



Lactic Acid Extraction from Aqueous Systems by Emulsion Liquid Membrane Separation Process Using Statistical Experimental Design

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Abstract

Box-Behnken design was utilized to obtain optimized process condition for maximizing lactic acid extraction efficiency and initial extraction rate by emulsion liquid membrane (ELM) process. A mixture of tri-n-octylamine and tri-n-decylamine (1:1, v/v) was employed as carrier in membrane phase of ELM for synergic facilitated lactic acid transport. The effect of different process parameters like lactic acid concentration in feed, sodium carbonate concentration in internal phase, carrier fraction, treatment ratio, phase ratio, stirring speed and contact time has been investigated. Extraction efficiency of 98.5% and 9.36×10^{-9} mol/cm².sec, initial extraction rate were found under optimized conditions of process parameters.

Keywords Emulsion liquid membrane · Box-Behnken design · Extraction · Response surface methodology · Tri-n-decylamine · Tri-n-octylamine

1 Introduction

Lactic acid, a naturally occurring organic acid has versatile applications in various industries such as brewing, food, cosmetic, pharmaceutical industries and as a chemical feed stock etc. (Pimtung et al. 2017; John et al. 2007). Recently, the utilization of L-lactic acid to produce polylactic acid (PLA), a biodegradable polymer and green solvent like lactate esters has led a remarkable increase in its worldwide demand year by year (Pimtung et al. 2017). PLA has given a breather to the worldwide environmental problems associated with the waste plastics disposal with its expected production capacity of 3 million tonne in 2020 (John et al. 2007; Venus et al. 2018).

Chemical synthesis and fermentation are the two routes for the LA production. The biotechnological production of lactic acid has drawn a significant interest of researchers from both environmental and economic viewpoint. The two key stages for lactic acid production are fermentation and product recuperation. Among the two, the product recovery poses the biggest challenge (Li and Shahbazi 2006). The separation,

purification and preconcentration of lactic acid produced biotechnologically are comparatively arduous tasks due to its chemical behavior. Its separation by distillation or solvent extraction process is difficult due to low volatility and its strong affinity towards water. The low activity of LA molecules towards water makes conventional extraction techniques unprofitable. Moreover, the urgent need for environmental sustainability and rapidly rising costs have underscored the requirement of novel alternative and effective energy efficient separation and recovery of fermentation products like organic acids and biochemicals of industrial importance.

An emerging and attractive novel separation technique involving emulsion liquid membrane (ELM) proposed by Li in 1968 has shown a considerable potential alternatives to the expensive conventional method for separating the metal ions, pollutants from waste streams and biochemical products with low concentrations (Hachemaoui and Belhamei 2017). ELM is a simplified extraction process (water-in-oil-in-water (w/o/w) emulsion system) with high extraction efficiency where in the primary water-in-oil (w/o) emulsion constituting of the internal and the membrane (organic) phase stabilized by the surfactant (responsible for reduction in free energy) is dispersed in the external feed phase (e.g. fermentation broth or aqueous phase containing solute/ions) (Ahmad et al. 2017; Hong et al. 2017). The solute transport during the ELM process from external phase to the internal phase across the membrane phase occurs due to the combined effect of extraction

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and stripping unit operations (Ahmad et al. 2017). Selectivity based on the difference in the permeation rate across the membrane phase of individual species present in feed phase is the key criteria for the mass transfer of targeted solute. Addition of carrier such as long chain tertiary amines, organophosphinic acids, phosphine oxides etc. in the membrane phase can further enhance the solute transportation rate by forming a solute-carrier complex selectively in the membrane phase (Berrios et al. 2010). Choosing a suitable carrier along with other operational conditions is one of the key factors that control the extraction efficiency (Garcia et al. 2013). The extraction efficiency can be further improved by utilizing a mixture of long chain tertiary amines as compared to pure tertiary amine (Uslu et al. 2009). ELM has an advantage of having a high surface area per unit volume ($1000\text{--}3000\text{ m}^2/\text{m}^3$) as well as high internal surface area per unit volume (typically $106\text{ m}^2/\text{m}^3$) resulting in very high mass rates with a considerably smaller working volumes of solvents requirement in comparison to conventional solvent extraction technique (Chanukya and Rastogi 2013; Rajasimman and Karthic 2010) and feasibility of economic continuous operation.

The LA extraction from aqueous phase and fermentation broths using the ELM technique has been studied by various researchers (Uslu et al. 2009; Hong and Hong 1999; Yankov et al. 2004; Gao et al. 2009; Garavand et al. 2017; Kyuchoukov et al. 2001). Although these works showed that ELM is efficient in removal of lactic acid from aqueous phase/fermentation broth, yet very few investigations have been reported on the comprehensive and detailed study on the interactive effect of process variables on response. A number of process parameters like carrier concentration, solute concentration in external phase, stripping reagent concentration in internal phase, treat ratio, internal to membrane phase ratio, surfactant concentration etc. may influence the LA extraction by ELM process from aqueous solution. Hence an effective suitable experimental technique has to be applied to investigate the effect of various process parameters, their interactive effect and to find optimized value of these process parameters for maximizing the LA extraction by ELM with minimum number of experiments (Yetilmezsoy et al. 2009; Goyal et al. 2011).

The conventional method for process parameters optimization is time consuming since it involves changing one independent variable while keeping all others unchanged at a fixed level. Moreover, it does not provide any information regarding combined effect of all the factors tested and does not often assured determination of optimum conditions. Response surface methodology (RSM) has been widely studied by many investigators for the design of experiments and optimization of process variables. It has been proven to be effective in substantially decreasing the experimental runs without affecting the interactions among the process parameters (Peng et al. 2012). Different types of RSM designs include 3-level

factorial design, central composite rotatable design (CCRD), Box-Behnken design (BBD), and D-optimal design. Among them CCRD and BBD are very useful (Chanukya and Rastogi 2013). Fewer experiments are needed with BBD and are less expensive to run in comparison to CCRD with the same number of factors (Babu et al. 2011).

The optimization of extraction efficiency of lactic acid by ELM from aqueous solution using response surface methodology (RSM) is scarce in the literature. Moreover no systematic investigation so far has been reported in the literature for optimization of LA initial extraction rate by ELM using RSM. Keeping in view the above, response surface methodology using BBD (a three-level factorial designs) has been utilized in this work for designing and analysis of experimental and parametric optimization of the initial lactic acid extraction rate and extraction efficiency of lactic acid from aqueous phase in a batch reactor using mixed tertiary amines consisting of trioctylamine (TOA) and tridecylamine (TDA).

2 Materials and Methods

2.1 Chemicals

Sorbitanmonooleate (Span 80), trioctylamine,(TOA), sulfuric acid and hydrochloric acid were the products of Merck, Germany. Tridecylamine (TDA) was a product of Sigma-aldrich. A commercial n-hexane was procured from Merk Pvt. Ltd., Mumbai, India. Lactic acid was the product of HiMedia Lab Pvt.,Mumbai. Na_2CO_3 , copper sulphate ($\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$) and p-phenyl phenol were received from the manufacturer M/s. Loba Chemie Pvt. Ltd., Mumbai, India. All the chemicals were of AR grade.

2.2 Experimental Design

The experiments were conducted for investigating the initial LA extraction rate and LA extraction efficiency in accordance with sets of experimental design obtained using Design-Expert 7.16 software (Statease Inc., Minneapolis, USA.) for Box-Behnken design (BBD) with seven variables at three levels each. The effect of lactic acid concentration in feed phase (c_f), [M], sodium carbonate concentration in internal phase (c_s) [M], carrier fraction in n-hexane (φ , % v/v), treatment ratio (ψ , v/v), phase ratio (Φ , v/v), stirring speed (ω , rpm), on the initial extraction rate (ξ_0) and extraction efficiency (η_{ext}) (whereas contact time (τ , min), was additional 7th variable, for the extraction efficiency) were investigated for the ranges as shown in Table 1. A total 62 experiments (Table 2) with various combinations process variables were conducted randomly in triplicate and average value was taken for statistical analysis.

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 [M], c_l	Sodium carbonate concentration [M], c_s	Fraction of carrier in n-hexane (%v/v), φ	Treatment ratio (v/v), ψ	Phase ratio (v/v), Φ	Stirring speed (rpm), ω	Contact time (min), τ
-1.000	0.05	0.025	0	0.5	0.25	100	0.5
0.000	0.275	0.1375	4	1.25	0.50	200	5.25
+1.000	0.5	0.25	8	2.0	0.75	300	10

2.3 Membrane Preparation

The membrane phase initially utilized for obtaining the ELM, (w/o/w) was consisted of 3–5% (v/v) Span 80 as stabilizer and 0–8% (v/v) of 1:1(v/v) mixture of tri-n-octylamine, and tri-n-decylamine as carrier in n-hexane which were stirred at constant speed (200 rpm) for 2 min. To this homogeneous membrane phase, 0.025–0.25 [M] stripping phase (Na_2CO_3 solution) was added drop wise slowly and simultaneously agitated (2000 rpm) at room temperature (25 ± 2 °C) for 20 min using a four blade impeller stirrer (Model: IKA RW 20; Cole-Parmer, India) while maintaining the desired phase (internal phase to organic phase volume) ratio (0.25–0.75 v/v) to obtain a stable ELM. Afterwards the emulsion thus obtained was washed with excess deionized water before transferring to settler to check its stability. On performing the experimental investigation, an emulsion constituted of 4% (v/v) Span 80 in n-hexane (χ), 0.25–0.75 (v/v) phase ratio (Φ), 0–8% (%v/v) of 1:1(v/v) mixture of tri-n-octylamine, and tri-n-decylamine as carrier in n-hexane (φ), and 0.025–0.25 [M] stripping phase concentration (c_s , Na_2CO_3 solution) stirred at 2000 rpm were very stable.

2.4 Lactic Acid Extraction

The extraction experiments was conducted batch-wise in a batch extractor at room temperature (25 ± 2 °C) containing freshly prepared ELM (100 ml) to which aqueous lactic acid (external phase) according to desired treatment ratio was added and stirred with the help of agitator as per the experimental design (Table 2). During the preparation of primary emulsion (w/o) of desired phase ratio, the organic phase volume was kept constant and the stripping phase volume was varied. Samples at different time intervals from the external feed phase during extraction process were drawn and analyzed for lactic acid concentration. While for initial extraction rate, (ξ_0), the samples were also drawn for analysis LA concentration in feed phase at contact times of 10, 20, 30 and 45 s in addition to desired contact times for each experiment as per experimental design (Table 2). After completion of extraction process, the emulsion and feed phases were separated by gravity settling and their respective volumes were measured.

2.4.1 Mass Transfer Mechanism

The schematic representation for the mass transfer of LA is shown in Fig. 1.

2.5 Statistical Analysis and Optimization

During the statistical analysis, at first, the regression equation is fitted to the experimental data for responses. The coefficients of the response model, their standard errors and significance are determined by regression analysis. The process behavior was represented and explained by the quadratic equation:

$$Y = b_0 + \sum_{i=1}^k b_i x_i + \sum_{i=1}^k b_{ii} x_i^2 + \sum_{i=1}^k \sum_{j=1}^k b_{ij} x_i x_j + \varepsilon \quad (1)$$

Where predicted response i.e. initial extraction rate/ extraction efficiency is represented by Y , b_0 , b_i , b_{ii} and b_{ij} represents offset term, linear effect, squared effect and interaction effect, respectively. x_i is i th independent variable (Yu et al. 2008) and ε is the random error. The transformation for coding the natural (uncoded) independent variables (X_1, X_2, \dots, X_k) while developing Eq. (1) has been utilized as

$$x_i = \frac{(X_i - X_{i0})}{\Delta X_i} \quad (2)$$

Where x_i , X_i , X_{i0} and ΔX_i are dimensionless coded value, uncoded value, uncoded value at center point and the step change value for the i th independent variable respectively (Yetilmesoy et al. 2009). After building the regression models, tests were performed for fitting of the models. The optimum values for process variables (within the experimental range) for maximizing initial extraction rate (ξ_0) and extraction efficiency (η_{ext}) were determined.

2.6 Analytical Method

Lactic acid concentration was determined through colorimetric method (Kimberley and Taylor 1996) by using a

Table 2 Box-Behnken design of process variables for experiment and values of experimental data for batch extraction of lactic acid using ELM

Coded process variables for experiments							Responses	
Lactic acid concentration (X_1)	Sodium Carbonate concentration (X_2)	Fraction of carrier in n-hexane (X_3)	Treatment ratio (X_4)	Phase ratio (X_5)	Stirring Speed (X_6)	Contact time (X_7)	Initial extraction rate $\times 10^{-9}$ (ξ_0)	Extraction efficiency (η_{ext})
0	1	1	0	0	1	0	5.85	59.71 \pm 0.52
-1	-1	0	1	0	0	0	1.14	24.41 \pm 0.35
0	0	-1	-1	0	0	1	4.53	47.04 \pm 0.51
1	0	0	0	0	1	1	4.45	20.74 \pm 0.32
-1	0	0	0	0	1	1	1.1	69.82 \pm 0.63
1	0	1	0	1	0	0	8.9	32.38 \pm 0.41
0	0	0	1	1	1	0	2.98	21.41 \pm 0.30
1	-1	0	-1	0	0	0	3.75	8.5 \pm 0.28
0	0	0	1	-1	1	0	1.96	6.87 \pm 0.13
0	-1	0	0	-1	0	1	1.68	3.14 \pm 0.11
0	0	1	1	0	0	-1	5.9	13.05 \pm 0.25
0	0	0	-1	-1	1	0	3.0	33.6 \pm 0.45
0	0	-1	1	0	0	-1	4.4	3.98 \pm 0.21
0	1	0	0	-1	0	-1	3.2	4.16 \pm 0.31
0	0	0	1	1	-1	0	2.75	23.39 \pm 0.43
0	-1	1	0	0	-1	0	1.82	4.16 \pm 0.29
-1	0	-1	0	1	0	0	1.3	48.75 \pm 0.61
0	0	0	-1	1	-1	0	3.9	56.22 \pm 0.64
-1	0	0	0	0	1	-1	1.1	28.88 \pm 0.33
-1	-1	0	-1	0	0	0	1.94	55.49 \pm 0.64
0	1	-1	0	0	-1	0	2.31	26.92 \pm 0.28
1	0	1	0	-1	0	0	5.3	10.54 \pm 0.21
-1	0	0	0	0	-1	-1	0.95	22.84 \pm 0.32
0	0	0	0	0	0	0	5.71	36.77 \pm 0.37
1	1	0	-1	0	0	0	7.98	65.03 \pm 0.71
-1	1	0	-1	0	0	0	2.8	95.42 \pm 0.82
0	0	-1	1	0	0	1	4.55	14.95 \pm 0.23
0	1	0	0	1	0	-1	6.68	22.92 \pm 0.22
0	0	0	-1	-1	-1	0	2.25	36.68 \pm 0.42
-1	0	0	0	0	-1	1	1.0	68.88 \pm 0.65
-1	0	1	0	-1	0	0	2.4	58.81 \pm 0.59
0	1	-1	0	0	1	0	3.59	28.74 \pm 0.31
1	0	-1	0	-1	0	0	2.54	5.7 \pm 0.2
0	0	0	0	0	0	0	5.75	37.64 \pm 0.45
0	0	0	0	0	0	0	5.69	36.29 \pm 0.39
1	0	0	0	0	-1	1	4.03	18.85 \pm 0.22
0	-1	-1	0	0	-1	0	0.45	2.69 \pm 0.16
0	0	0	-1	1	1	0	4.86	56.04 \pm 0.65
0	-1	0	0	1	0	-1	3.28	3.73 \pm 0.12
1	-1	0	1	0	0	0	2.43	2.42 \pm 0.14
0	-1	-1	0	0	1	0	0.5	4.51 \pm 0.21
0	0	1	1	0	0	1	6.9	20.02 \pm 0.31
0	-1	0	0	-1	0	-1	1.68	3.41 \pm 0.15
0	0	-1	-1	0	0	-1	4.51	7.51 \pm 0.19
1	0	-1	0	1	0	0	6.97	24.24 \pm 0.27
0	-1	1	0	0	1	0	1.94	5.87 \pm 0.21
0	1	0	0	-1	0	1	3.14	35.24 \pm 0.37
0	0	0	0	0	0	0	4.58	36.54 \pm 0.35
0	0	0	0	0	0	0	5.69	39.82 \pm 0.34
0	0	0	0	0	0	0	5.73	38.94 \pm 0.35
1	0	0	0	0	-1	-1	4.13	12.34 \pm 0.14
0	1	0	0	1	0	1	6.7	86.4 \pm 0.72
-1	1	0	1	0	0	0	1.64	44.64 \pm 0.52
0	0	1	-1	0	0	-1	8.0	36.32 \pm 0.48
-1	0	1	0	1	0	0	3.05	77.95 \pm 0.64
0	0	0	1	-1	-1	0	1.4	5.05 \pm 0.12
0	0	1	-1	0	0	1	8.02	79.51 \pm 0.76
1	1	0	1	0	0	0	6.92	23.75 \pm 0.25
1	0	0	0	0	1	-1	4.44	13.13 \pm 0.23
0	-1	0	0	1	0	1	3.3	10.3 \pm 0.18
0	1	1	0	0	-1	0	3.36	55.88 \pm 0.45
-1	0	-1	0	-1	0	0	0.91	29.61 \pm 0.38

UV/VIS spectrophotometer (model DR 5000 HACH, USA). The stability analysis of emulsion was confirmed by the pH method ((Jiao et al. 2013) by measuring the

pH of the aqueous solutions at different contact times of aqueous phase with emulsion using Eutech pH 5+, pH meter.

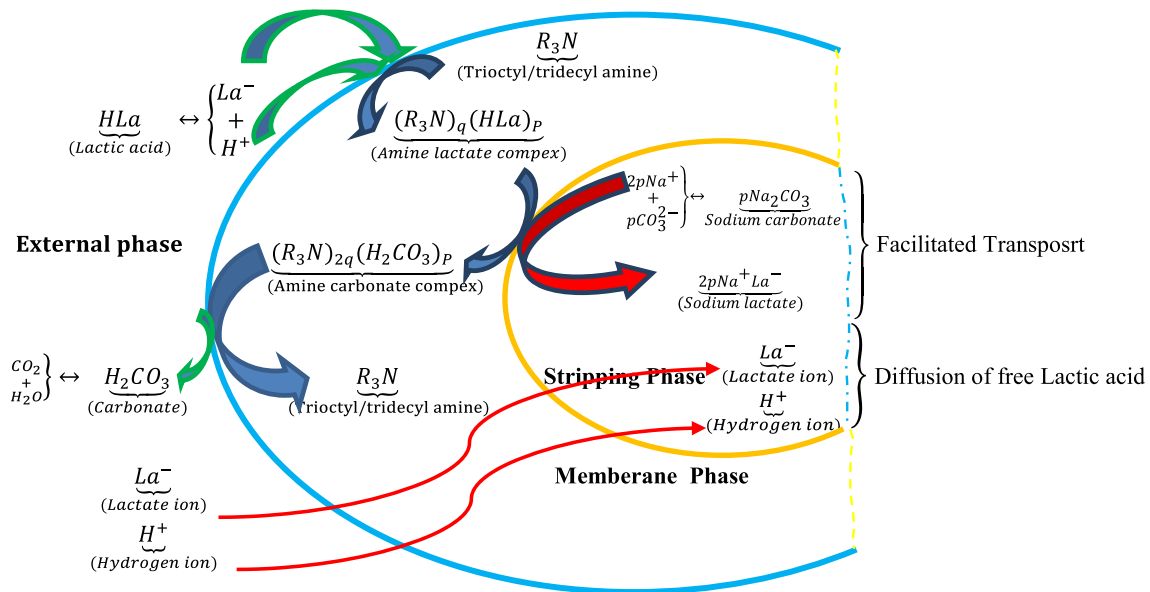


Fig. 1 Schematic representation of mass transfer mechanism

2.7 Mathematical Calculations

2.7.1 Calculation for Lactic Acid Extraction

The extraction efficiency had been calculated without considering any emulsion breakage and swelling using the equation:

$$\text{Extraction efficiency, } \eta_{ext} = \frac{C_{I0} - C_{I7}}{C_{I0}} \times 100 \quad (3)$$

Where C_{I0} and C_{I7} is the lactic acid concentration in feed phase initially at time $t = 0$, and at desired contact time as per design of experiment, (Table 2) respectively.

2.7.2 Calculation of Initial Lactic Acid Extraction Rate

During the preliminary experimentation, it has also been observed that lactic acid extraction is favored at the beginning of the experiment. The LA initial extraction rate, ξ_0 was determined as:

$$\text{Initial extraction rate, } \xi_0 = C_{I0} \left(\frac{V_F}{A} \right) \left(\frac{dE}{dt} \right) \quad (4)$$

Where V_F and A are the feed volume and interfacial area, respectively, (dE/dt) represents initial rate of change in LA extraction (≤ 20 s) and initial extraction rate is expressed in $[\text{mol cm}^{-2} \text{ s}^{-1}]$ (Basualto et al. 2006). The Souter mean diameter (d) in mm for calculating the emulsion area of interface was calculated using the correlation as described by S. Datta et al. (2003).

3 Results and Discussion

3.1 Regression Model

The quadratic models for the initial extraction rate (ξ_0) and extraction efficiency (η_{ext}) (in terms of coded forms) after the regression analyses were obtained explaining the role of each variable and their quadratic interaction:

$$\begin{aligned} \text{Initial extraction rate, } \xi_0 \times 10^9 = & 5.71 + 1.77^*(X_1) + 1.26^*(X_2) \\ & + 1.037^*(X_3) - 0.52^*(X_4) + 1.05^*(X_5) + 0.309^*(X_6) + 0.92^*(X_1)^*(X_2) \\ & + 0.87^*(X_1)^*(X_5) + 0.48^*(X_2)^*(X_5) + 0.45^*(X_2)^*(X_6) - 0.39^*(X_3)^*(X_4) \\ & - 0.99^*(X_1)^*(X_1) - 1.18^*(X_2)^*(X_8) - 0.80^*(X_5)^*(X_5) - 2.05^*(X_6)^*(X_6) \end{aligned} \quad (5)$$

$$\begin{aligned} \text{Extraction efficiency, } \eta_{ext} = & 38.58 - 16.16^*(X_1) + 17.5^*(X_2) + 8.73^*(X_3) \\ & - 15.56^*(X_4) + 9.62^*(X_5) + 0.64^*(X_6) + 12.61^*(X_7) + 2.21^*(X_1)^*(X_2) \\ & - 5.68^*(X_1)^*(X_3) + 4.31^*(X_1)^*(X_4) - 9.11^*(X_1)^*(X_7) + 7.13^*(X_2)^*(X_3) \\ & - 6.86^*(X_2)^*(X_4) + 7.81^*(X_2)^*(X_5) + 11.03^*(X_2)^*(X_7) - 5.89^*(X_3)^*(X_4) \\ & - 8.1^*(X_4)^*(X_7) + 4.91^*(X_5)^*(X_7) + 6.145^*(X_1)^2 - 5.46^*(X_2)^2 - 4.12^*(X_3)^2 \\ & - 4.27^*(X_5)^2 - 5.1^*(X_6)^2 - 7.35^*(X_7)^2 \end{aligned} \quad (6)$$

Where X_1 - lactic acid concentration, X_2 - sodium carbonate concentration, X_3 -fraction of carrier in n-hexane, X_4 - treatment ratio, X_5 -phase ratio, X_6 - stirring speed and X_7 - contact time.

The significance and models fittings (Eq. 6 & 7) were verified by ANOVA (analysis of variance). ANOVA results for initial extraction rate (ξ_0) and extraction efficiency (η_{ext}) are illustrated in Tables 3 and 4 respectively. The fishers variance ratio f value is a measure of data variation about the mean. The significant terms were considered as having p (probability) $> f$ values < 0.05 are (Tables 3 and 4). Smaller the magnitude of $p > f$ values, the more significant is the correlation with the corresponding coefficient.

Table 3 Regression model and ANOVA for initial lactic acid extraction rate using ELM (after backward elimination)

Source	Sum of squares	Degree of freedom	Mean square	<i>f</i> - value	<i>p</i> > <i>f</i>
Model	275.04	15	18.34	114.59	< 0.0001
Lactic acid concentration (X_1)	75.43	1	75.29	470.57	< 0.0001
Sodium carbonate concentration (X_2)	39.09	1	38.15	238.44	< 0.0001
Fraction of carrier in n-hexane(X_3)	25.86	1	25.79	161.19	< 0.0001
Treatment ratio (X_4)	6.51	1	6.58	41.14	< 0.0001
Phase ratio (X_5)	25.67	1	26.48	165.49	< 0.0001
Stirring speed (X_6)	2.17	1	2.29	14.33	0.0004
(X_1). (X_2)	6.42	1	6.77	42.31	< 0.0001
(X_1). (X_3)	6.13	1	6.12	38.17	< 0.0001
(X_2). (X_3)	1.805	1	1.82	11.39	0.0015
(X_2). (X_6)	1.63	1	1.62	10.12	0.0026
(X_3). (X_4)	1.13	1	1.22	7.65	0.0081
(X_1). (X_1)	13.28	1	13.89	86.82	< 0.0001
(X_2). (X_2)	19.21	1	19.87	124.17	< 0.0001
(X_3). (X_3)	9.186	1	9.16	57.29	< 0.0001
(X_6). (X_6)	60.34	1	60.16	376.01	< 0.0001
Residual	7.36	46	0.16		
Lack of Fit	5.76	29	0.199	2.12	0.0535
Pure Error	1.59	17	0.093		
Cor Total	282.40	61			
Standard Deviation = 0.400012				$R^2 = 0.973936$	
Mean = 3.77				Adjusted $R^2 = 0.965$	
Coefficient of variation (C.V. %) = 10.61				Predicted $R^2 = 0.952$	
Predicted residual error of sum of squares (PRESS) = 13.351				Adequate Precision = 42.39	

*non-significant at 5% level

The R^2 values were satisfactory (>0.97) for both the responses ($p \leq 0.05$) indicating a good agreement between experimentally observed and predicted values. The “Lack of Fit *f*-value” of 2.12 for ξ_0 and 1.73 for η_{ext} implies that it is not significantly relative to the pure error and signifies towards the model best fit (Yu et al. 2008). For ξ_0 and η_{ext} , the difference between adjusted R^2 and predicted R^2 is 0.0127 and 0.0147 respectively, confirming that models are in good agreement. The signal to noise ratio (adequate Percision) greater than 4 is desirable for using the models to navigate the design space and which is 226.077 and 42.39 for ξ_0 and η_{ext} respectively (Yu et al. 2008). No lack of fit has been observed in the ANOVA tables for any of the equation ($p \geq 0.05$). Better precision and reliability of the experiments conducted has also been confirmed by relatively lower value of the coefficient of variation (C.V. = 10.61% & 9.08% for ξ_0 and η_{ext} respectively) (Yu et al. 2008).

The response surface curves and the contour plots were drawn for these responses representing interactive effect within the experimental design of any two independent variables on responses while maintaining other variables values constant at zero coded values. Contours of parabolic nature indicate a quite significant interaction between two independent

variables (Goyal et al. 2011). The detailed analysis of both the responses is described as under.

3.2 Initial Lactic Acid Extraction Rate

The modified quadratic model represented by Eq. 6 satisfactorily explained the effect of six variables on initial extraction rate. The response surfaces 3D graphical shown in Figs. 2, 3, 4, 5 and 6 helped to visualize the interactive effect of variables on the initial extraction rate. Parabolic surface responses signify a significant interaction between them.

The effect of lactic acid concentration (c_l) and sodium carbonate concentration (c_s) on the initial extraction rate (ξ_0) is illustrated in Fig. 2. The surface plot illustrates that ξ_0 increases with the increase in c_l as well as with the increase in c_s .

It is due to the fact that an increase in c_s enhances the ability of stripping phase for stripping the solute from the carrier solute complex at the external surface of internal droplets within the emulsion leading to reduction in concentration polarization at the surface. Hence with an increase in c_l , the driving force in both, stagnant external aqueous film and membrane phase in accordance with the Fick’s law will be increased; hence the initial extraction rate has been observed

Table 4 Regression model and ANOVA for extraction efficiency (%) using ELM (after backward elimination)

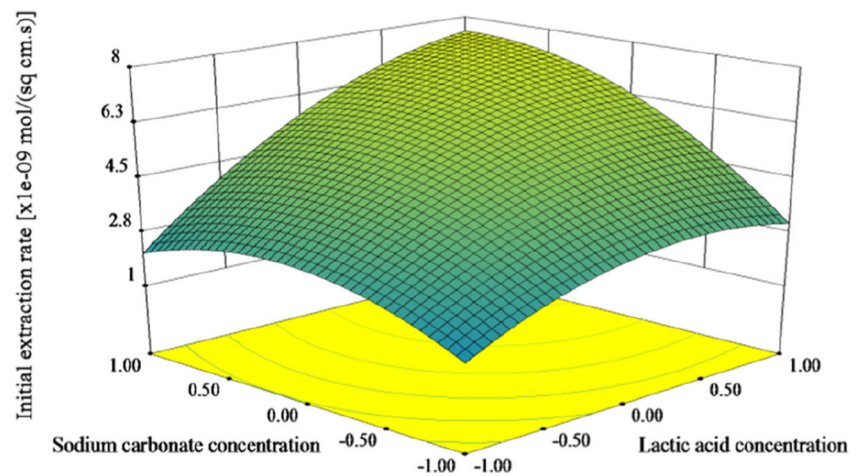
Source	Sum of squares	Degree of freedom	Mean square	<i>f</i> - value	<i>p</i> > <i>f</i>
Model	34,062.98	24	1419.29	181.51	< 0.0001
Lactic acid concentration (X_1)	6266.78	1	6268.78	801.69	< 0.0001
Sodium carbonate concentration (X_2)	7358.30	1	7356.30	940.77	< 0.0001
Fraction of carrier in n-hexane(X_3)	1832.84	1	1829.80	234.01	< 0.0001
Treatment ratio (X_4)	5810.18	1	5810.10	743.03	< 0.0001
Phase ratio (X_5)	2225.81	1	2221.83	284.14	< 0.0001
Stirring speed (X_6)	9.98	1	9.91	1.27	0.2676
Contact time (X_7)	3811.58	1	3815.78	487.98	< 0.0001
(X_1). (X_2)	40.06	1	39.16	5.01	0.0313
(X_1). (X_3)	257.81	1	257.87	32.98	< 0.0001
(X_1). (X_4)	146.68	1	148.78	19.03	< 0.0001
(X_1). (X_7)	665.50	1	663.57	84.86	< 0.0001
(X_2). (X_3)	409.59	1	407.55	52.12	< 0.0001
(X_2). (X_4)	377.65	1	376.75	48.18	< 0.0001
(X_2). (X_5)	484.23	1	487.34	62.32	< 0.0001
(X_2). (X_7)	975.78	1	973.72	124.52	< 0.0001
(X_3). (X_4)	275.79	1	277.77	35.52	< 0.0001
(X_4). (X_7)	526.61	1	524.55	67.08	< 0.0001
(X_5). (X_7)	194.22	1	192.47	24.61	< 0.0001
(X_1). (X_1)	524.07	1	522.61	66.83	< 0.0001
(X_2). (X_2)	410.73	1	412.45	52.74	< 0.0001
(X_3). (X_3)	235.17	1	235.12	30.068	< 0.0001
(X_5). (X_5)	248.56	1	251.80	32.20	< 0.0001
(X_6). (X_6)	358.96	1	359.67	45.99	< 0.0001
(X_7). (X_7)	744.78	1	747.96	95.65	< 0.0001
Residual	282.91	37	7.82		
Lack of Fit	279.09	32	8.72	4.26	0.0556*
Pure Error	10.23	5	2.05		
Cor Total	34,352.3	61			
Standard Deviation = 2.796				$R^2 = 0.971$	
Mean = 30.783				Adjusted $R^2 = 0.966$	
Coefficient of variation (C.V. %) = 9.084				Predicted $R^2 = 0.951$	
Predicted residual error of sum of squares (PRESS) = 1323.97				Adequate Precision = 55.53	

*non-significant at 5% level

increasing (Garcia et al. 2013). At low level of c_{s_s} , a slight decline in ξ_0 had been observed as c_l approaches high level. This can be explained with context to the advancing front model that with the further increase in c_l , (as it approaches high level) there is an increase in the diffusional path length due to which the emulsion globule mass transfer resistance contribution to the overall mass transfer resistance got augmented. Similarly at low level of c_l , a slight decrease in ξ_0 had been observed as c_s approaches high level. This may be attributed to swelling in internal droplets of membrane at high c_s , due to water transport along with lactic acid thorough the organic phase, causing coalesce of the internal droplets and hence reduction in mass transfer area (Datta et al. 2003).

It is evident from Fig. 3 that with enhancement in phase ratio, Φ and lactic acid concentration, c_l , ξ_0 increases. As the Φ increases from low level to high level, more proportion of internal stripping phase will be available for encapsulation of lactic acid and moreover the membrane thickness will be got reduced causing decrease in mass transfer resistance in membrane phase (Peng et al. 2012). On the other hand, at low c_l with the increase in Φ towards the high level, there is a slight decrease in ξ_0 . This may be attributed to the fact that the internal droplets size have increased causing reduction in the interfacial contact area between emulsion and feed phase, which may have started dominating the effect on mass transport with respect to the thinning of membrane phase continue

Fig. 2 Effect of sodium carbonate concentration and lactic acid concentration on initial extraction rate



with the increase of Φ . At low level of Φ , with the increase in c_l towards its high level, there is a slight decrease in ξ_0 , owing to the fact that the low level of Φ causes reduction in the hold-up capacity of the stripping phase, i.e. the emulsion globules, leading to simultaneously decrement in mass transfer interfacial area and LA encapsulating capacity of the internal stripping phase (Peng et al. 2012). Moreover at low level of Φ , high c_l causes more readily saturation of the internal droplet with LA in the peripheral region (Noah et al. 2016).

It can be observed from Fig. 4 that with the increase in phase ratio Φ and sodium carbonate concentration in internal phase c_s , ξ_0 increases due to the increase in availability of stripping agent and capacity of internal phase for encapsulating the lactic acid. However at low Φ , with the increase in c_s towards its high level, there is a slight decrease in ξ_0 , since high c_s will increase the pH of stripping phase and may result in osmotic swelling due to high pH difference between the external and stripping phase. This leads to water transportation from the external to internal phase causing enhancement in the internal emulsion volume, which in turn decreases the area for mass transfer and moreover diffusion resistance increases in

membrane phase due to the thickening of the membrane which tends to maintain the emulsion stability under low Φ (Ng et al. 2010). At low c_s , a slight decrease in ξ_0 , has also been observed with the increase in Φ at high level increases the ELM.

volume owing to the decrease in the contact area (Goyal et al. 2011) and due to the low difference of electrolyte concentration between the stripping and external phases.

The variation in the extent of ξ_0 due to the interactive effect of ω and c_s is represented in Fig. 5. Since the contours are parabolic which signify a quite significant interaction between both the parameters. ω and c_s are correlated to reach other by the fact that internal phase droplet size is a function of stirring speed and viscosity, while the latter is directly proportional to c_s (Goyal et al. 2011). The stirring speed governs the mass transfer of solute across the membrane phase (Mesli and Belkhouche 2018). ξ_0 tends to increase with the increase in both the variables upto a certain level, but towards the higher level of ω and c_s , ξ_0 decreases. With the increase in stirring speed during extraction, the shear force acting on the emulsion globule increases,

Fig. 3 Effect of phase ratio and lactic acid concentration on initial extraction rate

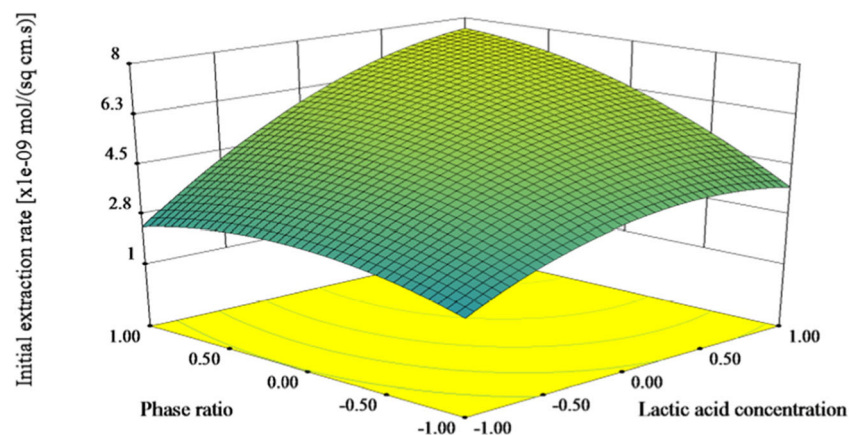
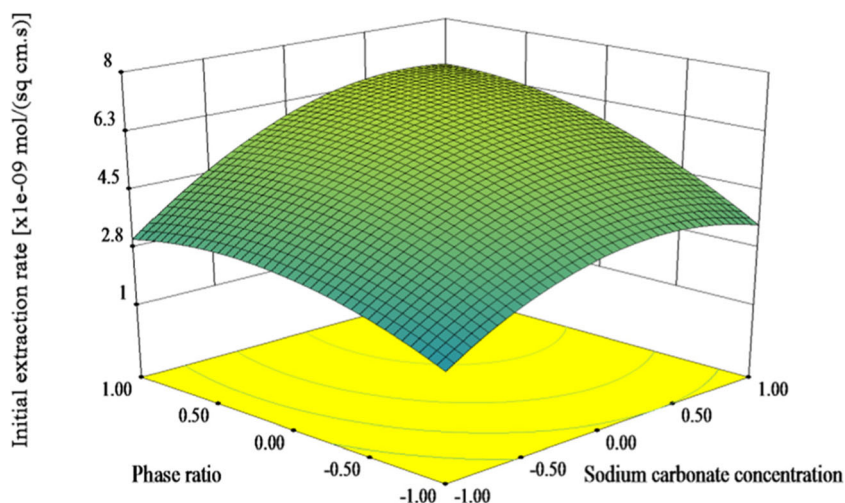


Fig. 4 Effect of phase ratio and sodium carbonate concentration on initial extraction rate



which in turn decreases the average emulsion globules radius. Hence thereby causing an increase in the mass transfer rate due to increase in the interfacial area between feed phase & the membrane phase and reduction in the LA diffusion path length within the globules (Kumbarar 2012; Eyupoglu and Kumbarar 2015). Since viscosity is directly proportional to stripping phase concentration, hence high c_s hinders the formation of smaller size emulsion globules at high ω . Moreover mass transfer resistance due to turbulence and the membrane swelling also got aggravated at higher ω (Peng et al. 2012; Mesli and Belkhouche 2018; Eyupoglu and Kumbarar 2015). At lower stirring speed, the interfacial contact area and mass transfer between external phase and emulsion decreases due to larger globule size. At low c_s , the stripping rate of lactic acid is the limiting step in the system. This could be caused by saturation of lactic acid in organic phase due to low stripping rate (Reis et al. 2011).

The Interactive effect of treatment ratio, ψ and fraction of carrier φ , on ξ_0 is illustrated in Fig. 6. ξ_0 increases with the decrease in ψ and increase in φ . It may account for the reason that though the increase in φ leads to a higher amount of carrier solute complex at external-organic membrane interface which improves the selectivity (Mousavi et al. 2012; Lee 2013; Kumbarar 2010), while decrease in ψ results in increase in the number of emulsion globules per unit external phase volume causing an increase in the membrane surface area, the emulsion phase hold up, along with simultaneously an increase in the amount of carrier and the transport capacity of the emulsion liquid membrane (Gao et al. 2009; Kumbarar 2012). This may have steered an increase in ξ_0 with the decrease in ψ and increase in φ . Minimum value of ξ_0 has been depicted by the figure at high level of ψ and low level of φ which indicated the carrier unavailability in the membrane phase due it saturation due to complex formation at the interface as the lactic acid amount in the external phase has in-

Fig. 5 Effect of stirring speed and sodium carbonate concentration on initial extraction rate

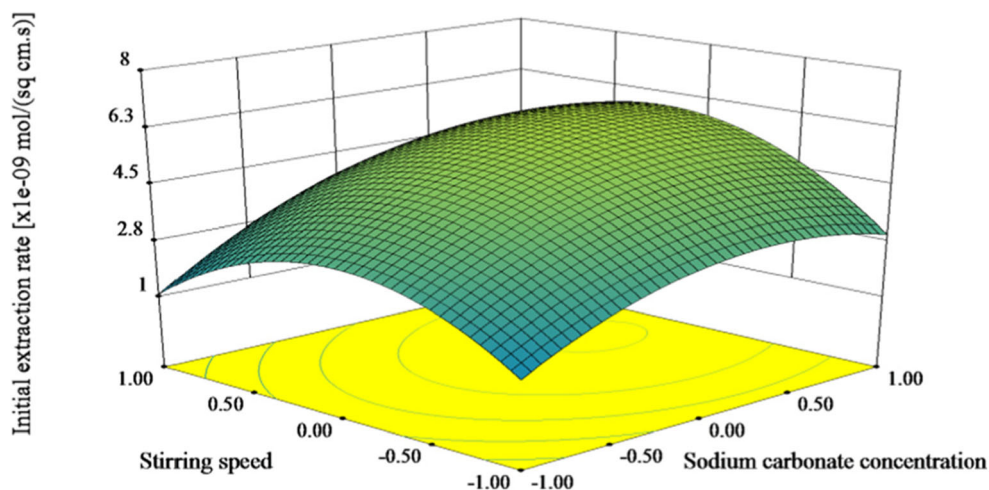
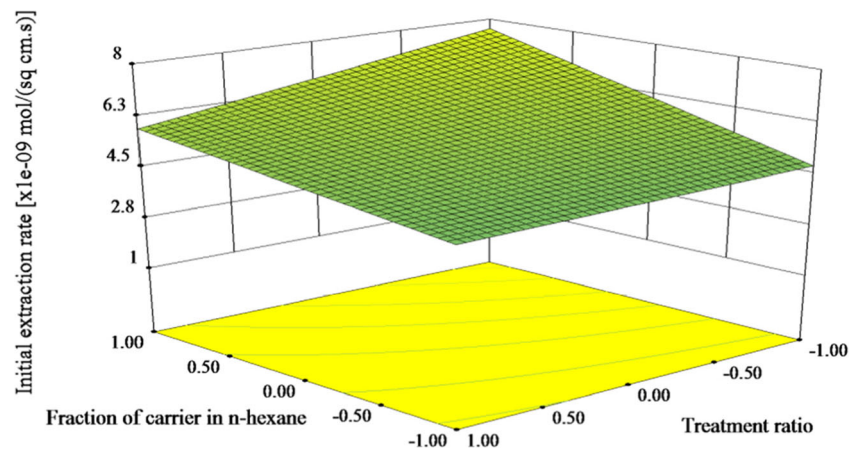


Fig. 6 Effect of fraction of carrier in n-hexane and treatment ratio on initial extraction rate



creased while that of carrier in the membrane phase has decreased (Noah et al. 2016).

3.3 Extraction Efficiency

The interactive effect of sodium carbonate concentration (c_s) and lactic acid concentration (c_l) on η_{ext} had been illustrated in Fig. 7. η_{ext} had been found to be increased with the increase in c_s irrespective of c_l , but more profoundly at low level of c_l . This may be attributed to the higher hydrogen ion difference between the feed and stripping phase due to the larger reaction potential of Na_2CO_3 with lactic acid at its higher initial concentration. The hydrogen ion difference will be higher for minimum c_l and maximum c_s (Lee 2011). η_{ext} had been found to decrease with the increase in c_l irrespective of c_s .

The 3D graphs depicts that decline in η_{ext} is more at low value of c_s . This can be explained with reference to the consideration of advancing front model for emulsion liquid membrane such that as the c_l in aqueous phase increases, internal droplets in the peripheral region of emulsion got saturated more rapidly causing increase in

the length of the diffusional path through the emulsion globule S_o , generating the necessity of more stripping reagent i.e. c_s (Reis et al. 2011). Hence mass transfer resistance in the membrane phase becomes important at high c_l , whereas, for low c_l , external mass transfer is rate controlling. Towards higher level of c_s , irrespective of c_l , η_{ext} tends to leveled off may be owing to the fact that initially increment in c_s causes decrease in the mean droplet size of emulsions but further increase in c_s after attaining its certain value, leads to increase in interfacial tension making emulsions unstable resulting in larger droplet size (Patti et al. 2012).

The effect of lactic acid concentration (c_l) and fraction of carrier in n-hexane (φ), on η_{ext} has been depicted in Fig. 8. It is observed that the effect of φ on η_{ext} is more significant at low values of c_l . For low values as well as high values of c_l the increment of c_l causes gradual decreasing of η_{ext} . At higher level of c_l the increasing of φ also leads to enhancement of η_{ext} , which is almost becoming constant at high level of φ . This may be due to reason that with the increase in carrier concentration, thickness of membrane wall increases due to increase in viscosity causing decrease in diffusion coefficient

Fig. 7 Effect of lactic acid concentration and sodium carbonate concentration on lactic acid extraction efficiency

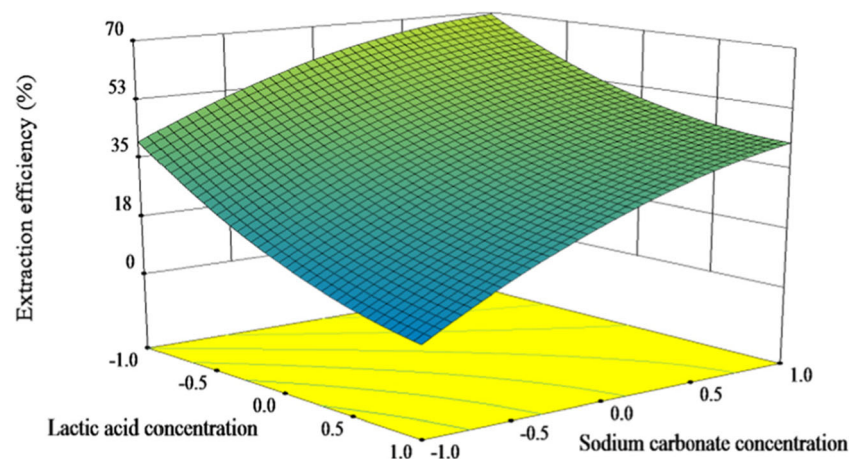
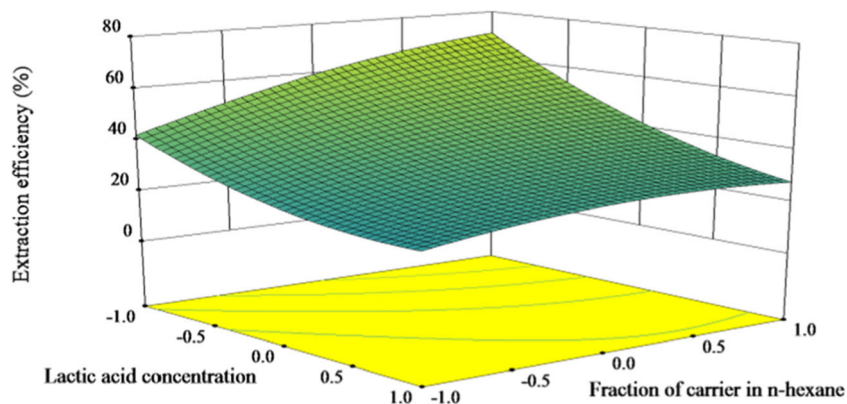


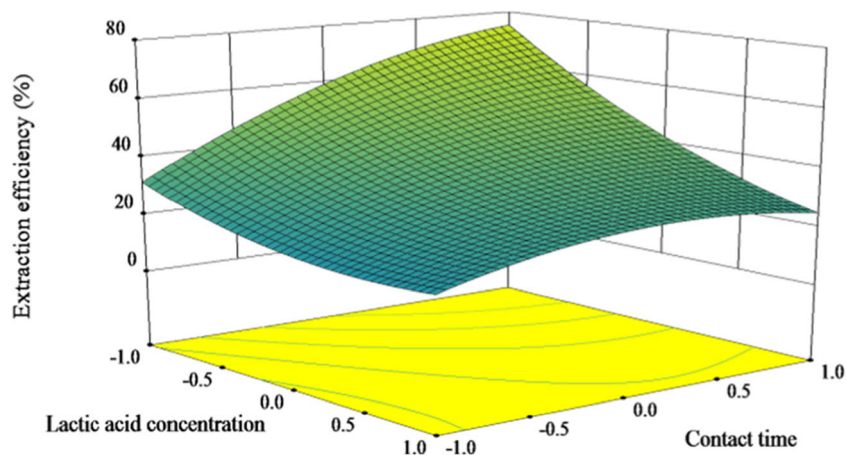
Fig. 8 Effect of lactic acid concentration and fraction of carrier in n-hexane on extraction efficiency



(Yordanov and Boyadzhiev 2004). Since the aqueous-organic interface has been flooded with lactic acid molecules at higher c_l and higher interfacial resistance would be spawned as surfactant and carrier molecules in larger number will be contending at the interface for the adsorption sites (Basualto et al. 2006). Moreover higher carrier concentration causes increase in interfacial tension causing formation of larger size emulsion globules hence lesser surface area availability for mass transfer (Benyahia et al. 2014).

The interactive effect of lactic acid concentration (c_l) and contact time, τ on extraction efficiency, η_{ext} is evident from Fig. 9. At low level of c_l , η_{ext} increases more rapidly with the incremental of τ in comparison to high level of c_l . It can be due to the fact that at high level of c_l during extraction, the peripheral region of emulsion could be got saturated by the earlier transported lactic acid into the stripping phase, and the lactic acid-amine complex now must diffuse to the more inner region of the emulsion through the membrane phase to liberate lactic acid into stripping phase Daas and Hamdaoui 2010). It is also evident from the figure that at any level of τ , the η_{ext} increases more rapidly at low level of c_l in comparison to high level of c_l , which may be owing to the fact that at high c_l concentration gradient at external phase-membrane phase interface is unfavorable causing carrier saturation effect (Anitha et al. 2015).

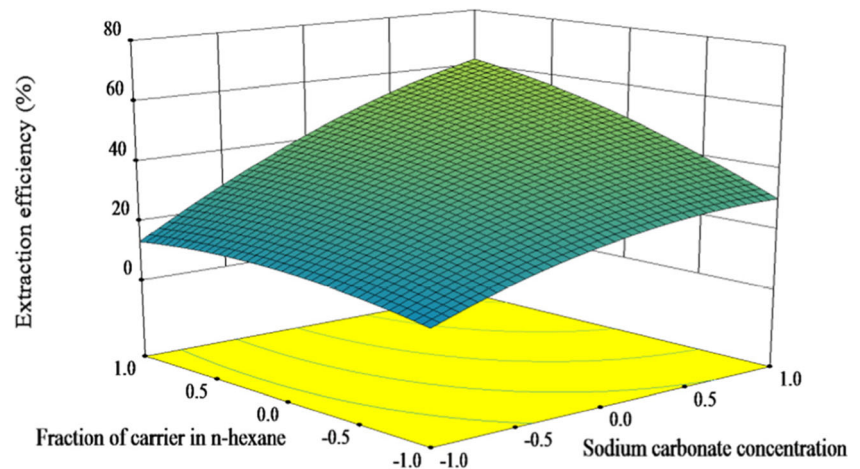
Fig. 9 Effect of lactic acid concentration and contact time on lactic acid extraction efficiency



In the ELM process, φ and c_s are the true representative of interactive extraction and stripping reaction processes in taking place in series respectively as both are the competitors for limiting reactant i.e. LA (Goyal et al. 2011). Extraction efficiency, η_{ext} has been found to rise with the increase in c_s for any value of φ (fraction of carrier in hexane) (Fig. 10), since the encapsulation capacity of lactic acid in stripping phase increases with the increase in c_s which makes it possible the faster regeneration of TOA/TDA molecules rendering it available at faster rate for carrier-solute complex formation at the external phase-membrane interface and lowers the accumulation of solute-carrier complex at the interfaces of membrane phase causing faster lactic acid extraction (Anitha et al. 2015). At high level of c_s , η_{ext} increases with the increase in φ , but at low level of c_s , η_{ext} doesn't show any significant increase may be owing to the fact that enough stripping agent was not available in the emulsion for the encapsulation of lactic acid.

The effect of contact time and sodium carbonate concentration on extraction efficiency has been illustrated in Fig. 11. η_{ext} increases initially slightly and then become steady state at high level with the incremental of contact

Fig. 10 Effect of fraction of carrier in n-hexane and sodium carbonate concentration on lactic acid extraction efficiency



time, τ at low level of c_s . This may be due the fact that the stripping agent present in the emulsion had got exhausted early.

At high level of c_s , η_{ext} increases with the incremental of τ owing to the normal permeation mechanism. η_{ext} had been found to be increasing with the decrease in treatment ratio, ψ for any level of φ (Fig. 12), though the increment is more at high level of φ in comparison to that of at low level of φ , since carriers provide high distribution coefficient due to their tendency to form ion pair association of the alkyl ammonium cation with the acid anion (Keshav et al. 2012). At high level of ψ , there was no significant increase in η_{ext} , due to lack of proper dispersion of emulsion globules for lactic acid encapsulation. At low level of ψ , η_{ext} shows an increasing trend with the incremental of φ , and tends to achieve a constant value towards higher level. Since, at higher external phase volume: membrane phase volume ratio (i.e. low treatment ratio) and higher carrier concentration in the membrane phase there is a tendency of emulsion swelling due to a hydrated surfactant, which facilitate the water diffusion across the membrane

along-with lactic acid, hence stopping the further increase in lactic acid extraction (Anitha et al. 2015).

It is evident from Fig. 13 that η_{ext} increases with the increment in τ and Φ . The increment in η_{ext} is higher at high level of τ and Φ in comparison to that at low level of τ and Φ . With the increase in Φ the thickness of the wall of the membrane globule decreases, causing decrease in distance to be traveled by the lactic acid-carrier complex relatively between the two interfaces, thereby increasing η_{ext} (Goyal et al. 2011a).

3.4 Optimization of Lactic Acid Extraction

The numerical optimization technique was applied for obtaining the optimum value of process variables to maximize the responses (initial extraction rate and extraction efficiency). The statistical optimization of six variables for ξ_0 and seven variables for η_{ext} was done separately. The optimum values of process variables, c_b , c_s , φ , ψ , Φ and ω obtained were 0.5 [M], 0.2 [M], 4.57 (%v/v), 0.50 (v/v), 0.70 (v/v) and 200 rpm respectively for ξ_0 , while for η_{ext} , the optimum values of

Fig. 11 Effect of contact time and sodium carbonate concentration on lactic acid extraction efficiency

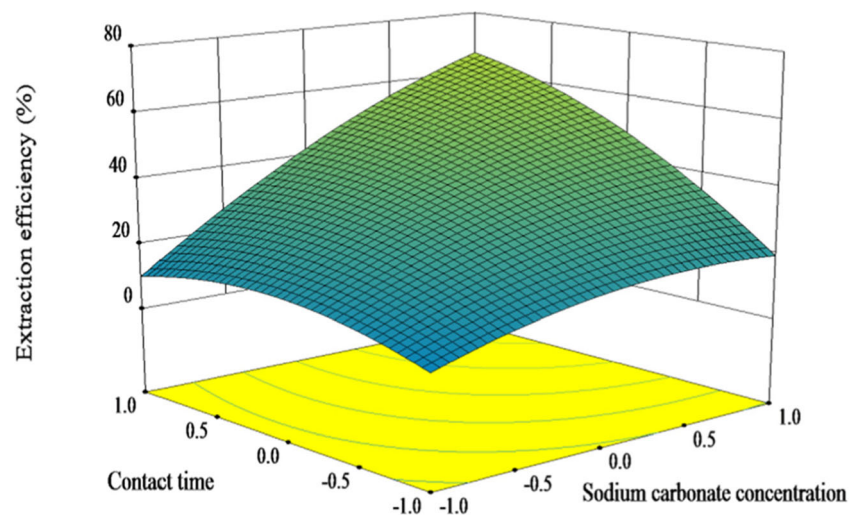
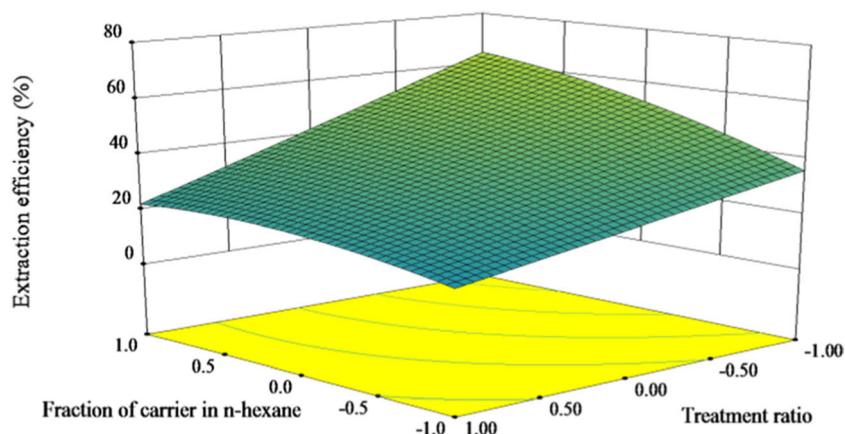


Fig. 12 Effect of fraction of carrier in n-hexane and treatment ratio on lactic acid extraction efficiency



process variables, c_t , c_s , φ , ψ , Φ , ω and τ were 0.16 [M], 0.25 [M], 3.20 (%v/v), 0.50 (v/v), 0.50 (v/v), 110 rpm and 9.75 min respectively. The initial extraction rate, ξ_0 and extraction efficiency, η_{ext} were predicted at the values of 9.36×10^{-9} [mol/cm²/s] and 98.5% under these optimized values, respectively. The synergy between the model predicted values for the process responses and those of experimentally observed values under optimized conditions has demonstrated that mass transfer phenomenon during the ELM process was adequately described by the respective mathematical models obtained during analysis of variance. So the design of experiments and subsequently optimization of process parameters by BBD for lactic acid extraction by ELM has shown a promising prospective on economical, environmental, time and technological aspects in comparison to conventional procedures/processes.

3.5 Validation of Results

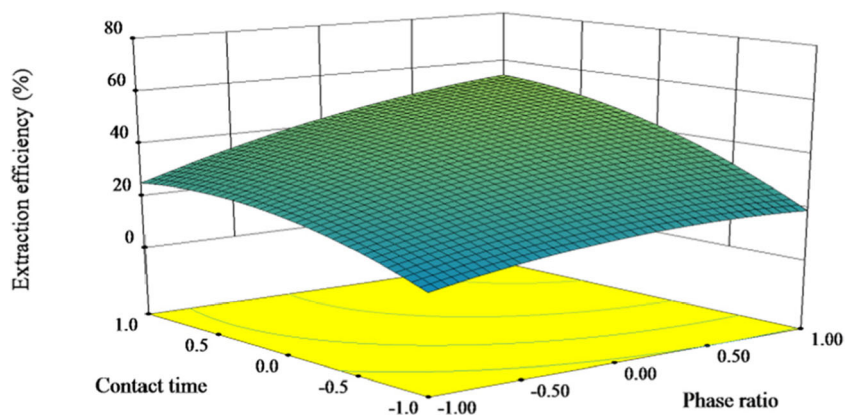
Experiments were performed in triplicate for validation of the results predicted by the model under the optimized conditions for initial extraction rate and extraction efficiency. A close agreement between the predicted model values and experimental results was observed. The relative error was found to be within $\pm 1.4\%$ and $\pm 1.5\%$ for the initial extraction rate and

extraction efficiency, respectively. It indicates that the process statistical modeling is appropriate and fulfills the optimization objective.

4 Conclusion

Response surface methodology has successfully optimized the LA extraction by emulsion liquid membrane technology. The experimental design, regression analysis, and quadratic models hence developed for the initial extraction rate and extraction efficiency were observed to be reasonably accurate and efficient in forecasting the response value within the ranges of the variables investigated. The optimum value of contact time of 9.75 min along with optimized conditions of other process parameters for achieving the 98.5% extraction efficiency with an initial rate of extraction of 9.36×10^{-9} [mol/cm²/s] has demonstrated the ability of ELM to achieve considerably high degree of separation at a very rapid rate. The contour and 3D graphs has provided the insight about the interactive effect of process parameters on the ELM process efficiency for lactic acid extraction under the synergic effect of mixture of tertiary amines.

Fig. 13 Effect of contact time and phase ratio on lactic acid extraction efficiency



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