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Response Surface Modeling of Lactic Acid Extraction by Emulsion Liquid Membrane: Box-Behnken Experimental Design

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***Abstract*—**Extraction of lactic acid by emulsion liquid membrane technology (ELM) using n-trioctyl amine (TOA) in n-heptane as carrier within the organic membrane along with sodium carbonate as acceptor phase was optimized by using response surface methodology (RSM). A three level Box-Behnken design was employed for experimental design, analysis of the results and to depict the combined effect of five independent variables, vizlactic acid concentration in aqueous phase (c_l), sodium carbonate concentration in stripping phase (c_s), carrier concentration in membrane phase (ψ), treat ratio (φ), and batch extraction time (τ) with equal volume of organic and external aqueous phase on lactic acid extraction efficiency. The maximum lactic acid extraction efficiency (η_{ext}) of 98.21%from aqueous phase in a batch reactor using ELM was found at the optimized values for test variables, c_l, $c_{s,}$ ψ, $\varphi$and τ as 0.06 [M], 0.18 [M], 4.72 (%,v/v), 1.98 (v/v) and 13.36 min respectively.

***Keywords*—**Emulsion liquid membrane, extraction, lactic acid, n-trioctylamine, response surface methodology.

I. Introduction

RECOVERY of carboxylic acids from aqueous solutions and fermentation broths, where it is present in dilute form (<10%), is always of interest to researchers [1]. Lactic acid (LA), an important carboxylic acid has received much attention in recent years as it can participate in a wide variety of chemical reactions leading to a host of products for use such as a preservative and acidulant in foods, controlled delivery of drugs in pharmaceutical agents, as a precursor for production of polymers like polylactic acid and as moisture agents in cosmetic etc. [2]. Due to increased environmental concerns, volatility and scarcity of fossil fuels' costs, regulatory initiatives, the need to reduce dependency on petroleum based feedstock; the worldwide demand of lactic acid has been increasing year by year. There has been a remarkable increase in the application of lactic acid as it is used to synthesize biodegradable polymers and green solvents, such as poly(lactic) acids (PLA) and lactate esters. Lactic acid can be produced by carbohydrate fermentation or chemical synthesis. Chemical synthesis process for lactic acid production from petroleum resources consistently yields a racemic mixture of DL-lactic acid, whereas the demand is for pure L(+) lactic acid, which is extensively used for the synthesis of PLA [3]. The most economical method for producing L(+) lactic acid as used worldwide is fermentation. Lactic acid is the most serious product inhibitor during its microbial production as it lowers the pH of fermentation broth. Removal of lactic acid from the fermentation broth is a preliminary step for separation & purification of lactic acid and a part of fermentation processes to remove a product inhibitor. The effects of end product inhibition can be reduced by in situ removal of lactic acid from fermentation broth by several methods [4]. 50% of the total production cost of lactic acid is due to involvement of a large number of separation and purification steps [3].Traditional purification methods recover lactic acid directly from a fermentation broth and include precipitation and physical extraction, but these poses environmental problems and are not economical, because the precipitation by calcium hydroxide or calcium carbonate produces a large amount of sludge and the organic solvents due to very low distribution coefficient in physical extraction. Hence, these traditional methods of recovery are expensive and unfriendly to the environment [5]. Thus development of a more economical purification method is required for success of the fermentation-based processes for the production of lactic acid. In recent years emulsion liquid membrane technology, which was initially proposed by Li [6] is a simplified extraction process with high extraction efficiency which combines both extraction and stripping stage to perform a simultaneous purification and concentration has been used as a one of the most promising novel approach to the extraction of low concentrations of organic acids, provides an attractive alternative to conventional extraction. ELM could be up to 40% cheaper than that of other solvent extraction methods [4]. ELM one of the most promising separation methods has been successfully employed by the various researchers for the separation of sugars, organic acids, amino acids, proteins and antibiotics [7]. The emulsion is made by dispersing the internal phase in membrane phase under high agitation provided by a homogenizer or ultrasonicator in the presence of a surfactant generating typically, the size distribution of the dispersed internal phase droplets of about 1 to 10 μm followed by the dispersion of prepared emulsion as emulsion globules (0.1-3 mm) into a third aqueous phase which contains a solute to be removed making it w/o/w type emulsion in which oil

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phase acts as a barrier between two aqueous phases and called as membrane phase. ELM processes are simple, relatively low energy consumption compared to other separation processes such as thermal evaporation, solvent extraction and pressure-driven membrane processes, provides high selectivity and allow very high mass transfer rate due to its large surface area within the emulsion globules and internal droplets at a greater speed and with a high degree of effectiveness [6], [8]. The selectivity can be enhanced by adding a carrier to the membrane phase such as trialkylamines, tributyl phosphate, quaternary ammonium salts, crown ethers and others [7]. Concentration of solute in a feed phase (or external phase) can be reduced to very low levels and it can be highly concentrated in a stripping phase (or internal phase) [9]. The extraction chemistry of ELM is similar in kind to the classical solvent extraction, but the transport process is governed by kinetic rather than equilibrium parameters, under non-equilibrium mass transfer [10]. The extraction yield depends on the operation conditions as well as solvent characteristics, surfactant, carrier type and concentration, among others [7]. Thus, the emulsion efficiency can be assumed to be controlled by the inherent membrane properties and the operating parameters [11]. Hence in order to have a better understanding of the dynamics of ELM process using TOA as carrier for the extraction of lactic acid from aqueous phase, the objective of this work is to experimentally study the major parameters influencing the extent of extraction and to determine the optimum conditions needed for the lactic acid extraction from aqueous phase by changing various experimental variables. From this point of view, it is important to select a suitable experimentation technique which will evaluate the effects of important parameters along with possible interactions, with minimum number of experiments [12].

Optimization of parameters by the conventional method involves changing one independent variable while unchanging all others at a fixed level. 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. Response surface methodology is a statistical tool available as software used to optimize the different processes and this methodology is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. In this technique, the main objective is to optimize the response surface that is influenced by various process parameters. It also has important applications in the design, development and formulation of new products as well as in improvements of existing products designs. Response surface methodology can identify and quantify the various interactions among different parameters [13]. Response surface methodology is used in modeling the relationship between one or two responses and a number of quantitative variables or factors and in locating the combination of the factor levels that give the optimum expected response.

Keeping in view the above, the lactic acid extraction from aqueous phase in a batch reactor by ELM was studied to develop an optimal ELM system using a three level Box-Behinken design.

II. Theory

The mass transfer in W/O/W double emulsions during the facilitated transport includes the migration of lactic acid through the oil film, diffusion and/or permeation through the oil membrane in the form of solute carrier complex as the molecules pass through thin lamellae of surfactants which partially form in the oil layer due to fluctuation of its thickness. The formation of solute-carrier complex is achieved by incorporating an organic soluble extractant known as carrier agent, which selectively combines with the solutes at the external interface. This complex will permeate through the membranes from the external to the internal interface. At the inner interface, the complex decomposes by the reversal of the equilibrium reaction and the solute ion is stripped from the complex by a stripping agent in the internal phase and the regenerated carrier goes back into the membrane phase. The physical extraction of lactic acid due to the "swelling–breakdown" & "reverse micelles" mechanism, as well as the acid dimerization and the water coextraction via hydrated surfactant can also take place along with the facilitated transport of lactic acid. However, the transport due to "reverse micelles" or via hydrated surfactant gets retarded if the oil film is extremely thin (<1 μm) [14].The extracting and stripping reactions take place during the extraction of lactic acid by ELM are as (Fig. 1).

A. Extraction Reaction

The type of mechanism during the interaction between a lactic acid (available in external aqueous phase) and a tertiary amine (available in the organic phase of emulsion) at the external interface, which will prevail depends on the pH of the lactic acid solution, the pK_a of the lactic acid, the amine concentrations, and the basicity of the amine with respect to the lactic acid [15] and has been realized by two mechanisms

a) through hydrogen bonding of non-dissociated acid molecule:

b) $$\underbrace{R_3N}_{(membrane\ phase)} + \underbrace{HLa}_{(external\ Phase)} \leftrightarrow \underbrace{R_3N{:}HLa}_{(membrane\ phase)} \quad (1)$$

or b) by ion-pair formation:

$$\underbrace{R_3N}_{(membrane\ phase)} + \underbrace{H^+ + La^-}_{(external\ phase)} \leftrightarrow \underbrace{R_3NH^+La^-}_{(membrane\ phase)} \quad (2)$$

where R_3N represents the tertiary amine (TOA) and HLa, H^+ and La^- represents lactic acid and its ions, respectively.

The other possibilities for the association of lactic acid molecules with the amine carrier in the membrane phase are

i) In case of un-dissociated lactic acid molecules [HLa] extraction, the equilibrium can be represented by a set of equations depicting the formation of different complexes having nacid molecules and one amine molecule:

$$\underbrace{HLa}_{(external\ phase)} + \underbrace{R_3N(HLa)_{n-1}}_{(membrane\ phase)} \leftrightarrow \underbrace{R_3N(HLa)_n}_{(memberane\ phase)} \quad (3)$$

ii) If more than one amine molecule takes part in the complex formation, the reaction mechanism can be expressed as

$$\underbrace{HLa}_{(external\ phase)} + \underbrace{nR_3N}_{(membrane\ phase)} \leftrightarrow \underbrace{HLa(R_3N)_n}_{(membrane\ phase)} \quad (4)$$

iii) If p molecules of the acid react with q molecules of the amine, the reaction mechanism can be given as:

$$\underbrace{pHLa}_{(external\ phase)} + \underbrace{qR_3N}_{(membrane\ phase)} \leftrightarrow \underbrace{(R_3N)_q(HLa)_P}_{(membrane\ phase)} \quad (5)$$

Generally, the reaction of the amines with un-dissociated lactic acid at the external interface can be expressed by the mechanism as described above by (5).

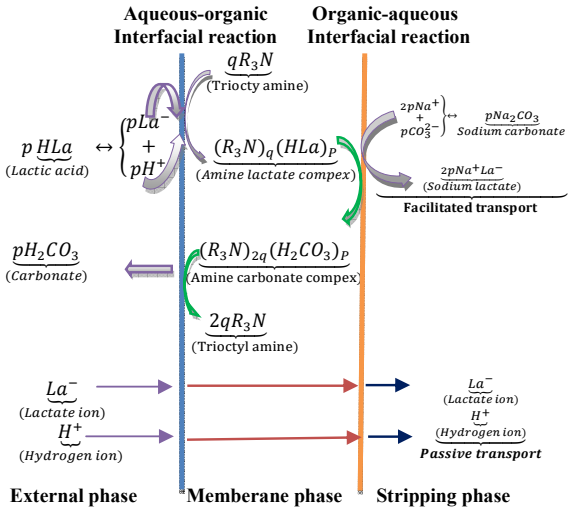

Fig. 1 Schematic representation of facilitated and passive mass transfer mechanism of lactic acid permeation

B. Stripping Reaction

The carrier-solute complexes diffuses onto the interface of the stripping phase, where it decomposes due to the high pH value in the stripping phase and reacts with the stripping reagent Na_2CO_3 to release lactate ion and carrier as

$$\underbrace{2(R_3N)_q(HLa)_P}_{(\text{membrane phase})} + \underbrace{pNa_2CO_3}_{(\text{stripping phase})} \rightarrow \underbrace{2pNa^+La^- + pH_2CO_3}_{(stripping\ phase)} + \underbrace{2qR_3N}_{(membrane\ phase)} \quad (6)$$

The free carrier ion is expected to reacts as follows to form amine carbonate complex and diffuses back to the aqueous-organic interface due to concentration gradient and dissociates into Carbon dioxide and water regenerating the free amine, which is again made itself available in the membrane phase to form complex with lactic acid and transport it many times, achieving a high degree of extraction.

$$\underbrace{pH_2CO_3}_{(stripping\ phase)} + \underbrace{2qR_3N}_{(membrane\ phase)} \leftrightarrow \underbrace{(R_3N)_{2q}(H_2CO_3)_P}_{(\text{membrane phase})} \quad (7)$$

$$\underbrace{(R_3N)_{2q}(H_2CO_3)_P}_{(\text{membrane phase})} \leftrightarrow \underbrace{2q(R_3N)}_{(memberane\ phase)} + \underbrace{pH_2O + pCO_2}_{(external\ phase)} \quad (8)$$

Lactic acid transport through the membrane can be visualized as a process of mass transfer affected by the equilibrium and kinetics of the extraction chemical reaction between the lactic acid ion and the amine carriers. The solvation of the whole carrier solute complex is based on dipole-dipole interaction, play an important role in the neutralization reaction between solute and carrier. The content of carrier extractant in the organic phase along with other parameters would then affect the chemical extraction reaction at the interface as well as the diffusion process through the membrane. Moreover pH difference (causes difference in chemical potential) between the external and the stripping phase also functions as a driving force for extraction of lactic acid in the system; hence it is possible to obtain a high extraction of lactic acid using the stripping phase of high Na_2CO_3 concentration.

III. Materials and Methods

A. Experimental Design

For the optimization of extraction efficiency, the experiments were conducted according to experimental design obtained from Box-Behnken design (BBD) with five variables at three levels each using Design-Expert 7.16 software (Statease Inc., Minneapolis, USA,). The effect of lactic acid concentration in aqueous phase (c_l), [M], sodium carbonate concentration in stripping phase (c_s) [M], fraction of carrier in n-heptane (ψ, % v/v), treat ratio (φ, v/v), and batch extraction time (τ, min) on the extraction efficiency (η_{ext})were investigated at the ranges as shown in Table I in the form of original values of each factor (un-coded) and their corresponding levels (coded). The experimental plan in coded and un-coded form of process variables is as shown in Table II. A total 45 experiments with various combinations of lactic acid concentration in aqueous phase, sodium carbonate concentration in acceptor phase, carrier concentration in membrane phase, treat ratio and batch extraction time were conducted randomly to minimize the effect of extraneous variables. All the experiments were conducted in duplicate and the average values of extraction efficiency were tabulated, as given in Table II.

TABLE I
Range of Different Variables for Lactic Acid Extraction Using ELM in Coded and Un-Coded Form

Codes values		-1.000	0.000	+1.000
Un-coded values	c_l, [M]	0.05	0.075	0.1
	c_s, [M]	0.1	0.15	0.2
	ψ, (%,v/v)	2	5	8
	φ, (v/v)	1	2	3
	τ, (min)	5	10	15

B. Membrane Preparation

The ELM used was a water-oil-water (w/o/w) type of emulsion and was prepared by mixing the internal stripping phase with membrane (organic) phase. The membrane phase initially tried contained 3-5% (v/v) Span 80 as stabilizer,0-10% (v/v) tri-n-octylamine (TOA), as carrier in n-heptane and 2% (v/v) cyclohexanone (to reduce water co-transportation

and hence the swelling of the membrane phase) [16] under constant stirring speed of 200 rpm for 2 min was prepared by using a magnetic stirrer. To this homogeneous membrane phase, 0.1-0.2 [M] stripping phase (Na_2CO_3 solution) with 1:1 (v/v) internal to organic phase ratio was added drop wise at a low stirring speed of 200 rpm. Subsequently, this mixture was stirred at 2000 rpm using a four blade impeller stirrer (Model: IKA RW 20, Digital Dual Range Mixer from Cole-Parmer, India) for 20 minute at room temperature (25 ± 2°C) to form a stable liquid emulsion membrane. Then emulsion was transferred to settler after washing the emulsion with excess deionized water to wipe out the internal reagents attached to the surface of emulsion if any and stored for an hour to check its stability. After several trials, for 1:1(v/v) phase ratio, emulsion containing 4 % (v/v) Span 80 in n-heptane (χ), 0-10% (%,v/v) tri-n-octylamine concentration in n-heptane (φ), 2% (v/v) cyclohexanone and 0.1-0.2 [M] stripping phase concentration (c_s, Na_2CO_3 solution) stirred at 2000 rpm were found to be very stable.

C. Extraction of Lactic Acid

The extraction was carried out in a 250 ml capacity batch extractor at 25±2◦C temperature with a variable speed four bladed agitator having diameter 30 mm, which was charged with ELM (50 mL) and to which aqueous lactic acid (external phase) was added according to treat ratio as per experimental design and stirred well at the stirring speed of 200rpm. Samples from the stirred batch reactor during the course of run at different time intervals as per experimental design (Table II) were drawn. The external phase of the samples was separated from the emulsion phase by filtration using a filter paper and was analyzed for lactic acid concentration.

D. Statistical Analysis and Optimization

Response surface and contour plots were generated for different interactions of any two independent variables while holding the values of the other variables 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 first analysis step in response surface methodology is to fit regression equation to the responses data obtained from the experimental work; a regression analysis is carried out to determine the coefficients of the response model, their standard errors and significance.

The behavior of the system was explained by the following quadratic equation:

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} b_{ij} x_i x_j + \varepsilon \quad (9)$$

where Y is the predicted response i.e. extraction efficiency, $b_0$is the offset term; b_i is the linear effect; $b_{i\ i}$is the squared effect; and b_{ij} is the interaction effect. x_i is ith independent variable [17] and ε is the random error or allows for discrepancies or uncertainties between predicted and measured values. In developing (1), the natural (uncoded) independent variables (X1, X2,. . .,Xk) are coded according to the following transformation

$$x_i = \frac{(X_i - X_{i0})}{\Delta X_i} \quad (10)$$

where x_i is dimensionless coded value of the ith independent variable, X_i is the uncoded value of the ith independent variable, X_{i0} is the uncoded ith independent variable at the center point, and $\Delta X_i$is the step change value [18].

The statistical analysis of the results was carried out by Analysis of Variance (ANOVA) which evaluates the model and interactions of the five factors on the lactic acid extraction efficiency through identifying the coefficients of each term given in (9). Statistical significance was verified by the *F*-test in the program. Model terms were selected or rejected based on the probability value with 95% confidence level [6].

After the regression models had been built, tests were performed to find out fitting of the models. The optimum level of variables (within the experimental range) to obtain the maximum extraction efficiency, η_{ext} were determined. The experiments were run using the optimum values for variables given by response optimization for confirmation of predicted values and maximum extraction efficiency, η_{ext} were confirmed. The same software was used to analyze the data, to estimate the coefficients of the regression equation and for the optimization of process variables.

E. Analytical Method

Lactic acid concentration was analyzed by a colorimetric method [19] using a (model DR 5000 HACH, USA) UV/VIS spectrophotometer.

F. Mathematical Calculations

The extraction efficiency has been calculated using the following equation:

$$\text{Extraction efficiency, } \eta_{ext} = \frac{C_{l\tau_0} - C_{l\tau}}{C_{l\tau_0}} x100 \quad (11)$$

where $C_{l\tau_0}$is the lactic acid concentration in aqueous phase initially at time, $\tau = 0$, before contacting it with the emulsion globules, and $C_{l\tau}$ is the concentration of the lactic acid in aqueous phase after contacting the aqueous phase with emulsion liquid membrane for desired time as per design of experiment.

IV. Results and Discussion

TABLE II
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					Response
Lactic acid concentration (X_1)	Sodium Carbonate concentration (X_2)	Fraction of carrier in n-heptane (X_3)	Treat ratio (X_4)	Batch extract-ion time (X_5)	Extraction efficiency (η_{ext})
0	0	-1	0	-1	58.55
0	0	1	0	-1	70.67
1	0	0	-1	0	70.30
0	-1	0	0	-1	63.01
0	1	0	0	-1	67.45
0	-1	1	0	0	74.23
0	0	0	-1	-1	64.67
0	0	1	1	0	86.76
0	-1	0	1	0	75.05
-1	0	-1	0	0	75.56
0	1	0	0	1	98.01
0	0	0	0	0	93.08
0	1	1	0	0	87.79
-1	0	0	-1	0	77.06
1	0	0	0	1	85.64
0	0	-1	-1	0	72.34
0	0	0	0	0	92.76
1	0	0	0	-1	62.20
0	0	1	-1	0	73.08
0	1	0	1	0	88.61
1	-1	0	0	0	68.61
-1	-1	0	0	0	75.87
0	-1	0	-1	0	66.55
0	0	0	0	0	92.98
0	0	0	0	0	93.16
-1	0	1	0	0	88.00
0	0	0	0	0	93.38
0	0	0	0	0	93.09
0	0	-1	1	0	75.66
1	0	1	0	0	74.72
0	-1	-1	0	0	68.31
1	0	-1	0	0	75.32
-1	1	0	0	0	88.93
-1	0	0	0	1	92.40
-1	0	0	0	-1	68.96
0	0	0	1	-1	63.61
1	1	0	0	0	82.67
0	1	-1	0	0	81.87
0	0	0	-1	1	78.55
0	-1	0	0	1	77.33
-1	0	0	1	0	85.56
0	0	0	1	1	96.61
0	0	1	0	1	87.91
0	0	-1	0	1	88.19
0	1	0	-1	0	80.11
1	0	0	1	0	78.80

A. Regression Model

The following regression equations were developed as a result by applying the multiple regressions (along with backward elimination regression with α to exit = 0.100) on experimental data the quadratic model (in terms of coded forms) explained the role of each variable and their quadratic interaction on extraction efficiency, η_{ext} is as follows:

$$Extraction\ efficiency, \eta_{ext} = 93.075 - 3.38 * X_1 + 6.66 * X_2 + 2.96 * X_3 + 4.25 * X_4 + 11.6 * X_5 + 0.25 * X_1 * X_2 - 3.26 * X_1 * X_3 + 4.06 * X_2 * X_5 + 2.59 * X_3 * X_4 - 3.1 * X_3 * X_5 + 4.78 * X_4 * X_5 - 6.81 * X_1^2 - 7.33 * X_2^2 - 7.78 * X_3^2 - 8.25 * X_4^2 - 9.05 * X_5^2 \quad (12)$$

where X_1- concentration of lactic acid, X_2- concentration of sodium carbonate, X_3- concentration of carrier, $X4$- treatment ratio and X_5-batch extraction time

The quadratic model (12) has sixteen terms which contain five linear terms, five quadratic terms and six two-factorial interactions. The significance of each coefficient was determined by F-value and P-value as listed in Table III. Out of these, the terms having p > F values less than 0.05 are significant terms. P-value greater than 0.1 indicates that the model term is insignificant. Probability p (p > F) values were used as a tool to check the significance of each of the coefficients. The smaller the magnitude of p values, the more significant was the correlation with the corresponding coefficient [6]. In this case the first-order main effects and the square effects of all factors are significant. It then can be concluded that all the factors play a significant role in the extraction of lactic acid from aqueous solutions by ELM. It also explains the interactive effects of c_l&c_s, cl&ψ, c_s&τ, ψ&φ, ψ&τ and φ&τ. ANOVA of the regression model demonstrates that the model is highly significant. The coefficient of determination values (R^2) were satisfactory (>0.98) for the response ($p\leq$ 0.05) indicating a good agreement between experimental observation and predicted values. The R^2 value also indicated that only 1% of the variation was not explained by the model. The "Lack of Fit F-value" of 2.12 for η_{ext} implies that it is not significant relative to the pure error and signifies towards the model best fit [17]. The difference between adjusted R^2 and predicted R^2 is 0.0108, which implies that the values for the models are in good agreement. For using the models to navigate the design space the signal to noise ratio (adequate Percision) greater than4 is desirable which is 240.91 [17]. There was no lack of fit in the equation ($p\geq$ 0.05). A relatively lower value of the coefficient of variation (C.V. = 3.47%) indicates better precision and reliability of the experiments carried out [17].

The response surface curves for the extraction of lactic acid from aqueous solutions by ELM using TOA as carrier are shown in Figs. 2-7. Each response surface curve represents the change in levels of two factors with the other three factors maintained at zero levels.

B. Extraction Efficiency

The interactive effect of lactic acid concentration (c_l) and sodium carbonate concentration (c_s) on η_{ext} had been illustrated in Fig. 2. η_{ext} had been found to increase with the increase in c_s irrespective of c_l. This may be attributed to the fact that due to the larger reaction potential of Na_2CO_3 at higher c_s with lactic acid causes a higher hydrogen ion difference between the feed & the stripping phase and hydrogen ion difference will be higher in case of minimum c_l and maximum c_s. [20]. From Fig. 2, it can be seen that as the c_s exceeds 0.5 (coded value), the increasing rate of extraction efficiency slows down and even shows slightly a downward trend at the higher level. This may be due to the fact that above this value, the enhanced concentration difference between the external phase and internal phase leads to less stabilized emulsion causing emulsion coalescence, hence a

decrease in specific surface area available for mass transfer and the process becomes mass transfer controlled [17]. Extraction efficiency gradually increases with the augmentation in C_l at low level. This behavior is in accordance to the Fick's law; an increase in the c_l will raise the lactic acid driving force in both, stagnant aqueous layer and organic phase, which in turn causes an increase in the overall lactic acid flux rate through the ELM [21]. Extraction efficiency, η_{ext} had been found to be decreasing with the further increase in c_l irrespective of c_s. the 3D response depicts that decrease in η_{ext} is more at low value of c_s. This can be explained by the fact that as the c_l increases the internal droplets containing stripping agent in the peripheral region got saturated more rapidly causing an increase in the length of the diffusional path through the emulsion globule and more stripping reagent is required to enhance the capacity of the emulsion for extraction [22].

The effect of the TOA concentration, ψ as well as lactic acid concentration, c_l on η_{ext} is illustrated in Fig. 3. With the increase in ψ towards higher level, irrespective of c_l, η_{ext} had been found to be increasing. Apparently, more LA-TOA complex formation takes place on increasing carrier concentration, hence increases the η_{ext}. At low level of ψ *(-1)*, the extraction due to passive transport of lactic acid along with the facilitated transport is also contributory as it got dissolved in the organic phase due to the concentration gradient between the external phase and organic phase (Fig. 1). This passive transport enables the diffusion of LA to stripping phase and which was stripped down by the stripping reagent in the emulsion [11]. At higher value of ψ with further increase in ψ there is a slight decrease in $\eta_{ext,}$ may be owing the fact that higher carrier concentration leads to a higher amount of aminelactic acid complex at feed aqueous-organic membrane interface and also increases the organic phase viscosity, which causes the decrease in diffusivities of carrier & its complex and an increase in emulsion drop size, hence η_{ext} decreases [21], [23].

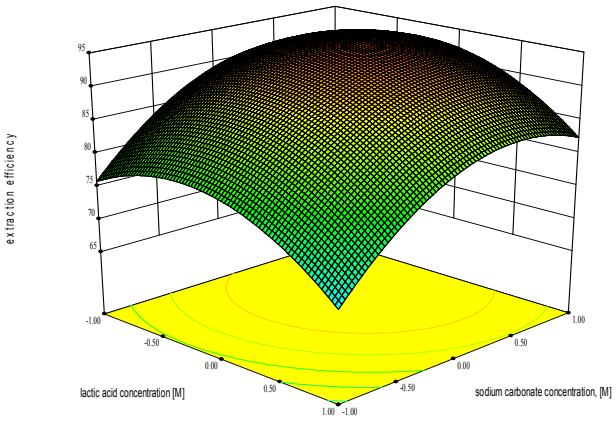

Fig. 2 Effect of lactic acid concentration and sodium carbonate concentration on lactic acid extraction efficiency

TABLE III
REGRESSION MODEL AND ANNOVA FOR EXTRACTION EFFICIENCY USING ELM (AFTER BACKWARD ELIMINATION)

Source	Sum of squares	Degree of freedom	Mean square	*f* - value	*p* >*f*
Model	5056.397	16	316.0248	4149.279	< 0.0001
Lactic acid concentration (X_1)	182.7904	1	182.7904	2399.965	< 0.0001
Sodium carbonate concentration (X_2)	708.6244	1	708.6244	9303.954	< 0.0001
Fraction of carrier in n-heptane (X_3)	140.1856	1	140.1856	1840.581	< 0.0001
Treat ratio (X_4)	289	1	289	3794.454	< 0.0001
Batch extraction time(X_5)	2151.104	1	2151.104	28243.14	< 0.0001
(X_1). (X_2)	0.25	1	0.25	3.2824	0.0804
(X_1). (X_3)	42.5104	1	42.5104	558.1445	< 0.0001
(X_2). (X_5)	65.9344	1	65.9344	865.6922	< 0.0001
(X_3). (X_4)	26.8324	1	26.8324	352.2986	< 0.0001
(X_3). (X_5)	38.44	1	38.44	504.7018	< 0.0001
$(X4)$. (X_5)	91.3936	1	91.3936	1199.961	< 0.0001
(X_1). (X_1)	404.8359	1	404.8359	5315.333	< 0.0001
(X_2). (X_2)	468.587	1	468.587	6152.359	< 0.0001
(X_3). (X_3)	528.361	1	528.361	6937.168	< 0.0001
(X_4). (X_4)	594.12	1	594.12	7800.557	< 0.0001
(X_5). (X_5)	714.3906	1	714.3906	9379.662	< 0.0001
Residual	2.20875	29	0.076164		
Lack of Fit	2.12	24	0.083333	1.996	0.2276*
Pure Error	0.20875	5	0.04175		
Cor Total	5058.606	45			
Standard Deviation = 0.275978			R^2 = 0.989		
Mean= 79.43413			Adjusted R^2 =0.989322		
Coefficient of variation (C.V.%) =0.34743			Predicted R^2 = 0.97849		
Predicted residual error of sum of squares (PRESS)= 7.63702			Adequate Precision = 240.9121		

*non-significant at 5 % level

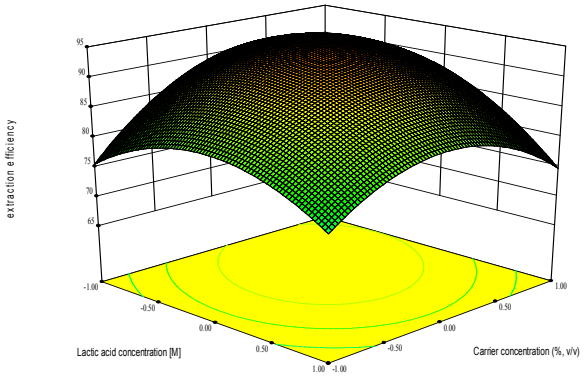

Fig. 3 Effect of lactic acid concentration and carrier concentration on extraction efficiency

The interactive effect of batch extraction time, τ and sodium carbonate concentration, c_s in stripping phase on extraction efficiency, η_{ext} has been illustrated in Fig. 4. η_{ext} had been found to be increasing with the increase in τ more profoundly at higher level of c_s. since high level ofc_s causes a higher hydrogen ion difference between the feed & the stripping phase in comparison to lower level of c_s. η_{ext} got levelled off at higher level of τ may be owing to the fact that batch extraction time is sufficient to get exhausted all the stripping reagent present in the internal droplet of the emulsion. Thus, at low level of c_s, the stripping rate of lactic acid was the limiting step in the process. The η_{ext} had been found to be first increasing and then decreasing with the increase in c_s, since with the increase in c_s the encapsulation capacity of the emulsion increase but at the higher c_s, due to the enhanced pH difference between the feed and the stripping phase, a large amount of osmotic pressure difference got induced. As a consequence, swelling takes place in emulsion liquid membrane which reduces the extraction efficiency [8].

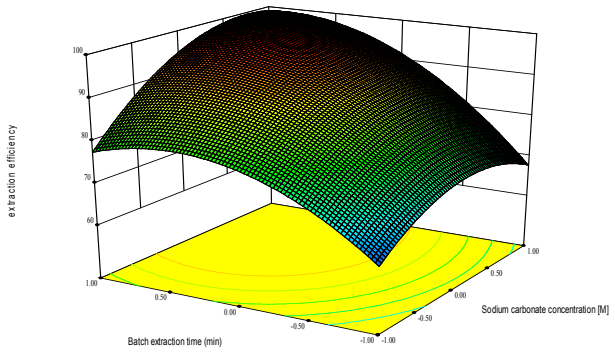

Fig. 4 Effect of batch extraction time and sodium carbonate concentration on lactic acid extraction Efficiency

The extraction efficiency, η_{ext} found to be increasing with the increase in φ and ψ towards the higher level (Fig. 5). At higher level of φ and ψ, η_{ext} had been found to be decreased. With the initial increase in the φ, the volume of the membrane as a whole decreases, this reduces the probability of the swelling. The effective concentration of LA per globule increases which enhances the rate of extraction at the interface of the aqueous (feed phase) and the organic phase. Hence, η_{ext} increases with increase in φ [8]. However, further increase in the φ affects the η_{ext} negatively may be owing to the fact that the number of emulsion globules per unit volume of feed phase and area for mass transfer decreases. Moreover increasing of φ may slightly increase the size of globules, which also contributes inversely a reduction in interfacial surface area [24].Though with the increase in ψ, there is a higher concentration of carrier at the interface between emulsion and external aqueous phase which promotes the transport of solute, but stripping rate remains almost constant during the whole process. Therefore, many LA-TOA complexes remain unstripped in the membrane phase causing a reduction in the extraction efficiency at higher level of ψ [8], [10].

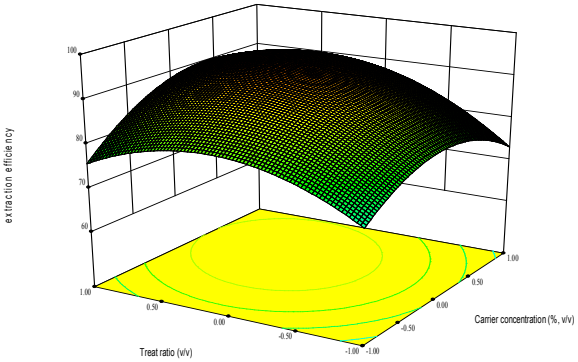

Fig. 5 Effect of treat ratio and carrier concentration on lactic acid extraction efficiency

η_{ext} had been observed to be increasing with the increase in ψ and τ (Fig. 6). However at higher level of ψ and τ there was a slight decline in η_{ext}. This may be owing to the reason that there was no more internal reagent left in the internal phase to react with the transported LA-TOA complex, results in a decrease in ψ, at the outer interface. Hence, the η_{ext} decreases [6].

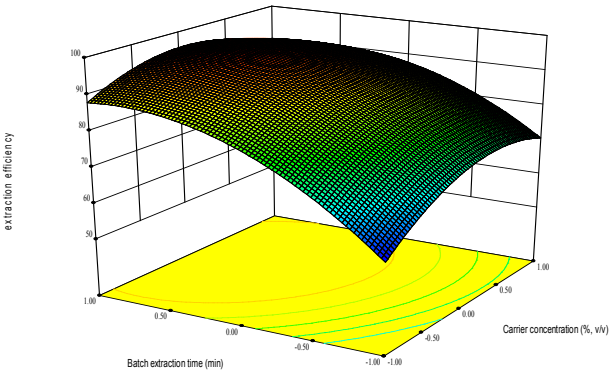

Fig. 6 Effect of batch extraction time and carrier concentration on lactic acid extraction efficiency

The 3D surface plot obtained under the operating conditions as per experimental design and analysis (Fig. 7) described the effects of batch extraction time, τ as a function of treat ratio, on the extraction efficiency η_{ext} and vice versa. At low level of φ, the emulsion dispersed in the external phase tends to form bigger droplets, leading to the decrease in the specific surface area between external aqueous phase and organic phase, hence lower extraction efficiency. Moreover, lower φ also add to the treatment cost [6].It is evident from the figure that η_{ext} increases with the increase in τ at a (any) fixed φ. However, at higher τ, the increase levels off asymptotically. With the increase in τ, the total mass transfer between the emulsion and feed phases increases. The 'leveling-off' of extraction efficiency at higher τ may be due to the physical phenomenon of exhausting of encapsulation capacity of emulsion.

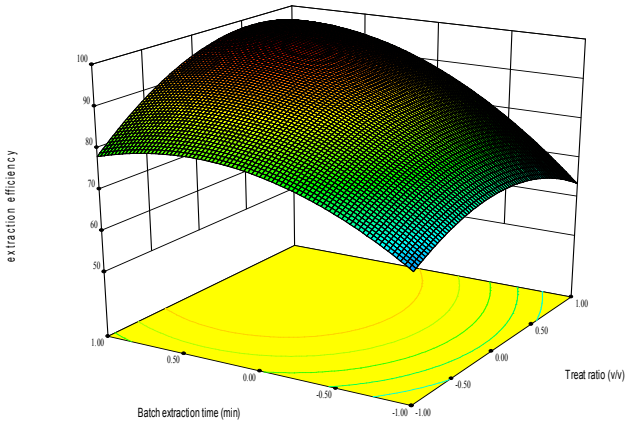

Fig. 7 Effect of batch extraction time and treat ratio on lactic acid extraction efficiency

C. Optimization of Lactic Acid Extraction

The numerical optimization technique was adopted for searching the optimum value of test variables by means of fitted models of input combinations of design variables that maximize the responses (extraction efficiency) i.e. Equation (12), was used for optimization of experimental conditions. The optimal values of the test variables were first obtained in coded units and then converted to the uncoded units. The statistical optimization of all the five variables for η_{ext} was carried out, which resulted in 10 different solutions each with having almost same optimum values in all of them for each response. With the consideration of the economy of the ELM process, since chemicals used as carriers are the most expensive chemicals in comparison with the rest [22], hence the solution with minimum carrier concentration was selected for each response. The uncoded optimum values for test variables, c_l, c_s, ψ, $\varphi$and τ are 0.06 [M], 0.18 [M], 4.72 (%,v/v), 1.98 (v/v) and 13.36 min respectively. The extraction efficiency, η_{ext} was predicted at the values of 98.33% under these optimized values.

D. Validation of Results

A set of experiments were performed to validate the results that the model predicted for the maximum extraction efficiency using different predicted optimum, values of variables. A close correspondence between the values predicted by the model and experimental data was observed. The absolute value of the relative error was found to be lower than 3% for the extraction efficiency. It indicates that the system modelling is appropriate and fulfills the objective function of the optimization.

V. Conclusion

Extraction of lactic acid by emulsion liquid membrane technology has been successfully optimized using response surface methodology. The experimental design, regression analysis, and quadratic models developed using response surface methodology according to Box–Behnken Design (BBD) for the extraction efficiency were noticed to be reasonably accurate and effective in predicting the value of the response within the limits of the factors investigated.

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