were the citric acid concentration in the inner and feed phases and inner phase swelling. Under these conditions, an extraction greater than 50 % and swelling equal to 80 % were obtained. Use of recycled membranes as well as extraction in multiple stages was also evaluated. Experiments of recycling revealed that the membranes can be reused for at least three times with good performance. Extraction in multiple stages showed high efficiency for the citric acid separation ($\sim 100 \%$) after three steps of operation.

Key words:

liquid surfactant membranes, citric acid, factorial designs, membrane recycling, multi-stage extraction

Introduction

The liquid surfactant membrane technique (LSM) is an extraction process developed by Norman N. Li in 1968,¹ which can be applied to separation of many chemical species.² Among these species, organic acids have been recovered and purified with good efficiency^{3–6} and, particularly, citric acid separation by the LSM process has presented promising results in the last few years.^{6–11}

Citric acid is an organic acid industrially produced by fermentation, widely applied in the food and beverage industries. Its recovery from the fermentation broth is performed by precipitation or solvent extraction. In both cases, the processes require many separation steps and, especially for precipitation, large quantities of residues are produced.¹² In this context, the study of other separation methods, such as LSM technique, aims to evaluate an alternative way of carrying out the citric acid recovery in order to search for better operating conditions to accomplish the separation.

In this paper, the study of the extraction of citric acid by LSM technique is reported. The aim of

this study was to establish suitable conditions to separate and concentrate citric acid from aqueous feed solutions by using two factorial designs (2^{5-1} and 2^3), and the evaluation of process efficiency through experiments of membrane recycling and extraction in multiple stages. This study comprises the first step for the definition of the initial conditions to study citric acid recovery in a pilot plant unit.

The present extraction utilised a primary emulsion with composition different from that used in the literature.^{6–8,11} This change was implemented in order to reduce some stability problems caused by the swelling of the emulsion and the rupture of the inner phase droplets usually present in this extraction system. Additionally, factorial designs were used to identify possible interactions between some important parameters that affect the LSM technique.

Basis of the LSM technique

A liquid surfactant membrane is a multiple emulsion system comprised of three phases as shown in Fig. 1.

According to this scheme, the LSM phases are the following: the feed, which contains one or more solutes to be concentrated and/or purified; the mem-

*Corresponding author: A. Salum, email: salum@deq.ufmg.br; phone: +55 31 34091781; fax: +55 31 34091789

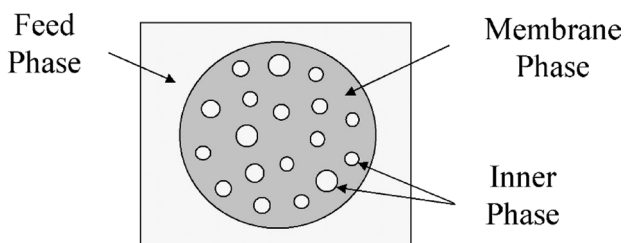


Fig. 1 – Schematic representation of the LSM phases

brane, usually composed of a carrier, a surfactant and a diluent, which is responsible for selective permeation of the solute(s) through the membrane; and the inner phase that acts as the receiver of the solute extracted from the feed phase. The multiple emulsion can be formed in two different ways: water/oil/water (W/O/W) or oil/water/oil (O/W/O).

The LSM separation process is performed in four stages,^{9,13,14} as presented in Fig. 2. At the emulsification stage, the inner phase is poured into the membrane phase under high stirring speed to produce the primary emulsion. Usually, these emulsions take a short time to prepare (1–10 minutes). At the permeation stage, the primary emulsion is dispersed into the feed phase under mild stirring conditions to form the multiple emulsion. While the stirring conditions persist, the solute permeates through the membrane phase, providing its transfer from the feed to the inner phase. As soon as permeation ends, usually in less than 30 minutes, the loaded primary emulsion is separated from the exhausted feed solution by settling. The settling time required to obtain a good separation basically depends on the difference between the densities of the loaded primary emulsion and the depleted feed phase. Generally, it takes up to 5 minutes to per-

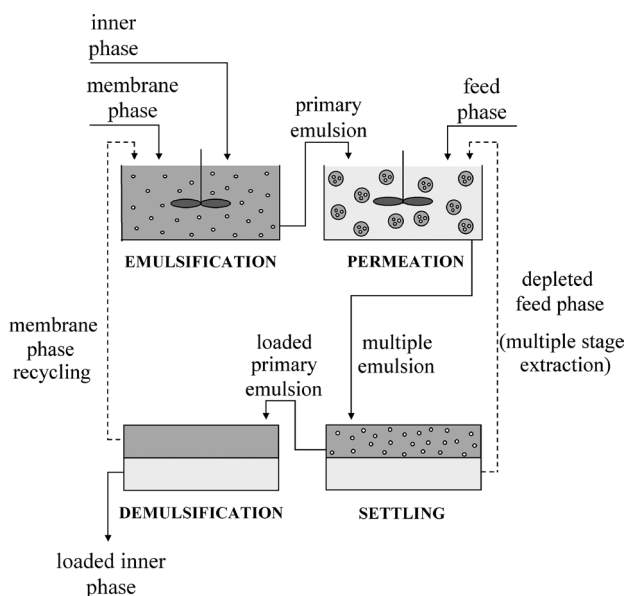


Fig. 2 – Stages of LSM process

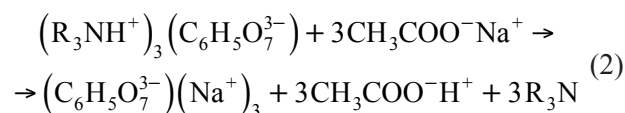
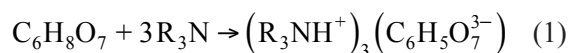
form this step. In the final stage known as demulsification, the emulsion is broken under action of a high-intensity electric field, providing the separation of the membrane and inner phases through the coalescence of the dispersed phase.

Remarkable advantages of the LSM technique are associated with small size equipment requirements, low reagent consumption, operation with reduced number of separation stages, extraction and stripping steps performed in a single device, high selectivity and high capacity to extraction from diluted solutions. The last characteristic is particularly useful in the recovery of species found at low concentrations, with promising applications in the extraction of metal ions,^{15,16} removal of ionic species from wastewater,^{17–19} and separation of carboxylic acids^{11,20,21} and aminoacids.^{22,23}

Additionally, two important limiting aspects that should be carefully observed in this technique are the swelling of the emulsion droplets and occlusion of the feed phase. Swelling, which is usually caused by osmosis, can lead to losses of the concentrated solution in the inner phase by rupture of the membrane, decreasing the process separation efficiency. The occlusion of the feed phase by the primary emulsion causes contamination of the inner phase and decreases the process selectivity. However, both effects can usually be reduced by choosing appropriate phase composition and suitable operating conditions.

Mechanism of citric acid permeation

The mechanism proposed to explain the citric acid extraction by liquid surfactant membrane with tertiary amines is classified as simple carrier transport with chemical reaction. This mechanism is shown in Fig. 3 and the extraction and stripping reactions involved in the permeation step, using sodium acetate solution as inner phase, are presented in eqs. (1) and (2).



In accordance with this mechanism, the citric acid molecule ($\text{C}_6\text{H}_8\text{O}_7$) diffuses from bulk feed phase towards external membrane interface, induced by the chemical potential gradient between phases. At the feed/membrane interface, the solute reacts with the carrier, in this case a tertiary amine (R_3N), forming the complex $(\text{R}_3\text{NH}^+)_3(\text{C}_6\text{H}_5\text{O}_7)^{3-}$. This new molecule diffuses through the membrane until it reaches the membrane/inner phase interface, where the citric acid is stripped with CH_3COONa

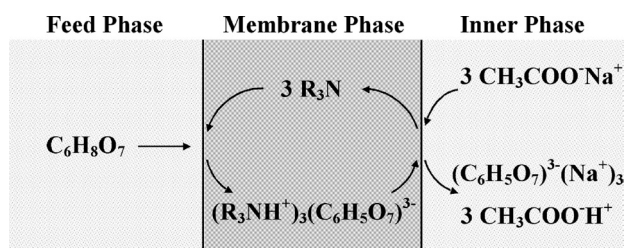


Fig. 3 – Mechanism of citric acid extraction by simple carrier transport with chemical reaction

into the inner phase. The extraction cycle is completed when the free carrier molecule returns to the feed/membrane interface to react again with the solute.⁹

It is important to emphasize that the proposed mechanism represents the expected stoichiometry for citric acid extraction and stripping by tertiary amines. However, studies on citric acid recovery by reactive liquid-liquid extraction with trioctylamine have shown that this stoichiometry can be changed in accordance with the composition of the organic phase and the temperature in which the reactions occur.²⁴

Experimental work

Materials

The apparatus used during the development of this work includes an emulsifier Walita Firenze, a mechanical stirrer Fisatom model 713 T, an incubator Fanem model 002 CB, an electrostatic demulsifier and an acrylic baffled reactor. The reagents, used as supplied by the manufacturers, were: anhydrous sodium acetate (> 99 % of purity – Riedel de Hæn and Reagen), anhydrous citric acid (> 99.5 % of purity – Vetec), sodium hydroxide (> 97 % of purity – Ecibra), Alamine 336 (> 95 % of tertiary amine – General Mills Chemicals), ECA 4360 (commercial grade with $w = 2.13$ % of nitrogen – Paramins) and Exxsol D240/280 (commercial grade – Exxon Chemicals). The composition of the system adopted to carry out the extraction experiments is presented in Table 1.

Table 1 – Composition of the extraction system

Phases	Composition	Volumes (mL)
Inner (I)	$\text{CH}_3\text{COONa} - 4 \text{ mol L}^{-1}$	20
	Alamine 336 (carrier)	
Membrane (II)	ECA 4360 (surfactant)	60
	Exxsol D 240/280 (diluent)	
Feed (III)	$\text{C}_6\text{H}_8\text{O}_7 - 0.1 \text{ g mL}^{-1}$	160

Methods

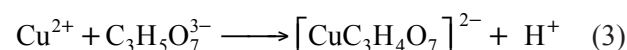
In the first part of this study, fractional and complete factorial designs were used to establish suitable operating conditions to carry out the citric acid separation. In the former case, a 2^{5-1} factorial with 4 center points, in a total of 20 experiments, was used to determine the most influential variables on the system and the more suitable range of operation for all studied factors with a reduced number of experiments. In the last one, a 2^3 complete factorial design was performed to define suitable operating conditions for the most important variables, resulting in 8 runs. The variables and operating conditions adopted in each design are presented in Table 2.

Table 2 – Levels of the 2^{5-1} and 2^3 factorial designs

Variables	2^{5-1} Factorial			2^3 Factorial	
	-1	0	+1	-1	+1
<i>pH</i>	1.5	2.5	3.5	1.5	2.5
w_c (%)	5	12.5	20	20	30
w_s (%)	2	4	6	–	–
<i>v</i> (rpm)	135	145	160	–	–
<i>t</i> (minutes)	10	20	30	3	10

In this table, the variable *pH* is initial pH of the feed phase; w_c and w_s are carrier and surfactant concentrations in the membrane phase, respectively; *v* is stirring speed, and *t* is permeation time. The variable responses used to evaluate the system were: final solute concentration in the inner (γ_f^I) and feed (γ_f^{III}) phases, and swelling percentage of the inner phase (*S*).

The concentration of citric acid in the aqueous phases was measured by complexometric titration of the citrate ions with Cu^{2+} , according to the 1:1 stoichiometric reaction^{25,26} presented in eq. (3). A detailed description of this analytical methodology is given in the literature.^{9,25}



The swelling percentage of the inner phase was calculated by:

$$S = \frac{(V_f^I - V_i^I) \cdot 100}{V_i^I}, \quad (4)$$

where, V_i^I and V_f^I are the initial and final volumes of the inner phase, respectively. The final volume of the inner phase was measured after the emulsion break-up in the demulsification step.

Statistical analysis of the data was performed by means of MINITAB® software, and the computer data outputs are presented in the Appendix A. The analysis of residuals (not presented) showed that the errors are normally and independently distributed with mean zero and constant variance for both designs.

All experiments were carried out in batch mode. In the emulsification stage, primary emulsions were prepared using a membrane phase/inner phase volume ratio equal to 3:1, under 13,000 rpm, for 5 minutes. In the permeation step, feed phase/primary emulsion ratio of 2:1 was used, giving a total volume of 240 mL per experiment. The settling was conducted at 50 °C in order to favour the depleted feed phase/loaded primary emulsion separation. The loaded primary emulsion was broken-up in an electrostatic demulsifier, at 1.7 kV and 5 kHz, using insulated electrodes.

Membrane recycling experiments were carried out under the best operating conditions defined from the 2³ factorial design results. The recycled organic phases (membrane phases after the demulsification step) were used without further treatment or after treating with sodium hydroxide or sodium acetate solutions to prepare new primary emulsions, which were used in the LSM process as described previously for the fresh membranes. The extraction results for fresh and recycled membranes were expressed in terms of the enrichment factor (*EF*) and swelling (*S*). The system enrichment factor (*EF*) was calculated by:

$$EF = \gamma_f^I / \gamma_i^{III}, \quad (5)$$

where, γ_f^I is final concentration of citric acid in the inner phase, and γ_i^{III} is initial concentration of this solute in the feed phase.

To carry out the multiple stage extraction, an aqueous solution of citric acid at 0.1 g mL⁻¹ was used in the first stage of the LSM separation process. The aqueous phase resulting from the settling step (see Fig. 2) was reused in the second permeation stage and this procedure was repeated until the feed phase was exhausted. The experiments were carried out using fresh and once recycled membranes without treatment.

Results and discussion

2⁵⁻¹ and 2³ Factorial Designs

In both designs, statistical analysis of the data was done using a significance level of 20 % ($\alpha = 0.20$), *i.e.*, factors and its interactions with *P*-value < 0.20 were considered potentially relevant to the process. This value was used instead $\alpha = 0.05$ to take into account all the important factors of the process at the beginning of the research.

These designs use simplified models to correlate the variables to each response by means of regression coefficients, and the *P*-value defines whether the variable should be included or not into the model. The regression coefficients associated with each variable are determined based on the *effect* (*E*) of the variable upon the response, and the sign of *E* is used to indicate how the responses would be affected by the factor, defining the most suitable level of operation, the lower (–) or the higher one (+). The proposed models, *P*-value (*P*) and *effect* (*E*) data for all responses are summarized in Appendix A.

Statistical analysis of the data obtained from the 2⁵⁻¹ fractional factorial design showed that the feed phase pH and carrier concentration are the most influential factors upon the final citric acid concentration in the inner phase (γ_f^I). The sign of the effects indicated that the low level of operation for pH ($pH = 1.5$) and the high level for carrier concentration ($w_c = 20\%$) provide the most concentrated inner phase solution for the evaluated levels, so these were chosen as the most suitable operating conditions to increase the γ_f^I .

In case of γ_f^{III} , the main factors *pH*, w_c , *t* and the interaction *pH*· w_c presented some influence upon the response. When some interaction occurs, it is not possible to evaluate the involved variables independently, and an interaction plot is used to determine in which levels of operation both factors can provide the best response. According to the interaction plot indicated in Fig. 4, the highest percentage of extraction is obtained at $pH = 1.5$ and $w_c = 20\%$, yielding the lowest final citric acid concentration in the depleted feed phase ($\gamma_f^{III} = 0.04$ g mL⁻¹), as desired. Factor *t* has presented a borderline *P*-value; therefore it was included as a possible influential variable. The *effect* data for this factor indicated that at higher level of operation ($t = 30$ minutes),

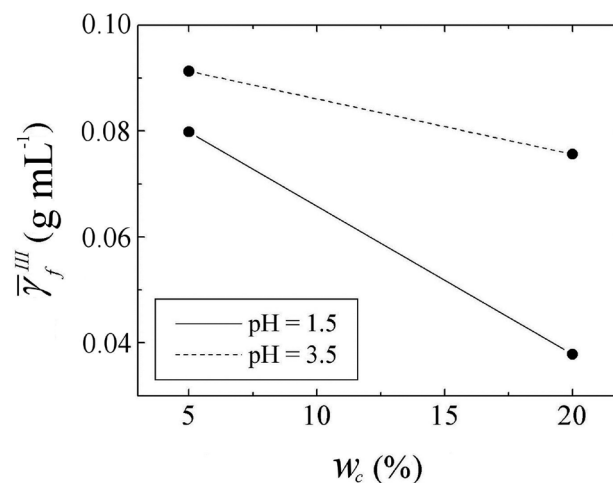


Fig. 4 – Interaction between *pH* and carrier concentration (*pH*· w_c)

more solute is extracted from the feed phase, decreasing γ_f^{III} .

The analysis for the inner phase swelling (S) is more complicated because it is affected by two main factors, the stirring speed and carrier concentration, and a great number of interactions between the two factors. To define the best operating conditions to minimise the swelling, it is necessary to establish the suitable values for each factor from the interaction plots, as described above. From the eight interaction plots generated from this analysis, it was possible to define the most suitable levels to reduce the swelling for each interaction, as summarized in Table 3. The interaction plots were omitted for simplicity.

Table 3 – Suitable operating conditions chosen from the interaction plots for S response

Interactions	Operating Conditions				
	pH	v (rpm)	w_s (%)	w_c (%)	t (minutes)
$pH \cdot v$	3.5	160	–	–	–
$pH \cdot t$	1.5	–	–	–	10
$v \cdot w_s$	–	160	2	–	–
$v \cdot w_c$	–	135	–	20	–
$v \cdot t$	–	160	–	–	10
$w_s \cdot w_c$	–	–	2	20	–
$w_s \cdot t$	–	–	2	–	30
$w_c \cdot t$	–	–	–	20	10

Establishment of the most suitable conditions was based on the modal value obtained for each factor. Except for pH , for which it was not possible to define a unique value ($pH = 1.5/3.5$), the other conditions were set at $v = 160$ rpm, $w_s = 2$ %, $w_c = 20$ %, $t = 10$ minutes.

Table 4 presents the chosen experimental conditions that minimise S and γ_f^{III} and maximise the γ_f^I responses.

Table 4 – Experimental conditions that minimise S and γ_f^{III} and maximise γ_f^I

Variables	Best Operating Conditions		
	γ_f^{III}	γ_f^I	S
pH	1.5	1.5	3.5/1.5
v (rpm)	–	–	160
w_s (%)	–	–	2
w_c (%)	20	20	20
t (minutes)	30	–	10

To define the best operating values for each variable, which present a different influence upon each response, some criteria were adopted to make the right choice. The first one is based on the extraction mechanism, which enables better separation efficiency at low values of pH (1.5). The second criterion is associated with the membrane stability, which is impaired if high values of v and t are used. In the case of v , an intermediate value (145 rpm) was chosen because too low stirring speeds produce bad homogenisation of the system and high values can lead to significant breakage rates of the emulsion globules, thus yielding low efficiency of citric acid recovery. The permeation time was defined in the low value (10 minutes) because the longer the t value is, the lower is the system stability, although the separation efficiency is usually enhanced. For the variable w_c , all responses present the best results at 20 %, and for w_s , suitable conditions for recovery of the solute are obtained at 2 %. Based on these results, a new region was defined to carry out a complete factorial design around the point $pH = 1.5$, $w_s = 2$ %, $w_c = 20$ %, $v = 145$ rpm and $t = 10$ minutes.

To perform the 2^3 factorial design, the variables v and w_s were set at 145 rpm and 2 %, respectively, because both factors revealed a slight influence upon the responses. The variables pH , w_c and t were included into this design, adopting new operating levels, in accordance with the data presented in Table 2.

The statistical analysis of the data obtained from 2^3 design, summarized in Appendix A, indicated that the variables w_c and t affect the citric acid concentration in the inner phase (γ_f^I), although this influence is quite limited because of the narrow range of the studied values. Evaluating the signal of the effects, the best values of γ_f^I are obtained choosing higher concentrations of carrier ($w_c = 30$ %) and longer permeation times ($t = 10$ minutes).

In the case of γ_f^{III} , the main factors pH , w_c , t and the interactions $pH \cdot w_c$ and $pH \cdot t$ were significant to the response. As explained in the 2^{5-1} factorial design, interaction plots were necessary to define the best operating levels for this response. The analysis of respective interaction plots, which are not presented here, indicated $pH = 1.5$, $w_c = 30$ % and $t = 10$ minutes as the suitable operating conditions to minimise the γ_f^{III} .

For the swelling, all main factors pH , w_c and t presented some significant effect upon the system. Evaluating the signal of the effects, the best conditions to minimise the swelling are obtained operating at $pH = 2.5$, $w_c = 30$ % and $t = 3$ minutes. The best conditions for each response are summarized in Table 5.

Table 5 – Best operating conditions established for responses γ_f^I , γ_f^{III} and S

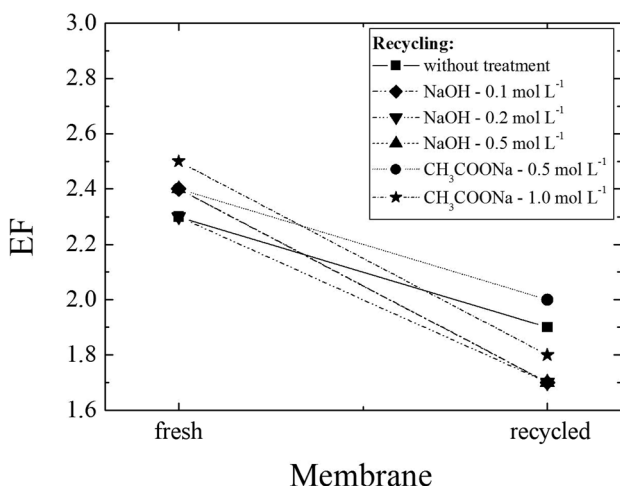
Variables	Best Operating Conditions		
	γ_f^I	γ_f^{III}	S
pH	–	1.5	2.5
w_c (%)	30	30	30
t (minutes)	10	10	3

The ideal conditions to operate the system should be set at maximum value of γ_f^I and minimal values of γ_f^{III} and S . Nevertheless, the results of both factorial designs have shown that is not possible to satisfy these criteria in a unique set of experimental conditions. Besides, at $w_c = 30$ %, in which the most promising results were obtained for all responses, problems with handling and coalescence of the emulsions were found due to their high viscosity. Thus, the choice of the most suitable conditions was restricted to values of w_c up to 20 %. Among the remaining conditions, the best results were obtained at $pH = 1.5$, $w_c = 20$ % and $t = 10$ minutes, with fixed factors set at $v = 145$ rpm and $w_s = 2$ %, yielding $\gamma_f^I = 0.25$ g mL⁻¹, $\gamma_f^{III} = 0.04$ g mL⁻¹ and $S = 80$ %.

Membrane recycling

The membrane recycling experiments were performed under the best conditions defined from the 2³ factorial design. The results for fresh and recycled membranes are expressed in terms of the enrichment factor (EF) versus the membrane condition, as presented in Fig. 5.

In this figure, the enrichment factor (EF) of the system decreases when the recycled membranes are used. In the experiments performed with fresh membranes, the mean value of the enrichment factor is EF

Fig. 5 – Enrichment factor (EF) versus membrane condition

= 2.4, while in the tests with recycling the mean value obtained is $EF = 1.8$. These data show a 25 % decrease in the concentration capacity of the system when a recycled membrane phase is used. The swelling showed small difference from fresh to recycled membrane, presenting mean values equal to $S = 73$ % for fresh and $S = 81$ % for recycled.

The decrease in the EF value when a recycled membrane is used is probably due to partial loading of the organic phase with the solute extracted in the first membrane extraction. As a result, the amount of solute that remains attached to the carrier molecules in the subsequent stages reduces the quantity of the citric acid removed from the feed phase, decreasing the extraction percentage, and consequently the enrichment factor.

To complement the results obtained for recycled membranes, new experiments were performed to evaluate the effect of the number of recycling stages on the separation efficiency using the same membrane. Membrane recycling was carried out without treatment because the enrichment factor obtained in this condition ($EF = 1.9$) was very close to the mean value ($EF = 1.8$), and no swelling changes were observed after recycling ($S \sim 70$ %). In each stage, fresh feed solutions containing 0.1 g mL⁻¹ of citric acid were used. The results are presented in Fig. 6.

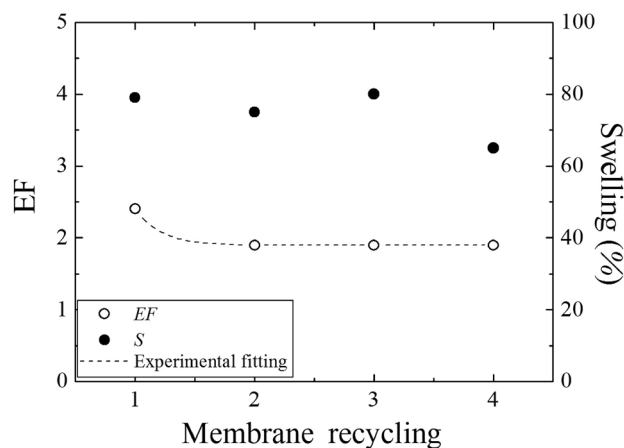


Fig. 6 – Enrichment factor and inner phase swelling as a function of membrane recycling

As expected, the EF data presented in Fig. 6 show a decrease in the extraction efficiency of the system after the first recycling of the membrane phase, remaining approximately constant for the other stages. From the second recycling onward, the membrane phase is already saturated with solute and, consequently, the extraction of citric acid remains unchanged.

The swelling data do not show significant dependence on the condition of the membrane phase,

presenting a stable value between 75 and 80 %, except in the fourth stage, where a more pronounced decrease is observed, probably related to the inner phase losses during the process since the EF value remained constant.

Multistage extraction

The efficiency of the LSM process was also evaluated in terms of citric acid extraction in multiple stages. Two sequences of experiments were carried out using a fresh feed phase for each sequence, using firstly fresh, and secondly the recycled membranes. The results are presented in Figs. 7 and 8.

In Fig. 7, it is possible to observe that extraction with the fresh membrane occurs more quickly than with the recycled membranes in the first and second stages. However, from the third stage onward, the citric acid concentration in the feed phase (γ_f^{III}) is re-

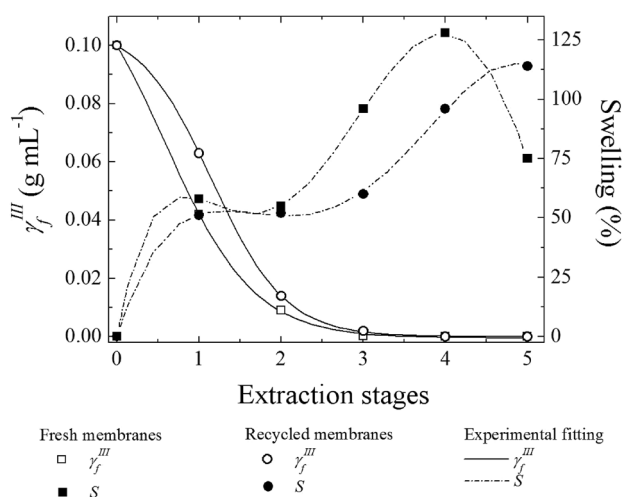


Fig. 7 – Final citric acid concentration in feed phase (γ_f^{III}) and swelling (S) of the inner phase as a function of the number of extraction stages

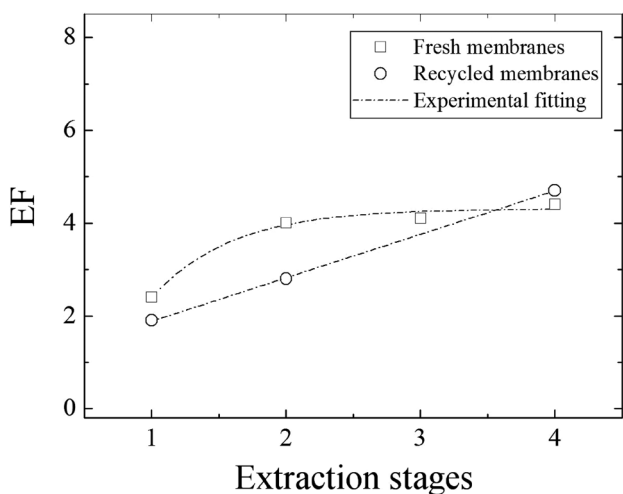


Fig. 8 – Enrichment factor (EF) versus the number of extraction stages

duced to almost null value, regardless of membrane phase condition. In case of swelling, fresh membranes present more pronounced S until the fourth stage, while for recycled membranes this occurs at the fifth stage. The increase in swelling with extraction stage is expected because the ionic force difference between aqueous phases increases as soon as the citric acid is extracted from the feed phase. In order to reduce this difference, the osmotic phenomenon induces water transport to the inner phase, producing the observed swelling increase. The decrease in swelling at the fifth stage of extraction for fresh membranes could be caused by the loss of the inner phase because the ionic force difference between aqueous phases at the fourth and the fifth stages is approximately the same. Consequently, the effect of the osmosis upon the swelling should be the same.

Besides the fact that extraction with fresh membranes is greater than with recycled membranes, the swelling in the former case leads to stabilisation of the EF value as the number of the stages increases, as shown in Fig. 8. In the case of recycled membranes, in spite of the EF value rising slower in the first and second stages, the smaller swelling in most experiments provides a higher value of the enrichment factor in the fourth stage.

Conclusions

In this work, suitable operating conditions for performing the citric acid separation from aqueous solutions, using the liquid surfactant membrane technique, were defined. Two factorial designs were used to conduct the first part of the experiments, which revealed the influence of the variables pH of the feed phase, carrier concentration in organic phase, and permeation time on final concentration of the citric acid, in the feed and inner phase, and on the swelling. Both surfactant concentration and stirring speed presented only a slight influence on these responses. The best conditions were defined at $pH = 1.5$, $w_s = 2\%$, $w_c = 20\%$, $v = 145$ rpm and $t = 10$ minutes.

The influence of pH and w_c on the extraction was somewhat expected because the pH directly interferes in the facilitated transport of the solute carried out by the Alamine 336. However, the interaction observed between pH and carrier concentration reported through factorials, permitted the evaluation of both variables at the same time to define the most suitable operating conditions for carrying out the extraction. Although the influence of permeation time on the extraction was also predictable, the use of the fractional factorial design indicated that its effect on the swelling is much more complex, and the use of a short time was more favourable for this system. Furthermore, the use of factorials, in gener-

al, permitted the definition of a starting point to evaluate the behaviour of each variable separately, which will be discussed in a forthcoming paper.

The study of membrane phase recycling showed that, after the first step of recycling, the system presented a decrease in the enrichment factor probably caused by the partial loading of the organic phase with the solute extracted in the first membrane extraction. From the second recycling onward, the system remained unchanged, presenting the same extraction efficiency and good stability.

The solute extraction in multiple stages showed that approximately 100 % of the citric acid present in the feed phase could be recovered after three stages, regardless of membrane condition. However, the application of recycled membranes is more advantageous in terms of the inner phase swelling, which is 37.5 % smaller, as well as in terms of reduced costs with replenishment of reagents and treatment of organic phase residues.

Nomenclature

Symbols

- w_c – carrier mass fraction in membrane phase (%)
 w_s – surfactant mass fraction in membrane phase (%)
 E – effect (dimensionless)
 EF – enrichment factor (dimensionless)
 P – P -value (dimensionless)
 pH – pH of feed phase (dimensionless)
 S – inner phase swelling (%)
 V – volume (mL)
 v – permeation stirring speed (rpm)
 t – permeation time (minutes)

Subscripts

- i – initial
 f – final

Superscripts

- I – inner phase
 II – membrane phase
 III – feed phase

Greeks

- α – significance level (dimensionless)
 γ – citric acid concentration in aqueous phase (g mL⁻¹)

Abbreviations

- LSM – liquid surfactant membranes
 O/W/O – oil/water/oil emulsions
 W/O/W – water/oil/water emulsions

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APPENDIX A: Statistical Analysis Output

A1. 2⁵⁻¹ Fractional Factorial Design

Coded variables:

$$pH' = \frac{pH - 2,5}{1,0}; w_c' = \frac{w_c - 12,5}{7,5}; w_s' = \frac{w_s - 4}{2};$$

$$v' = \frac{v - 147,5}{12,5}; t' = \frac{t - 20}{10}$$

Analysis of final citric concentration in inner phase (γ_f^I)

Complete Model

Table A1 – Estimated effects and coefficients for C_f^I ($C_f^I = 100\gamma_f^I$) (fractional factorial fit 2⁵⁻¹)

Term	Effect	Coef	Std Coef	t-value	P
Constant		16.036	1.380	11.62	0.000
pH'	-7.134	-3.567	1.543	-2.31	0.082
v'	-0.029	-0.014	1.543	-0.01	0.993
w_s'	-1.599	-0.799	1.543	0.52	0.632
w_c'	9.179	4.589	1.543	2.98	0.041
t'	1.944	0.972	1.543	0.63	0.563
$pH' \cdot v'$	-0.104	-0.052	1.543	-0.03	0.975
$pH' \cdot w_s'$	-1.399	-0.699	1.543	0.45	0.674
$pH' \cdot w_c'$	-3.931	-1.966	1.543	-1.27	0.272
$pH' \cdot t'$	0.589	0.294	1.543	0.19	0.858
$v' \cdot w_s'$	1.081	0.541	1.543	0.35	0.744
$v' \cdot w_c'$	-0.711	-0.356	1.543	-0.23	0.829
$v' \cdot t'$	-0.926	-0.463	1.543	-0.30	0.779
$w_s' \cdot w_c'$	-0.776	-0.388	1.543	-0.25	0.814
$w_s' \cdot t'$	0.244	0.122	1.543	0.08	0.941
$w_c' \cdot t'$	-0.224	-0.112	1.543	-0.07	0.946

Simplified Model

Table A2 – Estimated regression coefficients for C_f^I ($C_f^I = 100\gamma_f^I$) (response surface regression 2⁵⁻¹)

Term	Coef	Stdev	t-ratio	P
Constant	21.548	1.3099	16.450	0.000
pH'	-3.567	0.6549	-5.446	0.000
w_c'	4.589	0.6549	7.007	0.000
$pH' \cdot pH'$	-6.889	1.4645	-4.704	0.000

Regression Analysis

The regression equation is:

$$\gamma_f^I = (21.5 - 3.57 pH' + 4.59 w_c' - 6.89 pH' \cdot pH')/100$$

$$s = 0.0262$$

$$R^2 = 86.3 \%$$

$$R^2(\text{adj}) = 83.7 \%$$

Analysis of final citric concentration in feed phase (γ_f^{III})

Complete Model

Table A3 – Estimated effects and coefficients for C_f^{III} ($C_f^{III} = 100\gamma_f^{III}$) (fractional factorial fit 2⁵⁻¹)

Term	Effect	Coef	Std Coef	t-value	P
Constant		6.772	0.3413	19.84	0.000
pH'	2.457	1.229	0.3816	3.22	0.032
v'	-0.243	-0.121	0.3816	-0.32	0.767
w_s'	0.037	0.019	0.3816	0.05	0.963
w_c'	-2.888	-1.444	0.3816	-3.78	0.019
t'	-1.170	-0.585	0.3816	-1.53	0.200
$pH' \cdot v'$	0.130	0.065	0.3816	0.17	0.873
$pH' \cdot w_s'$	0.160	0.080	0.3816	0.21	0.844
$pH' \cdot w_c'$	1.310	0.655	0.3816	1.72	0.161
$pH' \cdot t'$	0.432	0.216	0.3816	0.57	0.601
$v' \cdot w_s'$	-0.065	-0.033	0.3816	-0.09	0.936
$v' \cdot w_c'$	-0.035	-0.017	0.3816	-0.05	0.966
$v' \cdot t'$	-0.087	-0.044	0.3816	-0.11	0.914
$w_s' \cdot w_c'$	0.045	0.023	0.3816	0.06	0.956
$w_s' \cdot t'$	-0.058	-0.029	0.3816	-0.08	0.944
$w_c' \cdot t'$	-0.273	-0.136	0.3816	-0.36	0.739

Simplified Model

Table A4 – Estimated regression coefficients for C_f^{III} ($C_f^{III} = 100\gamma_f^{III}$) (response surface regression 2^{5-1})

Term	Coef	Stdev	t-ratio	P
Constant	5.407	0.16609	32.559	0.000
pH'	1.229	0.08304	14.797	0.000
w_c'	-1.444	0.08304	-17.386	0.000
t'	-0.585	0.08304	-7.045	0.000
$pH' \cdot w_c'$	0.655	0.08304	7.888	0.000
$pH' \cdot pH'$	1.705	0.18569	9.182	0.000

Regression Analysis

The regression equation is:

$$\gamma_f^{III} = (5.41 + 1.23 \text{ pH}' - 1.44 \text{ } w_c' - 0.585 \text{ } t' + 0.655 \text{ pH}' \cdot w_c' + 1.71 \text{ pH}' \cdot \text{pH}')/100$$

$$s = 0.0033 \quad R^2 = 98.1 \% \quad R^2(\text{adj}) = 97.4 \%$$

Analysis of inner phase swelling (S)

Complete Model

Table A5 – Estimated effects and coefficients for S (fractional factorial fit 2^{5-1})

Term	Effect	Coef	Std Coef	t-value	P
Constant		112.75	6.274	17.97	0.000
pH'	8.75	4.38	7.014	0.62	0.567
v'	-25.00	-12.50	7.014	-1.78	0.149
w_s'	18.75	9.37	7.014	1.34	0.252
w_c'	-53.75	-26.87	7.014	-3.83	0.019
t'	1.25	0.62	7.014	0.09	0.933
$pH' \cdot v'$	-41.25	-20.63	7.014	-2.94	0.042
$pH' \cdot w_s'$	-2.50	-1.25	7.014	-0.18	0.867
$pH' \cdot w_c'$	-15.00	-7.50	7.014	-1.07	0.345
$pH' \cdot t'$	-52.50	-26.25	7.014	-3.74	0.020
$v' \cdot w_s'$	46.25	23.12	7.014	3.30	0.030
$v' \cdot w_c'$	36.25	18.13	7.014	2.58	0.061
$v' \cdot t'$	58.75	29.37	7.014	4.19	0.014
$w_s' \cdot w_c'$	27.50	13.75	7.014	1.96	0.122
$w_s' \cdot t'$	32.50	16.25	7.014	2.32	0.081
$w_c' \cdot t'$	32.50	16.25	7.014	2.32	0.081

Simplified Model

Table A6 – Estimated regression coefficients for S (regression analysis 2^{5-1})

Term	Coef	Stdev	t-ratio	P
Constant	88.750	7.726	11.49	0.000
pH'	4.375	3.863	1.13	0.309
v'	-12.500	3.863	-3.24	0.023
w_s'	9.375	3.863	2.43	0.060
w_c'	-26.875	3.863	-6.96	0.001
t'	0.625	3.863	0.16	0.878
$pH' \cdot v'$	-20.625	3.863	-5.34	0.003
$pH' \cdot t'$	-26.250	3.863	-6.80	0.001
$v' \cdot w_s'$	23.125	3.863	5.99	0.002
$v' \cdot w_c'$	18.125	3.863	4.69	0.005
$v' \cdot t'$	29.375	3.863	7.60	0.001
$w_s' \cdot t'$	16.250	3.863	4.21	0.008
$w_c' \cdot t'$	16.250	3.863	4.21	0.008
$w_s' \cdot w_c'$	13.750	3.863	3.56	0.016
$pH' \cdot pH'$	30.000	8.638	3.47	0.018

Regression Analysis

The regression equation is:

$$S = 88.8 + 4.37 \text{ pH}' - 12.5 \text{ } v' + 9.37 \text{ } w_s' - 26.9 \text{ } w_c' + 0.62 \text{ } t' - 20.6 \text{ pH}' \cdot v' - 26.2 \text{ pH}' \cdot t' + 23.1 \text{ } v' \cdot w_s' + 18.1 \text{ } v' \cdot w_c' + 29.4 \text{ } v' \cdot t' + 16.3 \text{ } w_s' \cdot t' + 16.3 \text{ } w_c' \cdot t' + 13.8 \text{ } w_s' \cdot w_c' + 30.0 \text{ pH}' \cdot \text{pH}'$$

$$s = 15.45 \quad R^2 = 98.4 \% \quad R^2(\text{adj}) = 94.1 \%$$

A2. 2³ Complete Factorial Design

Coded variables:

$$pH'' = \frac{pH - 2,0}{0,5}; \quad w_c'' = \frac{w_c - 25}{5}; \quad t'' = \frac{t - 6,5}{3,5}$$

Analysis of final citric concentration in inner phase (γ_f^I)

Complete Model

Table A7 – Estimated effects and coefficients for C_f^I ($C_f^I = 100\gamma_f^I$) (fractional factorial fit 2^3)

Term	Effect	Coef	Std Coef	t-value	P
Constant		24.1313	0.3412	70.71	0.009
pH''	-1.3825	-0.6913	0.3412	-2.03	0.292
t''	4.0075	2.0038	0.3412	5.87	0.107
w_c''	2.6725	1.3363	0.3412	3.92	0.159
$pH'' \cdot t''$	1.4325	0.7162	0.3412	2.10	0.283
$pH'' \cdot w_c''$	-0.1925	-0.0962	0.3412	-0.28	0.825
$t'' \cdot w_c''$	-0.8225	-0.4112	0.3412	-1.21	0.441

Simplified Model

Table A8 – Estimated regression coefficients for C_f^I ($C_f^I = 100\gamma_f^I$) (response surface regression 2³)

Term	Coef	Stdev	t-ratio	P
Constant	24.1313	0.3135	76.974	0.000
pH''	-0.6913	0.3135	-2.205	0.115
t''	2.0038	0.3135	6.392	0.008
w _c ''	1.3363	0.3135	4.262	0.024
pH'' · t''	0.7162	0.3135	2.285	0.106

Regression Analysis

The regression equation is:

$$\gamma_f^I = (24.1 - 0.691 \text{ pH}'' + 2.00 \text{ t}'' + 1.34 \text{ w}_c'' + 0.716 \text{ pH}'' \cdot \text{t}'')/100$$

$$s = 0.8867 \quad R^2 = 95.8 \% \quad R^2(\text{adj}) = 90.3 \%$$

Analysis of final citric concentration in feed phase (γ_f^I)

Complete Model

Table A9 – Estimated effects and coefficients for C_f^III ($C_f^III = 100\gamma_f^III$) (fractional factorial fit 2³)

Term	Effect	Coef	Std Coef	t-value	P
Constant		5.2250	0.005000	1045.00	0.001
pH''	0.9900	0.4950	0.005000	99.00	0.006
t''	-1.8300	-0.9150	0.005000	-183.00	0.003
w _c ''	-0.7300	-0.3650	0.005000	-73.00	0.009
pH'' · t''	-0.2100	-0.1050	0.005000	-21.00	0.030
pH'' · w _c ''	0.1200	0.0600	0.005000	12.00	0.053
t'' · w _c ''	-0.0000	-0.0000	0.005000	-0.00	1.000

Simplified Model

Table A10 – Estimated regression coefficients for C_f^III ($C_f^III = 100\gamma_f^III$) (response surface regression 2³)

Term	Coef	Stdev	t-ratio	P
Constant	5.2250	0.06052	86.337	0.000
pH''	0.4950	0.06052	8.179	0.001
t''	-0.9150	0.06052	-15.119	0.000
w _c ''	-0.3650	0.06052	-6.031	0.004

Regression Analysis

The regression equation is:

$$\gamma_f^III = (5.22 + 0.495 \text{ pH}'' - 0.915 \text{ t}'' - 0.365 \text{ w}_c'')/100$$

$$s = 0.0017 \quad R^2 = 98.8 \% \quad R^2(\text{adj}) = 97.9 \%$$

Analysis of inner phase swelling (S)

Complete Model

Table A11 – Estimated effects and coefficients for S (response surface regression 2³)

Term	Effect	Coef	Std Coef	t-value	P
Constant		56.250	1.250	45.00	0.014
pH''	-12.500	-6.250	1.250	-5.00	0.126
t''	25.000	12.500	1.250	10.00	0.063
w _c ''	-10.000	-5.000	1.250	-4.00	0.156
pH'' · t''	5.000	2.500	1.250	2.00	0.295
pH'' · w _c ''	5.000	2.500	1.250	2.00	0.295
t'' · w _c ''	2.500	1.250	1.250	1.00	0.500

Simplified Model

Table A12 – Estimated regression coefficients for S (response surface regression 2³)

Term	Coef	Stdev	t-ratio	P
Constant	56.250	1.976	28.460	0.000
pH''	-6.250	1.976	-3.162	0.034
t''	12.500	1.976	6.325	0.003
w _c ''	-5.000	1.976	-2.530	0.065

Regression Analysis

The regression equation is:

$$S = 56.2 - 6.25 \text{ pH}'' + 12.5 \text{ t}'' - 5.00 \text{ w}_c''$$

$$s = 5.590 \quad R^2 = 93.4 \% \quad R^2(\text{adj}) = 88.4 \%$$

