Parametric Optimization of Lactic Acid Extraction from Aqueous Solution in a Mixed Flow Reactor Using Emulsion Liquid Membrane by Response Surface Methodology

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A statistical programme using Box-Behnken design, which applies a response optimization algorithm, was used to calculate and optimize simultaneously the lactic acid extraction by emulsion liquid membrane (ELM) in a mixed flow reactor. A 3-level Box-Behnken design with seven variables i.e. lactic acid concentration, internal reagent concentration, Alamine 336 fraction in oleyl alcohol, stirring speed, fraction of acceptor phase containing internal reagent in emulsion, feed: emulsion ratio and residence time was used to identify a significant correlation between the effect of these variables on lactic acid extraction from aqueous phase since the conventional practice of single factor optimization by maintaining other factors at an unspecified constant level does not depict the combined effect of all the factors involved. The experimental values were found to be in good agreement with predicted values. The analysis of the variance (ANOVA) shows that all the extraction process parameters significantly affect the performance, as well as shows that there are some interactions between the extraction parameters. The contribution of feed: emulsion ratio and stirring speed on extraction efficiency was more than other factors and the fraction of acceptor phase in emulsion has minimum contribution. The optimum value of the process parameters for the maximization of extraction of lactic acid from aqueous phase using ELM in MFR by the application of Box-Behnken design has been found. The recommended optimal conditions have been verified by conducting confirmation experiments. It can be concluded that the Box-Behnken experimental design provides a suitable means of optimizing and testing the robustness of lactic acid extraction in a MFR using emulsion liquid membrane and 100 % lactic acid extraction in MFR using ELM from aqueous feed can be achieved in few minutes within the specified range of independent process parameters.

Key words:
Emulsion liquid membrane, lactic acid, extraction, mixed flow reactor, response surface methodology

Introduction

Lactic acid (2-hydroxypropionic acid) is a versatile organic chemical being an acid and alcohol. Lactic acid has huge market potential as a feedstock for the synthesis with a high added value. Lactic acid esters are used for preparation of a polylactates, biodegradable polymers with common industrial use. Biotechnologically produced lactic acid, its salts and esters are extensively used in food, animal feed, in leather tanning, textile dyeing etc.[1] Lactic acid exists as two optical isomers, D- and L-lactic acid. Several novel processes are being developed for the production and purification of lactic acid. The conventional recovery processes of lactic acid from fermentation broth are quite complicated, expensive and unfriendly to the environment, account up to 50 % of the production costs. A number of processes like solvent extraction, membrane bioreactor, liquid surfactant membrane extraction, adsorption, direct distillation, electrodialysis, reverse osmosis, anion exchange, etc. for lactic acid recovery from fermentation broth without precipitation have been studied and reported in the literature.[2,1] The use of extractive ultra filtration for lactic acid extraction has been found useful in batch processing; however for a continuous operation the process has a serious limitation of organic phase extraction capacity.[25] The separation, purification and pre-concentration of lactic acid obtained by fermentation is rather difficult due its chemical behavior as 2-hydroxypropionic acid, strong affinity to water and low volatility, which renders difficult its separation by solvent extraction or distillation.[3] The high cost of current lactic acid production technology is mainly due to the expensive recovery and purification of lactic acid from crude fermentation. Aiming at the significant reduction of production costs and the production of high-purity lactic acid, the development of novel bioseparation techniques for recovering and purifying lactic acid and other biological component can have a major impact on reducing the production cost.[4] Reactive extraction of lactic acid by a suitable extractant has been found to be a promising alternative to the conventional process. Moreover, the capacities of treating dilute solutions make the liquid membrane technique an attractive alternative to solvent extraction.[5] The combination and integration of recovery by liquid emulsion membrane will lead to a high-performance process for economic production of lactic acid. The foremost condition of an economic recovery by extraction is high distribution coefficient. Amine extractants have been extensively studied because of their high efficiency and selectivity. Different amines and diluents have been used for lactic acid extraction. Among the tertiary amines tri-*n*-octylamine, Alamine 336, tri-iso-octylamine and tridodecylamine are the most often utilized as carriers. The frequently applied diluents are octanol, decanol, oleyl alcohol, butyl acetate, chloroform, methylisobutyl ketone, hexane, toluene, paraffin oil.[6] It has been reported that long-chain tertiary amines are suitable for the recovery of carboxylic acid from aqueous solutions. Alamine 336 in oleyl alcohol gives the highest distribution coefficient.[7] For carrier (extractant) facilitated transport, the carrier in the membrane phase, which belongs to surface active agents can also cause permeation swelling of ELMs. It has been suggested that the swelling phenomena during lactic acid extraction could be explained by the surfactant solubilization–diffusion mechanism combined with the carrier–solute and reaction–solubilization–diffusion mechanism.[26,28] Statistical factorial experiments on extraction of lactic acid from clarified fermentation broth using Alamine 336 as carrier in membrane phase have been performed, however, the extraction efficiency from the fermentation broth was lower than that from aqueous phase.[27]

It is evident from the literature survey that a number of researchers have carried out the study on extraction of organic solutes from aqueous solutions using ELM in a batch reactor and such studies are few in flow reactors.[5–18,26] To the best of our knowledge, no effort has been made so far for optimization of lactic acid extraction by ELM in MFR. For the success of lactic acid extraction by the ELM process, it is necessary to establish the influence of all the parameters involved in the design of the process, so that the most suitable conditions to effectively achieve the extraction of lactic acid can be defined. Experimental design is a very powerful tool for the search of the variables that predominantly affect the extraction process.[30] Many statistical experimental designs have been recognized as useful techniques to optimize the process variables. Optimization of parameters by the conventional method involves changing one independent variable while unchanging all others at a fixed level. Conventional practice of single factor optimization by maintaining other factors at an unspecified constant level does not depict the combined effect of all the factors involved. Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. It also has important applications in the design, development and formulation of new products as well as in improvements of existing product design. Response surface method is used to examine the relationship between one or two response variables and a set of quantitative variables or factors. Different types of RSM designs include 3-level factorial design, central composite design (CCD), Box-Behnken design, and D-optimal design. A modified central composite experimental design, Box-Behnken design, is an independent, rotatable or nearly rotatable quadratic design (contains no embedded factorial or fractional factorial design), in which the treatment combinations are at the midpoints of the edges of the process space and at the center.[20] Among all the RSM designs, we had employed a response surface method (RSM) in the form of the Box-Behnken design (BBD) to optimize lactic acid extraction in a mixed flow reactor because they offer advantages in comparison with central composite designs, i.e. fewer experiments are needed, they are more efficient, they can be moved through the experimental domain and they can even be easily contracted or expanded.[21] The Box-Behnken approach is a class of three-level partial factorial designs for ascertaining parameters in a second-order model. Merging two-level factorial designs and balanced incomplete block designs in a systematic way form the Box-Behnken designs. Keeping in view the above, in this work experimental and parametric optimization of lactic acid extraction by ELM in MFR using BBD has been carried out, which has not been done earlier.

Materials and methods

Experimental design

For the optimization of lactic acid extraction from aqueous solution using the ELM in a MFR, the experiments were conducted according to Box-Behnken design with seven variables at three levels each. The design was composed of 62 runs, no blocking, six center points, and seven factors.

Table 1 – *Range of different variables for lactic acid extraction using ELM in coded and un-coded form*

Coded values	Un-coded values						
	lactic acid concentration c/mol L^{-1}	sodium carbonate concentration c/mol L^{-1}	Alamine 336 fraction in oleyl alcohol φ/%, v/v	feed: emulsion ratio Ψ/v/v	stirring speed rpm	fraction of acceptor phase in emulsion φ/%, v/v	residence time τ/min
–1.000	0.001	0.1	10	10	200	0.125	10
0.000	0.0055	0.55	20	15	300	0.3215	35
+1.000	0.01	1.0	30	20	400	0.5	60

The design was generated by commercial statistical package, Design-Expert version 6.01 (Statease Inc., Minneapolis, USA, Trial version). The variables were lactic acid concentration, sodium carbonate concentration (internal reagent), Alamine 336 fraction in membrane phase φ (% v/v), feed to emulsion ratio Ψ (v/v), stirring speed (rpm), fraction of acceptor phase in emulsion φ (% v/v) and residence time τ/min. The low level and high level in the actual (un-coded) form were taken as (Table 1). The ranges of these variables were selected on the basis of preliminary experiments by using one variable at a time approach. The experiments plan in coded form of process variables is as given in Table 2. The experiments were conducted randomly to minimize the effect of extraneous variables.

Apparatus

Experimental setup consists of homogenizer with a variable speed of 50–6000 rpm used for the preparation of stable w/o emulsion made of Alamine 336 diluted in oleyl alcohol as membrane phase and internal reagent, aqueous sodium carbonate as acceptor phase. The emulsion immediately washed with excess water to remove any internal reagent attached to the surface of emulsion globule and transferred to the settler. Then the emulsion is pumped with the help peristaltic pump to a cylindrical glass vessel having stirring arrangement with the help four blade agitator along with two inlet at the top and one outlet at the lower portion which was used as mixed flow reactor (MFR) by controlling the inlet and outlet flow rate with the help of valves. The continuous phase was transferred to the MFR with the help of pneumatic pressure applied in the vessel containing aqueous lactic acid of desired concentration. In the MFR emulsion phase was dispersed in continuous phase with the help of stirring. Mixture obtained from the outlet of reactor was immediately transferred the funnel containing Whatman 42 filter paper to separate the extract enriched emulsion from raffinate.[8] The raffinate was analyzed for lactic acid concentration.

Experimental procedure

The membrane phase was prepared by mixing surfactant φ = 4 % (v /v) span 80 in organic solvent consists of Alamine 336 and oleyl alcohol in the homogenizer under constant stirring speed of 500 rpm for 2 min. Then emulsion phase was prepared by adding internal reagent in the membrane phase and emulsifying by stirring with the help of four blade agitator at 2500 rpm for 10 min. Then emulsion was transferred to settler after washing the emulsion with excess deionised water to wipe out the internal reagents attached to the surface of emulsion if any. The emulsion was transferred to MFR at constant flow rate in accordance with the residence time with the help of peristaltic pump, E. The aqueous phase containing known concentration of LA was introduced at precalibrated flow rate to maintain the required F:E ratio. The continuous phase (aqueous LA) was allowed to contact with emulsion in the MFR by constantly stirring the contents at known speed in the MFR. The flow rate of the outlet is maintained with the help of valve to achieve steady state in the MFR. Then the emulsion enriched with extractant was separated from the mixture obtained from the outlet of MFR[8] and concentration of lactic acid in the raffinate was analyzed. The experiments were repeated twice to check the reproducibility of the results and average value was taken for the statistical analysis and optimization.

Statistical analysis and optimization

The response surface and contour plots were generated for different interactions of any two independent variables while holding the values of the other variables as constant. Such three-dimensional surfaces could give accurate geometrical representation and provide useful information about the behavior of the system within the experimental design. The optimization of the extraction was aimed at finding the levels of independent variables, viz. lactic acid concentration in aqueous phase, sodium carbonate concentration, Alamine 336 fraction φ (% v/v) in membrane phase, feed: emulsion ratio, stirring speed, fraction of acceptor phase in emul-

Table 2 – *Box-Behnken design of process variables and value of experimental data for lactic acid extraction using ELM in MFR*

Coded variables				Response			
lactic acid concentration (X_1)	sodium carbonate concentration (X_2)	Alamine 336 fraction in oleyl alcohol (X_3)	feed: emulsion ratio (X_4)	stirring speed (X_5)	fraction of acceptor phase in emulsion (X_6)	residence time (X_7)	extraction (%) (Y)
0.000	0.000	0.000	-1.000	-1.000	-1.000	0.000	92.00
0.000	0.000	0.000	1.000	-1.000	-1.000	0.000	84.97
0.000	0.000	0.000	-1.000	1.000	-1.000	0.000	95.65
0.000	0.000	0.000	1.000	1.000	-1.000	0.000	94.88
0.000	0.000	0.000	-1.000	-1.000	1.000	0.000	93.54
0.000	0.000	0.000	1.000	-1.000	1.000	0.000	86.68
0.000	0.000	0.000	-1.000	1.000	1.000	0.000	95.28
0.000	0.000	0.000	1.000	1.000	1.000	0.000	95.00
-1.000	0.000	0.000	0.000	0.000	-1.000	-1.000	84.82
1.000	0.000	0.000	0.000	0.000	-1.000	-1.000	81.53
-1.000	0.000	0.000	0.000	0.000	1.000	-1.000	87.04
1.000	0.000	0.000	0.000	0.000	1.000	-1.000	82.60
-1.000	0.000	0.000	0.000	0.000	-1.000	1.000	96.18
1.000	0.000	0.000	0.000	0.000	-1.000	1.000	93.67
-1.000	0.000	0.000	0.000	0.000	1.000	1.000	96.67
1.000	0.000	0.000	0.000	0.000	1.000	1.000	93.58
0.000	-1.000	0.000	0.000	-1.000	0.000	-1.000	75.34
0.000	1.000	0.000	0.000	-1.000	0.000	-1.000	79.70
0.000	-1.000	0.000	0.000	1.000	0.000	-1.000	88.14
0.000	1.000	0.000	0.000	1.000	0.000	-1.000	86.17
0.000	-1.000	0.000	0.000	-1.000	0.000	1.000	88.95
0.000	1.000	0.000	0.000	-1.000	0.000	1.000	95.10
0.000	-1.000	0.000	0.000	1.000	0.000	1.000	94.90
0.000	1.000	0.000	0.000	1.000	0.000	1.000	95.00
-1.000	-1.000	0.000	-1.000	0.000	0.000	0.000	97.03
1.000	-1.000	0.000	-1.000	0.000	0.000	0.000	93.88
-1.000	1.000	0.000	-1.000	0.000	0.000	0.000	95.36
1.000	1.000	0.000	-1.000	0.000	0.000	0.000	94.84
-1.000	-1.000	0.000	1.000	0.000	0.000	0.000	92.43
1.000	-1.000	0.000	1.000	0.000	0.000	0.000	84.82
-1.000	1.000	0.000	1.000	0.000	0.000	0.000	95.98
1.000	1.000	0.000	1.000	0.000	0.000	0.000	91.30
0.000	0.000	-1.000	-1.000	0.000	0.000	-1.000	87.40
0.000	0.000	1.000	-1.000	0.000	0.000	-1.000	88.99
0.000	0.000	-1.000	1.000	0.000	0.000	-1.000	80.00
0.000	0.000	1.000	1.000	0.000	0.000	-1.000	82.02
0.000	0.000	-1.000	-1.000	0.000	0.000	1.000	96.00
0.000	0.000	1.000	-1.000	0.000	0.000	1.000	96.40
0.000	0.000	-1.000	1.000	0.000	0.000	1.000	95.05
0.000	0.000	1.000	1.000	0.000	0.000	1.000	95.59
-1.000	0.000	-1.000	0.000	-1.000	0.000	0.000	88.99
1.000	0.000	-1.000	0.000	-1.000	0.000	0.000	83.13
-1.000	0.000	1.000	0.000	-1.000	0.000	0.000	92.47
1.000	0.000	1.000	0.000	-1.000	0.000	0.000	86.91
-1.000	0.000	-1.000	0.000	1.000	0.000	0.000	94.58
1.000	0.000	-1.000	0.000	1.000	0.000	0.000	92.92
-1.000	0.000	1.000	0.000	1.000	0.000	0.000	94.79
1.000	0.000	1.000	0.000	1.000	0.000	0.000	93.00
0.000	-1.000	-1.000	0.000	0.000	-1.000	0.000	90.69
0.000	1.000	-1.000	0.000	0.000	-1.000	0.000	95.61
0.000	-1.000	1.000	0.000	0.000	-1.000	0.000	94.90
0.000	1.000	1.000	0.000	0.000	-1.000	0.000	95.12
0.000	-1.000	-1.000	0.000	0.000	1.000	0.000	91.60
0.000	1.000	-1.000	0.000	0.000	1.000	0.000	96.02
0.000	-1.000	1.000	0.000	0.000	1.000	0.000	95.12
0.000	1.000	1.000	0.000	0.000	1.000	0.000	95.93
0.000	0.000	0.000	0.000	0.000	0.000	0.000	94.50
0.000	0.000	0.000	0.000	0.000	0.000	0.000	94.50
0.000	0.000	0.000	0.000	0.000	0.000	0.000	94.50
0.000	0.000	0.000	0.000	0.000	0.000	0.000	94.80
0.000	0.000	0.000	0.000	0.000	0.000	0.000	94.15
0.000	0.000	0.000	0.000	0.000	0.000	0.000	94.50

sion, residence time, which would give maximum extraction of lactic acid from aqueous phase. Response surface methodology was applied to the experimental data using a commercial statistical package, Design-Expert version 6.01 (Statease Inc., Minneapolis, USA, Trial version) for the generation of response surface and contour plots. The same software was used for the optimization of process variables. The first analysis step in RSM is to fit regression equation to the responses. After the regression models built by, tests were performed to find out, whether the regression models satisfy the normality and constant variance assumptions. The optimum level of variables (within the experimental range) to obtain the maximum extraction were determined by running the experiments using the optimum values for variables given by response optimization for confirmation of predicted values and maximum extraction was confirmed.

Analytical method

Lactic acid concentration was measured by a calorimetric method using UV/VIS – spectrophotometer model DR 5000 HACH, USA.[22]

Mathematical calculations

Calculation of lactic acid extraction

When the emulsion membrane is brought in contact with aqueous phase, the concentration of lactic acid in the aqueous phase starts decreasing with time because of solute transfer across membrane into internal phase i.e., Extraction of solute has been carried out. Extraction (%) had been determined as below.

Extraction efficiency (%)

$$\eta_{\text{ext.}} = \frac{c_{0_{\text{aq}}} - c_{t_{\text{aq}}}}{c_{0_{\text{aq}}}} \cdot 100$$

where, $c_{0_{\text{aq}}}$ is the lactic acid concentration in aqueous phase initially at time, $t = 0$, before contacting it with the emulsion globules.

$c_{t_{\text{aq}}}$ is the lactic acid concentration in aqueous phase after contacting the aqueous phase with emulsion liquid membrane for time t.

Results and discussion

Regression model

For extraction efficiency (%), the fit summary recommended that the quadratic model is significant for analysis. The ANOVA for a quadratic model before elimination of non-significant terms had thirty-five terms which contain seven linear terms, seven quadratic terms and twenty-one two-factorial interactions. Probability $p > f$ values were used as a tool to check the significance of each of the coefficients. The terms having $p > f$ values more than 0.05 are insignificant terms, means it have negligible effect on the extraction. The smaller the magnitude of p values, the more significant was the correlation with the corresponding coefficient. To fit the quadratic model for extraction appropriately; the non-significant terms are eliminated by backward elimination process. Table 3 represents the ANOVA table for a quadratic model after backward elimination with alpha out 0.0500. The reduced model results indicated that the model is significant (R^2 and adjusted R^2 are 99.82 % and 99.68 % respectively), lack of fit is non-significant. Fig. 1 displays the normal probability plot of the studentized residuals for extraction lactic acid in MFR.

After elimination the non-significant terms the final response equation for extraction (%) is given as follows (In terms of coded factors)

$$\begin{aligned}
&\text{Extraction (\%)} = 94.28179 - 1.84 \cdot X_1 + \\
&+ 1.180417 \cdot X_2 + 0.802083 \cdot X_3 - 1.98542 \cdot X_4 + \\
&+ 3.022083 \cdot X_5 + 0.376667 \cdot X_6 + 5.555833 \cdot X_7 - \\
&- 1.05141 \cdot X_1^2 - 2.32829 \cdot X_5^2 + 0.233586 \cdot X_6^2 - \\
&- 4.03141 \cdot X_7^2 + 0.695 \cdot X_1 \cdot X_2 - 1.0775 \cdot X_1 \cdot X_4 + \\
&+ 0.99625 \cdot X_1 \cdot X_5 - 0.21625 \cdot X_1 \cdot X_6 + \\
&+ 0.26625 \cdot X_1 \cdot X_7 - 1.03875 \cdot X_2 \cdot X_3 + \\
&+ 0.3425 \cdot X_2 \cdot X_4 - 1.5475 \cdot X_2 \cdot X_5 + \\
&+ 0.4825 \cdot X_2 \cdot X_7 - 0.87125 \cdot X_3 \cdot X_5 - \\
&- 0.33375 \cdot X_3 \cdot X_7 + 1.605 \cdot X_4 \cdot X_5 + \\
&+ 1.57625 \cdot X_4 \cdot X_7 - 0.4375 \cdot X_5 \cdot X_6 - \\
&- 1.6775 \cdot X_5 \cdot X_7 - 0.36125 \cdot X_6 \cdot X_7
\end{aligned} \tag{I}$$

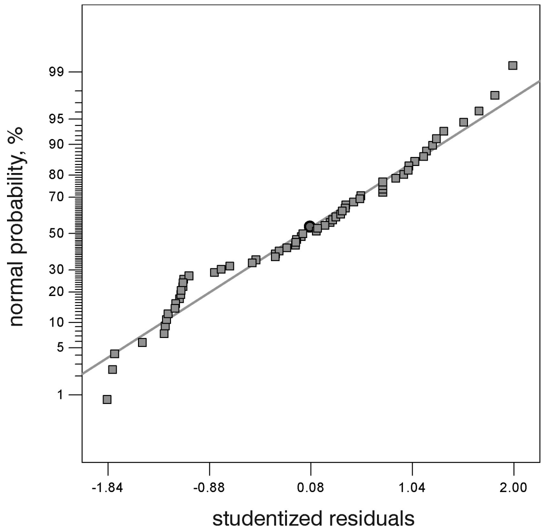

Fig. 1 – *Normal probability plot of the studentized residuals for lactic acid extraction (%)*

Table 3 – *Regression model and annova for lactic acid extraction using ELM in MFR (after backward elimination)*

Source	Sum of squares	Degree of freedom	Mean square	f – value	$p > f$
Model	1625.651	27	60.20931	700.2938	< 0.0001
lactic acid concentration (X_1)	81.2544	1	81.2544	945.069	< 0.0001
sodium carbonate concentration (X_2)	33.4412	1	33.4412	388.9543	< 0.0001
Alamine 336 fraction in oleyl alcohol (X_3)	15.4401	1	15.4401	179.5837	< 0.0001
feed: emulsion ratio (X_4)	94.6051	1	94.6051	1100.351	< 0.0001
stirring speed (X_5)	219.1917	1	219.1917	2549.416	< 0.0001
fraction of acceptor phase in emulsion (X_6)	3.405067	1	3.405067	39.60429	< 0.0001
residence time (X_7)	740.8148	1	740.8148	8616.409	< 0.0001
$(X_1) \cdot (X_1)$	15.80588	1	15.80588	183.838	< 0.0001
$(X_5) \cdot (X_5)$	77.50774	1	77.50774	901.4917	< 0.0001
$(X_6) \cdot (X_6)$	0.780129	1	0.780129	9.073667	0.0049
$(X_7) \cdot (X_7)$	232.3733	1	232.3733	2702.731	< 0.0001
$(X_1) \cdot (X_2)$	3.8642	1	3.8642	44.94447	< 0.0001
$(X_1) \cdot (X_4)$	9.28805	1	9.28805	108.0292	< 0.0001
$(X_1) \cdot (X_5)$	7.940112	1	7.940112	92.35136	< 0.0001
$(X_1) \cdot (X_6)$	0.374112	1	0.374112	4.351298	0.0446
$(X_1) \cdot (X_7)$	0.567112	1	0.567112	6.596079	0.0148
$(X_2) \cdot (X_3)$	8.632013	1	8.632013	100.3988	< 0.0001
$(X_2) \cdot (X_4)$	14.41845	1	14.41845	167.7008	< 0.0001
$(X_2) \cdot (X_5)$	19.15805	1	19.15805	222.8271	< 0.0001
$(X_2) \cdot (X_7)$	1.86245	1	1.86245	21.66214	< 0.0001
$(X_3) \cdot (X_5)$	6.072612	1	6.072612	70.63049	< 0.0001
$(X_3) \cdot (X_7)$	0.891112	1	0.891112	10.36452	0.0028
$(X_4) \cdot (X_5)$	20.6082	1	20.6082	239.6938	< 0.0001
$(X_4) \cdot (X_7)$	19.87651	1	19.87651	231.1835	< 0.0001
$(X_5) \cdot (X_6)$	1.53125	1	1.53125	17.80995	0.0002
$(X_5) \cdot (X_7)$	22.51205	1	22.51205	261.8374	< 0.0001
$(X_6) \cdot (X_7)$	1.044013	1	1.044013	12.1429	0.0014
Residual	2.923225	34	0.085977		
Lack of fit	2.711142	29	0.093488	2.204031	0.1929*
Pure error	0.212083	5	0.042417		
Corrected total	1628.575	61			

Standard Deviation = 0.29

Mean = 91.50

Coefficient of variation = 0.32

Predicted residual error of sum of squares (PRESS) = 10.14

$R^2 = 0.9982$

Adjusted $R^2 = 0.9968$

Predicted $R^2 = 0.9936$

Adequate Precision = 108.674

*non-significant at 5 % level

where X_1 – lactic acid concentration, X_2 – sodium carbonate concentration, X_3 – Alamine 336 fraction, X_4 – feed: emulsion ratio, X_5 – stirring speed, X_6 – fraction of internal reagent in emulsion and X_7 – residence time.

It can be seen from the Fig. 1 that errors are normally distributed, since the residuals are falling on straight line. From Fig. 2 it can be easily concluded that regression model is fairly well fitted with observed values. The contour and response surface plots were drawn based on these responses for different interaction of any two independent variables while holding the values of other variables constant at coded values of 0.000. Such three-dimensional surfaces provide useful information regarding the behavior of the system within the experimental design. As per analysis of the variance, regression and linear effect, the outputs were quite significant for the extraction of lactic acid by emulsion liquid membrane in MFR. The *p* values (Table 3) and coefficient of variables in the regression model indicates that the sodium carbonate concentration in acceptor phase, fraction of Alamine 336 in membrane phase, stirring speed, fraction of internal phase in emulsion and residence time have significant and positive effect on the extraction of lactic acid by ELM in MFR i.e. lactic acid extraction will increase with the increase of these parameters; while concentration of lactic acid and feed: emulsion ratio have significant and negative effect on the extraction i.e. significantly decrease in lactic acid extraction with the increase in lactic acid concentration in aqueous phase and feed: emulsion ratio.

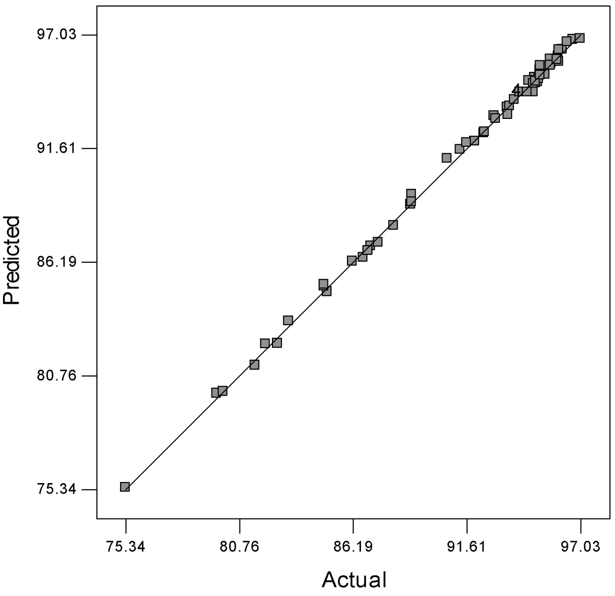

Fig. 2 – *Plot of predicted vs. actual response of lactic acid extraction (%) data*

Extraction of lactic acid

Mass transfer mechanism

A diffusing species is transported by incorporating a carrier (or extractant) in the membrane phase. The carrier reacts reversibly with the diffusing species to form a complex at the interface of external and membrane phase, which in turn also diffuses in addition to the diffusing species, thereby augmenting the flux of the diffusing species through the membrane. This facilitation is known as facilitated transport (Fig. 3), and was applied to the extraction of lactic acid by ELMs. In this study, we have used Alamine 336, a water insoluble trioctyl/decyl amine as carrier for the facilitated transport of lactic acid. Generally, the reaction of the amines with un-dissociated lactic acid at the external and the internal interfaces can be expressed by *n* moles of un-dissociated lactic acid (HLa) reacts with *m* moles of carrier (R_3N) at the external interface to form 1 mole of complex $[(R_3N)_m(HLa)_n]$. The carrier–solute complex diffuses onto the interface of the acceptor phase,

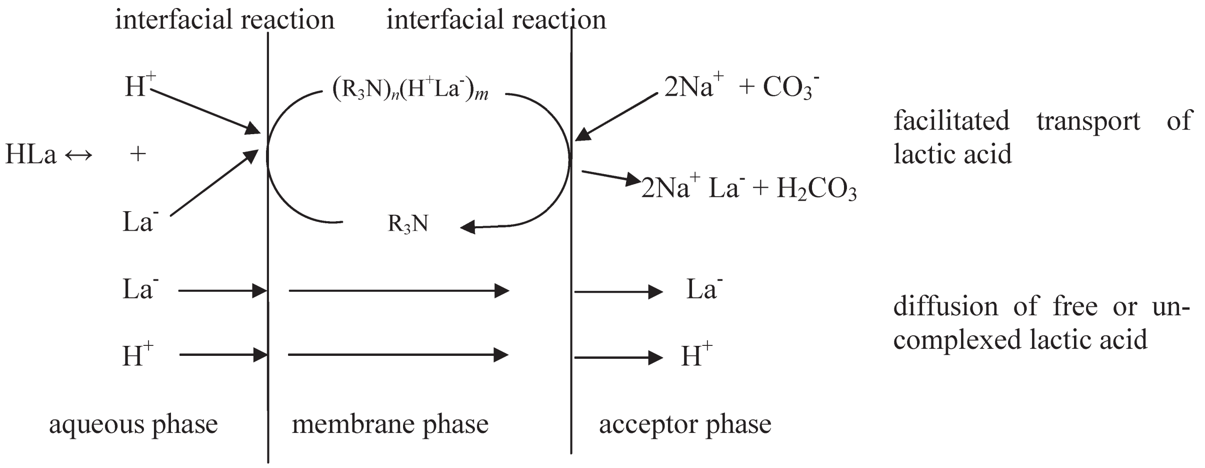

Fig. 3 – *Schematic representation of mass transfer mechanism of lactic acid facilitated permeation using Alamine 336 as carrier*

where it decomposes due to the high pH value in the acceptor phase and reacts with the stripping reagent Na_2CO_3 to release lactate ion and carrier[32] and the uncharged amine diffuses back. During lactic acid (HLa) extraction by ELMs, since pH difference between the external and the acceptor phase functions as a driving force for extraction of lactic acid in the system, it is possible to obtain a high extraction of lactic acid using the acceptor phase of high Na_2CO_3 concentration.

Effect of different variables

The model chosen satisfactory explained the effect of seven variables on the lactic acid extraction (eq. (I)). Significant interactions were noted between different variables as evident from Table 3. Graphical representation of response surfaces shown in Figs. 4–15 helped to visualize the effect of lactic acid concentration, sodium carbonate concentration, Alamine 336 fraction φ (% v/v) in oleyl alcohol, feed: emulsion ratio, stirring speed, fraction of acceptor phase in emulsion and residence time on lactic acid extraction. The extraction increases with the increase in sodium carbonate concentration in acceptor phase and with the decrease in lactic acid concentration in the aqueous phase. The maximum extraction can be obtained for maximum sodium carbonate concentration in the acceptor phase and minimum lactic acid concentration (Fig. 4). Because the capacity of the acceptor phase has got increased with the increase in sodium carbonate concentration in acceptor phase hence the extraction increases. With the increase in lactic acid concentration in the aqueous phase the extraction decreases indicating a nonlinear process with respect to lactic acid concentration. By considering the advancing front model[8] for the lactic acid diffusion in the ELM, it can be predicted that the extraction decrease is attributed to mass transfer resistance in the emulsion globule. Since at high concentration of lactic acid in aqueous phase the saturation of the internal droplets in the peripheral region of the emulsion is attained more rapidly and the lactic acid-Alamine 336 complex must diffuse through the membrane phase to the more inner region of the globule to release lactic acid in the acceptor phase.[31] Fig. 5 indicates that maximum extraction is possible with minimum lactic acid concentration as well as minimum feed: emulsion ratio. Decrease in feed: emulsion ratio makes increase in emulsions globules per unit volume; hence more surface area available for mass transfer and less external transfer distance for lactic acid molecule, which in turn gives maximum extraction.[4] Fig. 6 indicates that increase in extraction may be obtained with the increase in stirring speed and decrease in lactic acid concentration. With the increase in stirring speed the mass transfer coefficient in the continuous phase increases and the emulsion globule size decreases since the globule size inversely dependent on stirring speed;[8] hence providing more surface area for mass transfer and lowers the resistance to mass transfer in continuous phase owing to increase in lactic acid extraction with the stirring speed. Fig. 7 shows that with the increase in fraction of acceptor phase in emulsion and decrease in lactic acid concentration the extraction increases. The emulsions having lower fraction of acceptor phase have lower density and hence have a tendency to float in the external phase[4] causing lesser extraction. The effect of lactic acid concentration is more as compared to fraction on extraction. The extraction increases with the increase in residence time and decrease in lactic acid concentration (Fig. 8). With increase in residence time, the time of contact between emulsion and feed and hence the mass transfer of solute increases. At higher residence time the leveling off trend for extraction of lactic acid has been observed, which may be explained on the basis of advancing front model, since the characteristics diffusion time of Alamine 336-lactic acid complex within the un-reacted zone of emulsion increases. Hence, the lactic acid extraction gradually becomes diffusion controlled and independent of the residence time.[8] It can be observed from Fig. 9 that with the increase in residence time and sodium carbonate concentration the extraction will increase. The increase rate is higher when the residence time is small and leveled off at higher residence time. It is quite evident from Fig. 10 that minimum extraction will be achieved for minimum stirring speed as well as Alamine 336 fraction in oleyl alcohol. At higher Alamine 336 fraction and higher stirring speed the extraction slightly decreases after achieving the maximum. This may be because with the increase in carrier concentration membrane wall thickness increases causing decrease in diffusion coefficient[14] and also increase in the carrier concentration leads to the decrease in the stripping reaction rate. In addition, swelling of emulsion increases with the increase in carrier concentration; thereby diluting the stripping phase[29] and also causes an increase in diffusion distance in the membrane.[28] Fig. 11 indicated that extraction increases with the increase in Alamine 336 fractions as well as residence time. With the decrease in feed: emulsion ratio and increase in stirring speed and residence time the extraction increases (Figs. 12 and 13). The extraction increases with the increase in residence time as well as stirring speed and extraction labeled off at higher residence time and stirring speed (Fig. 14). The extraction increases with residence time and fraction of acceptor phase in emulsion. The extraction with the increase in fraction is quite independent at higher residence time (Fig. 15).

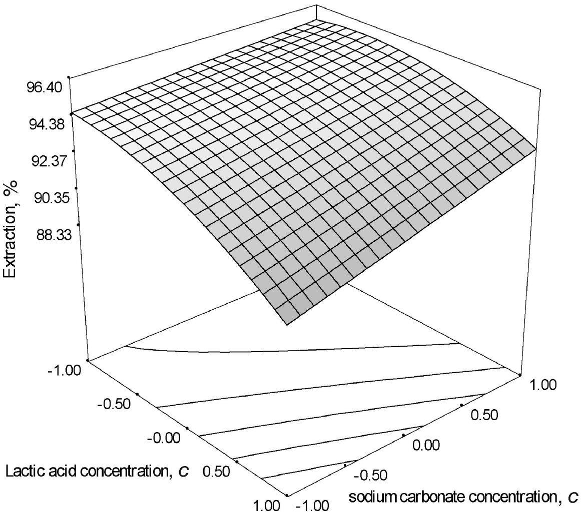

Fig. 4 – *Effect of lactic acid concentration and sodium carbonate concentration on lactic acid extraction (%)*

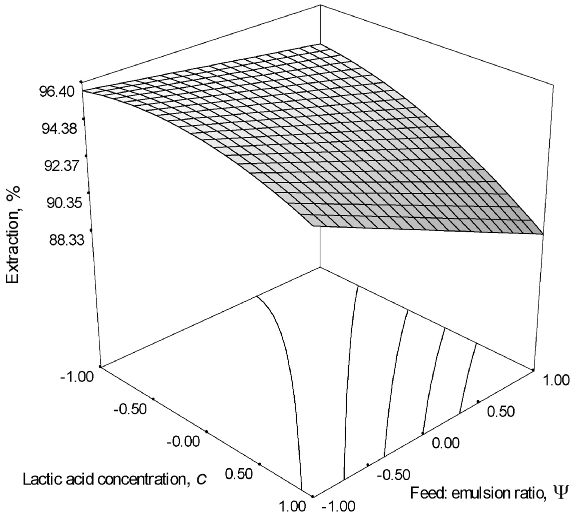

Fig. 5 – *Effect of lactic acid concentration and feed: emulsion ratio on lactic acid extraction (%)*

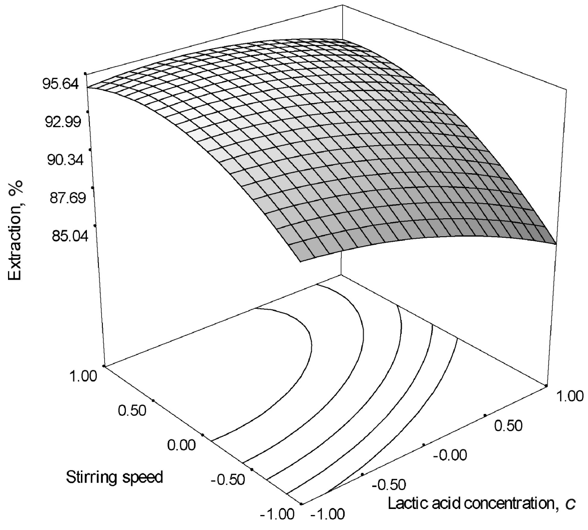

Fig. 6 – *Effect of stirring speed and lactic acid concentration on lactic acid extraction (%)*

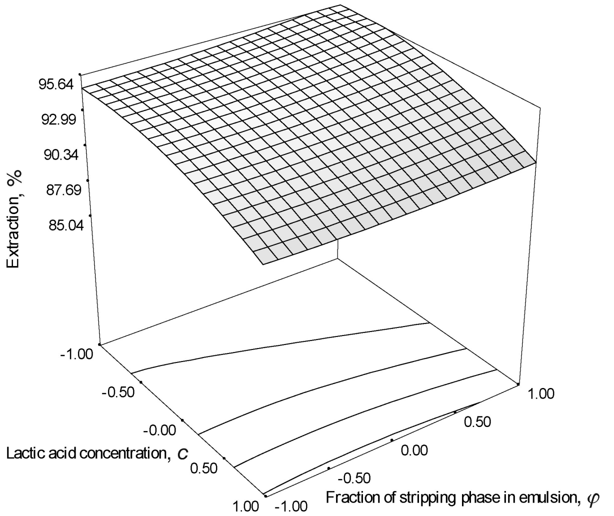

Fig. 7 – *Effect of lactic acid concentration and fraction of internal reagent in emulsion on lactic acid extraction (%)*

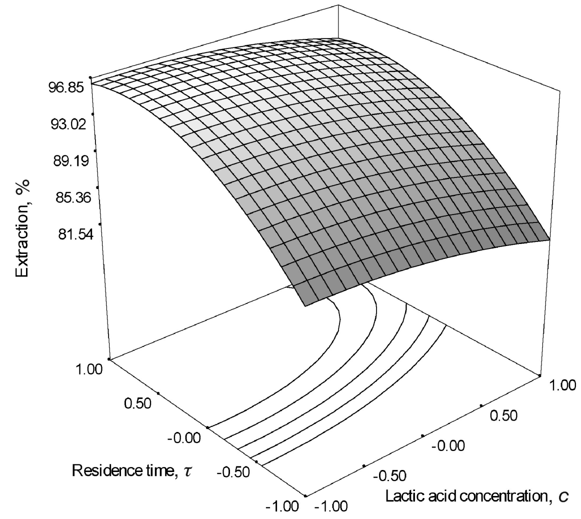

Fig. 8 – *Effect of residence time and lactic acid concentration on lactic acid extraction (%)*

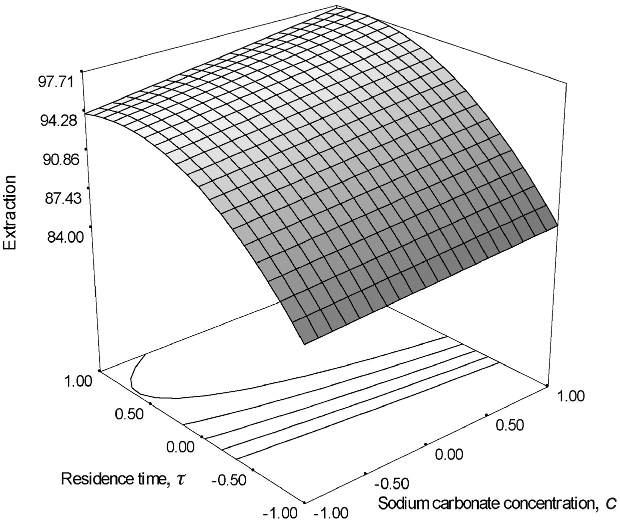

Fig. 9 – *Effect of residence time and sodium carbonate concentration on lactic acid extraction (%)*

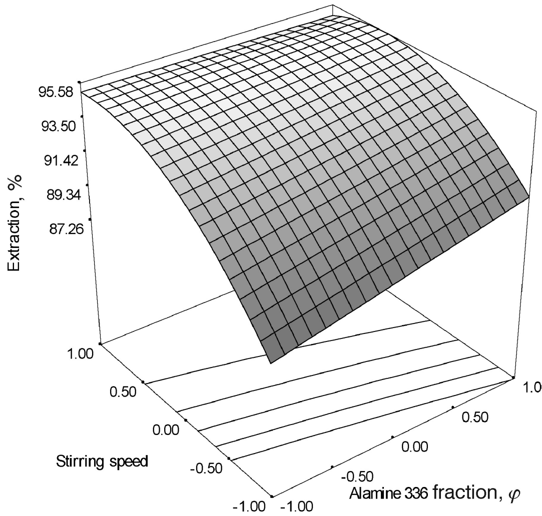

Fig. 10 – *Effect of stirring speed and Alamine 336 fraction on lactic acid extraction (%)*

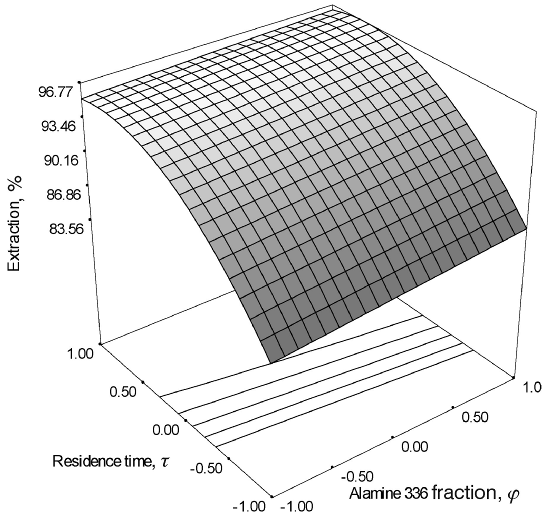

Fig. 11 – *Effect of residence time and Alamine 336 fraction on lactic acid extraction (%)*

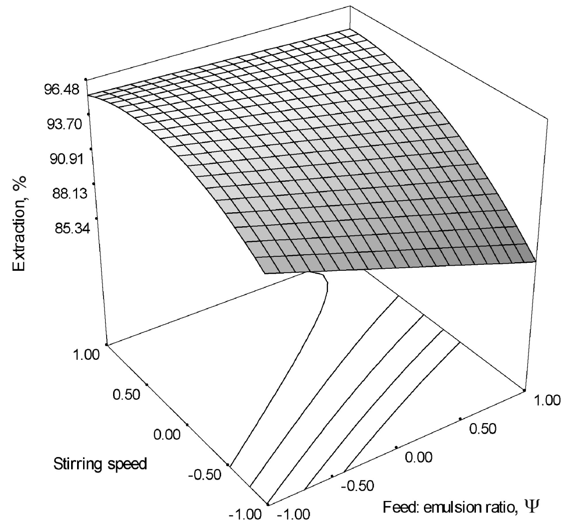

Fig. 12 – *Effect of stirring speed and feed: emulsion ratio on lactic acid extraction (%)*

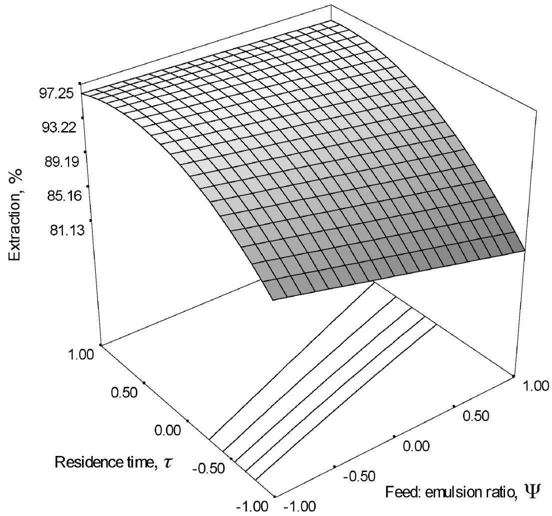

Fig. 13 – *Effect of residence time and feed:emulsion on lactic acid extraction (%)*

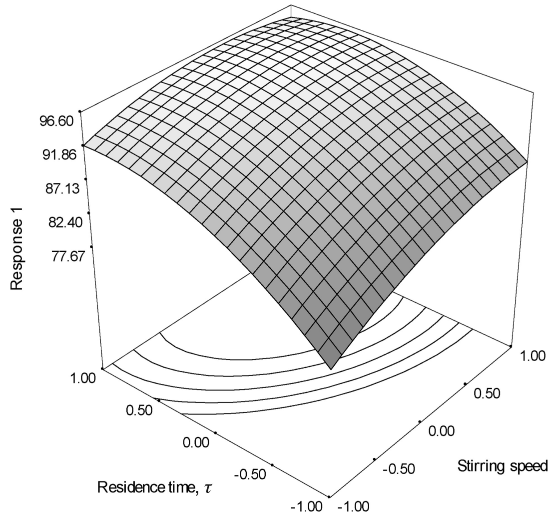

Fig. 14 – *Effect of stirring speed and residence time on lactic acid extraction (%)*

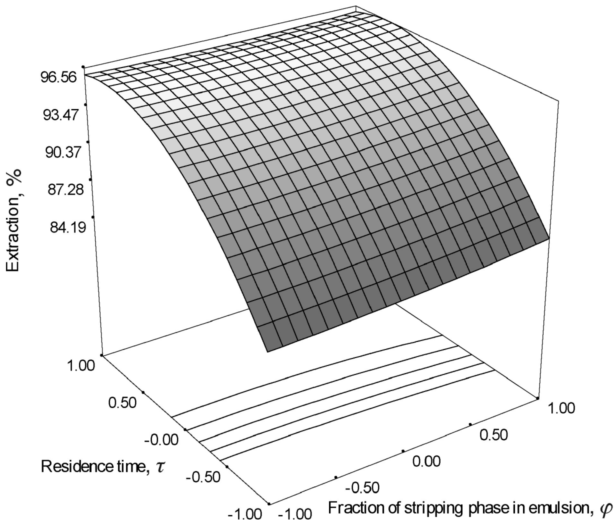

Fig. 15 – *Effect of residence time and fraction of internal reagent in emulsion on lactic acid extraction (%)*

Optimization of extraction of lactic acid

A numerical multi-response optimization technique was adopted to determine the workable optimum conditions for the extraction of lactic acid. In order to optimize the process conditions, equal importance of three was given to all the four process parameters and process responses. The main criterion for constraints optimization was maximum possible extraction in MFR using ELM. These constraints resulted in optimum conditions for maximum lactic acid extraction as c = 5.0 mmol L^{-1} lactic acid in aqueous phase, c = 0.99 mol L^{-1} sodium carbonate in acceptor phase, φ = 10.03 % v/v Alamine 336 in oleyl alcohol, φ = 19.89 % v/v feed: emulsion ratio, 354.80 rpm stirring speed, 0.1360 fraction of acceptor phase in emulsion and τ = 57.33 min residence time.

Conclusions

Extraction of lactic acid by emulsion liquid membrane in mixed flow reactor has been successfully optimized using the Box-Behnken design. The regression models were found to predict the lactic acid extraction, which has led to the following conclusions about the variation in response parameters in terms of independent parameters within the specified range. The analysis of the variance (ANOVA) shows that all the extraction process parameters significantly affect the performance, and that there are some interactions between the extraction parameters. The contribution of feed: emulsion ratio and stirring speed on extraction efficiency was more than other factors and the fraction of acceptor phase in emulsion has minimum contribution. The lactic acid extraction increases with the increase in stirring speed, residence time, sodium carbonate concentration, Alamine 336 fraction, fraction of internal phase in emulsion while it decreases with the increase in feed: emulsion ratio and lactic acid concentration in aqueous feed. The optimum value of the process parameters for the maximization of extraction of lactic acid from aqueous phase using ELM in MFR by the application of Box-Behnken design have been found and 100 % lactic acid extraction in MFR using ELM from aqueous feed can be achieved in few minutes within the specified range of independent process parameters.

List of symbols

c – concentration, mol L^{-1}
t – time, min
η – extraction efficiency, %
τ – residence time, min
φ – volume fraction, % (v/v)
Ψ – volume ratio

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