

Parametric Study of Lactic Acid Extraction Using Tri-N-Octyl Amine and Hexane through Emulsion Liquid Membrane

Thakur, Avinash^{*+}

Research Laboratory-III, Department of Chemical Engineering, Sant Longowal Institute of Engineering and Technology, Longowal, INDIA

Panesar, Parmjit Singh

Biotechnology Research Laboratory, Department of Food Engineering and Technology, Sant Longowal Institute of Engineering and Technology, Longowal, INDIA

Singh, Manohar

Research Laboratory-III, Department of Chemical Engineering, Sant Longowal Institute of Engineering and Technology, Longowal, INDIA

Kumar, Anil

Global Group of Institutes Amritsar, Punjab, INDIA

ABSTRACT: In this current research work, a detailed parametric study has been reported for the Lactic Acid (LA) extraction from the aqueous solution through Emulsion Liquid Membrane (ELM). A designed ELM loaded with tri-n-octyl amine (as a carrier), oleyl alcohol (as a membrane modifier), cyclohexanone (to reduce water co-transportation), hexane (as a diluent), sodium carbonate (as an internal stripping phase reagent), and span 80 (as an emulsifying agent) was formulated and prepared through mechanical agitation mode. The effect of operating conditions of various process parameters affecting the LA extraction efficiency through ELM was examined and elucidated in detail. The results have shown that more than $95 \pm 1.5\%$ of LA were successfully extracted within 20 min at the optimum conditions of 0.05 [M] LA concentration, 2000 rpm emulsification speed, 2.0 (v/v) treat ratio, 4% (v/v) span 80 concentration, 1.0 (v/v) phase ratio, 200 rpm stirring speed, 0.25 [M] stripping phase concentration (Na_2CO_3), 2% (v/v) cyclohexanone, 1 [N] sulphuric acid concentration, and TOA concentration: 10 % (v/v). Hence, it could be concluded that these optimized ELM constituents as well as optimized ranges of various desired process parameters may be considered for efficient ELM formulation and LA extraction.

KEYWORDS: Lactic acid; Organic phase; Process parameters; Emulsion liquid membrane; Separation.

* To whom correspondence should be addressed.

+ E-mail: avin_thakur@sliet.ac.in

1021-9986/2023/7/2233-2247

15\$/6.05

INTRODUCTION

Recently, the demand for “Lactic Acid” (LA) is gaining momentum due to the continuous rise in its industrial applications. LA is an eco-friendly product as it is obtained from fermentable sugars of renewable resources [1-3]. LA is non-volatile, odorless, and mildly acidic in taste beside other food acids [4]. LA is applicable to both food (as an acidulant, preservative, buffering agent, pH regulator, and for mineral fortification of staple food products) and various non-food industries (such as cosmetic (as a moisturizer) and pharmaceutical (for making parental solutions) industries, so as to produce chemicals (oxygenated) as plant growth regulators and special chemical intermediates) [5-7]. Although it can be produced by either chemical synthesis or biologically by LA fermentation currently, most of the LA worldwide is produced by bacterial fermentation process [3, 8]. The chemical synthesis route resulted in an impure racemic mixture of L & D-(lactic acid) while the biotechnological process resulted in optically pure LA used for biodegradable polymer Poly Lactic Acid (PLA) [9]. The growing demand of LA (market value (in 2020): 2.7 billion Dollar and compound growth expectation (during 2021-28): @ 8% per year) particularly for environment-friendly PLA to replace the non-biodegradable plastics has led the global hunt for economical production of the LA [10, 11]. Downstream processing (purification/separation/ recovery) of LA is known as the expensive step of the LA production [12]. Continuous efforts are made by various researchers for the economical separation and purification of LA by exploring various methods [12, 13]. Previously, there were various methods [Precipitation [14], adsorption [15], extraction with niosomes and microfiltration [16], and reactive extraction [17] which had been effectively used for LA separation and purification. These techniques have some disadvantages such as high operating expenses and cause secondary environmental problems. Hence, an effective way for extracting low concentrations of LA ions must be developed. Such issues have led to the consideration of the Emulsion Liquid Membrane (ELM) technology as an option which is the most economical separation technology [2, 18]. Since the inception of this technique by Dr. Norman Li in 1968, it has been explored for its many applications in different fields of chemistry, chemical & biochemical engineering, and environmental sciences [19, 20].

ELM offers several advantages over the conventional separation processes like low extractant/solvent inventory requirement, low energy, high interfacial mass transfer area per unit volume, high permeability rate through membrane phase, simultaneous solute extraction and stripping within a single-step, high-efficiency, and simple operation [21-23]. It involves only chemical energy as a driving force and is usually not constrained by the phase equilibrium [20, 24]. In ELM, the oil phase acts as a membrane phase that has surfactants, extractants/ carriers, and organic diluents as its constituents [25]. It surrounds the aqueous stripping phase as the homogenization of both phases leads to the formation of water-in-oil (W/O) type emulsion. The dispersion of this water-in-oil (W/O) emulsion in the stirred aqueous external feed phase having solute gives rise to water-in-oil-in-water (W/O/W) type double emulsion system and hence, the oil phase separates the aqueous external feed phase and internal stripping phase [24, 26]. The solute molecules from the external feed phase get transported selectively across the membrane phase by facilitated (due to the formation of carrier solute complex) or/and unassisted (in the absence of carrier) transportation mechanism and diffuses across the interface of membrane-internal stripping phase to get stripped out by reacting with the reagent present in the internal stripping phase forming a product which cannot permeate backward through membrane phase [22, 23]. The transportation rate and selectivity of solute across the membrane phase can be enhanced by selecting the suitable extractant making it useful to be utilized for extracting solutes of low concentrations [27, 28]. Finally, the separation of the oil phase from the stripping aqueous phase takes place enabling the recovery of the enriched solute from the stripping phase [29]. In this current study, a detailed investigation on the effects of various operating parameters viz. type of internal reagent and its concentration, type of diluents, extractant concentration, surfactant concentration, phase ratio, treat ratio, agitation speed, oleyl alcohol as the membrane additive, and sulphuric concentration in external phase on LA extraction through ELM was performed. The main goal of this work is to elucidate the parametric effect of key process parameters and study the feasibility of various ELM constituents (hexane, span 80, tri-n-octyl amine, sodium carbonate, cyclohexanone, and oleyl alcohol) for LA extraction from aqueous solution through ELM.

EXPERIMENTAL SECTION

Reagents

All the chemicals (such as span 80, tri-n- octyl amine (TOA), cyclohexanone, lactic acid, n-hexane, n-heptane, kerosene, oleyl alcohol, sulphuric acid, sodium carbonate, etc.) used during this present study for experimental investigations were analytical grade (HPLC grade for HPLC analysis) and were used without any further purification. These were procured from Hi Media Laboratories Pvt. Limited, Mumbai (India), Merk India Ltd., Mumbai (India), Fluka Goldie Chemika-Biochemica, Mumbai (India) and Sigma Aldrich (USA). Lactic acid solutions of the desired concentration [mentioned in Table 1] were prepared by dissolving LA in de-ionized water to obtain an external aqueous feed phase. The stripping phase solution of the desired concentration [mentioned in Table [1] was obtained by dissolving the stripping reagent in de-ionized water.

W/O Emulsion preparation

The membrane phase was prepared by mixing Span 80 as a stabilizer, tri-n- octyl amine (TOA) as a carrier, and cyclohexanone (to reduce water co-transportation) in diluent i.e., hexane at 200 rpm for 2 min using a magnetic stirrer. Then the emulsion was prepared by mixing the stripping reagent with the membrane phase. Stripping reagent of desired concentration was added dropwise with requisite (v/v) internal to organic phase ratio and was stirred at 2000 rpm using a four-blade impeller stirrer for 20 min at room temperature (25 ± 2 °C) to form a stable Emulsion Liquid Membrane (ELM). Then emulsion was transferred to the settler after washing the emulsion with excess deionized water to wipe out the internal reagents attached to the surface of the emulsion (if any) and stored for an hour to check its stability and for its further utilization for extraction.

Extraction process

The Lactic Acid (LA) extraction was carried out in a 250 mL capacity glass batch reactor at 25 ± 2 °C temperature with a variable speed [50-2000 rpm] four bladed agitators which was charged with ELM (20 mL) and to which aqueous external feed phase was added according to the desired treat ratio [as mentioned in Table 1 and stirred well at the particular agitation speed for the appropriate time. Samples from the stirred batch reactor

during the course of run at different time intervals (5 mins) were drawn using a syringe. The external phase samples were separated from the emulsion phase by filtration using a filter paper (Brand: Whatman) for LA concentration measurement. The experiments were performed in triplicates and are represented by an error in each Figure. In Fig.1, the ELM formulation and method of preparation have been elucidated for LA extraction through ELM.

Experimental conditions

The experimental conditions and ELM constituents influencing the extraction of LA such as surfactant concentration, extractant concentration, LA concentration in external phase, stripping phase concentration, type of internal phase reagents, stirring speed, phase ratio, treatment ratio, and diluents type. Oleyl alcohol (as a membrane modifier) concentration and H₂SO₄ concentration in an external phase were also studied. The range and fixed values of process parameters for LA reactive extraction through ELM have been mentioned in Table 1.

Analytical method

The LA concentration measurement in the external aqueous feed phase was examined by the HPLC method [30] employing Shimadzu LC 2010 CHT (Shimadzu Corporation, Kyoto, Japan) equipped with a low-pressure quaternary gradient pump along with the dual-wavelength UV-Visible detector and column i.e., C₁₈ oven. The LA extraction efficiency was calculated using the equation:

$$\text{LA extraction efficiency } \eta_{\text{ext}} = \frac{C_{IF0} - C_{IF\tau}}{C_{IF0}} \times 100 \quad (1)$$

Where C_{IF0} is the LA concentration in the external aqueous feed phase initially at time $t = 0$, and $C_{IF\tau}$ is the LA concentration in the external aqueous feed phase after the extraction by contacting the aqueous phase with the ELM at elapsed time $t = \tau$.

Reaction mechanism of LA transportation

ELM is characterized by interfacial extraction/stripping reactions and transport kinetics which play a major role during the encapsulation of low-concentration solute molecules from the feed phase. The LA is transported from the external aqueous feed phase through the membrane phase through coupled facilitated (due to the presence of carrier, i.e., TOA) transportation

Table 1: Experimental conditions and hold values for the LA extraction through ELM

Experimental Conditions for LA Extraction through ELM				
S. No	Process Parameters	Range		Units
		Low (-)	High (+)	
1	LA concentration	0.05	0.50	[M]
2	Na ₂ CO ₃ concentration	0.15	0.30	[M]
3	Span 80 concentration	3	8	%, v/v
4	Extractant concentration	0	15	%, v/v
5	Phase ratio (IP: OP) ^a	1/2	2/1	v/v
6	Treat ratio (EP: MP) ^a	2/1	4/1	v/v
7	Stirring speed	100	300	rpm
8	Oleyl alcohol (as a modifier) concentration	0	7.5	%, v/v
9	H ₂ SO ₄ concentration in external phase	0	2	[N]
10	Internal phase reagents	Na ₂ CO ₃ , NaOH, NaCl, and NH ₄ OH		
11	Types of diluents	n-hexane, n-heptane, and kerosene		
Hold Values of ELM Parameters				
12	Extraction temperature	25±2		°C
13	Emulsification time	20		min
14	Emulsification speed	2000		rpm

^a IP-Internal Phase; OP- Organic Phase; EP- External Phase; MP-Membrane Phase



Fig. 1: Schematic diagram of ELM formulation and preparation for LA extraction

In the membrane phase to the internal stripping phase where it is accumulated after reacting with the internal reagent (sodium carbonate) molecules. It can be elucidated through the series of many unit processes:

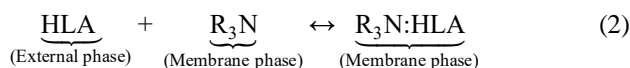
- i. Dissociation of LA in the bulk of feed phase as lactate ion and hydrogen ion.
- ii. Transportation of lactate ion as well as un-dissociated (HLA) LA from feed phase bulk to stagnant layer of feed phase surrounding the w/o emulsion.
- iii. In the Diffusion of lactate ion and undissociated LA through the stagnant thin layer and interfacial reactions between the charged species of LA and carrier at the outer interface, i.e., between external-membrane phase

to generate LA-carrier complex.

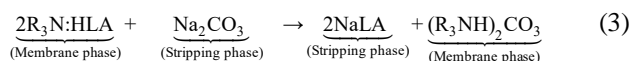
- iv. Diffusion of LA-carrier complexes across the membrane phase towards the stripping phase due to concentration gradient.
- v. Stripping reaction of LA- carrier complex with the internal reagent molecules at the inner interface i.e., between membrane-stripping phase.
- vi. Back diffusion of the carrier (TOA) through the membrane phase towards the outer interface owing to the concentration gradient.

While assuming that only the undissociated part of LA is extracted by carrier (TOA) in ELM process, the reaction mechanism can be depicted by Eqns. (2), (3) and (4). The

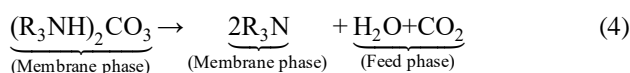
transportation of LA from feed phase to the membrane phase during the ELM process can be related to the formation of LA-TOA complex in the membrane phase as if one molecule of the acid (HLA) react with one molecule of the amine (R_3N).



LA got stripped itself in the vicinity of the membrane-stripping interface from the LA-TOA complex loaded organic phase due to the stripping reaction using Na_2CO_3 stripping solution as



and finally, the amine carbonate complex formed as above will diffuse back to the feed-membrane phase interface due to concentration gradient where it will be dissociated into water and carbon dioxide and regenerating free amine in membrane phase for further formation of LA-TOA complex as



RESULTS AND DISCUSSION

Experimental results of effect of various process parameters are provided in the form of extraction percentages and are presented in Figs 3-13. From the previously published results/findings it was found that hexane (used as a diluent) and sodium carbonate (used as a stripping agent) are best suitable for extracting low concentrated LA from feed phase. This outcome confirmed the ability of hexane and sodium carbonate to extract LA through ELM. Therefore, Hexane and sodium carbonate are selected for the ELM organic phase formulation in this work. To obtain the highest LA extraction through ELM, the optimum process conditions of the influencing process parameters are needed. The detailed discussions on each process parameter are appropriately elucidated.

Effect of various types of stripping agents

The stripping agent has a key role during the extraction of solute molecules through ELM process. Hence, the appropriate assortment for the right internal/stripping agent is of great importance in order to reach the highest

possible extraction of LA from aqueous solution. Generally, the solute molecules complexed by amines can be stripped from the protonated amine by the removal of a proton using neutral or alkaline solutions [31, 32]. Therefore, various kinds of internal phase agents ($NaOH$, Na_2CO_3 , NH_4OH , and $NaCl$) were tested (as shown in Fig.3) during the stripping process for the LA extraction from the LA loaded organic solution. The stripping reaction at the membrane-stripping interface depends on the stripping phase composition. It plays an important role in the extraction/encapsulation of solute transported from the feed solution during the ELM process.

Although in the preliminary experiments, sodium carbonate solution had been utilized as internal stripping phase, the effect of other alkaline substances as stripping reagent in the stripping phase solution for the extraction of LA were also examined. As evident from Fig.3, findings elucidated that more than 95 % of LA was effectively stripped out from the LA loaded organic phase. Such phenomenon can be discussed in terms of the basicity effect which has reduced in this trend: $NaCl < NaHCO_3 < Na_2CO_3 < NaOH$. Principally, the stripping behavior of internal phase agents enhances proportionally with their basicity. According to this trend, $NaOH$ is known as the strongest base, and it is able to produce the large chemical potential among the organic and aqueous stripping phase [32]. But in the case of sodium carbonate, two sodium ions are available which means high affinity of the sodium ion to complex with the LA molecule from the LA-extractant complex. It also favors the high decomplexation of the LA-TOA at the organic-stripping interface. The extraction efficiency of the different stripping reagents follows the order as $Na_2CO_3 > NaOH > NaCl > NH_4OH$ as evident from Fig.3. Several research studies were also reported in literature regarding the use of sodium carbonate as internal phase reagent [33-35]. Therefore, considering the above observations of Fig.3, it was concluded to use Na_2CO_3 as a suitable stripping reagent in the w/o/w system for obtaining high LA extraction.

Effect of various types of diluents

The performance of many liquid membrane systems depends on the appropriate selection of the organic diluents. Generally, these different diluents (n-hexane, n-heptane, and kerosene) were applied to change the physical properties of the extraction system (such as viscosity, density, and surface tension) for separating out

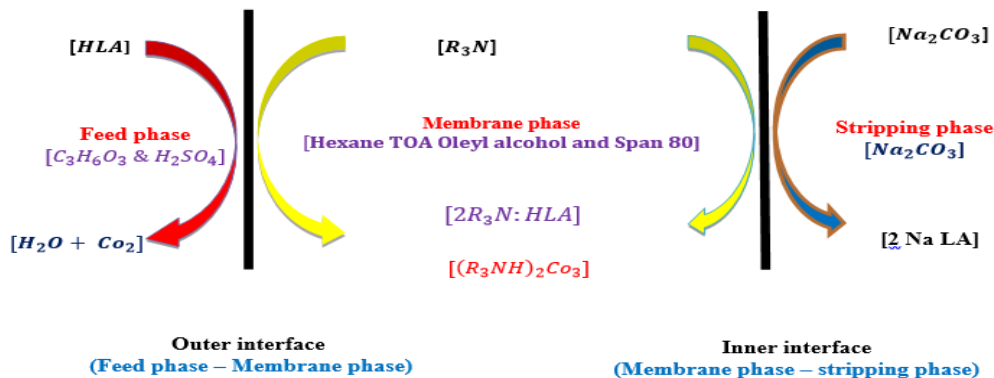


Fig. 2: Schematic representation of the LA reaction mechanism during its extraction through ELM

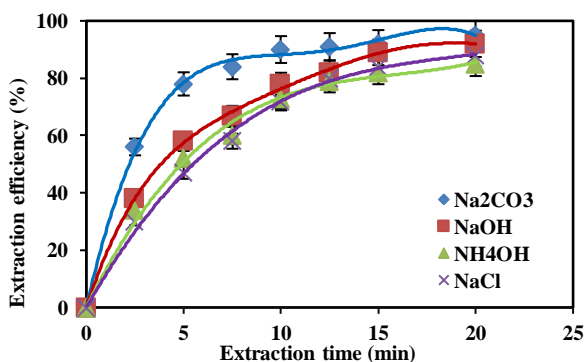


Fig. 3: Effect of stripping reagents on LA extraction efficiency through ELM. [Experimental conditions: LA concentration: 0.05 [M]; emulsion volume: 20 mL; treat ratio: 2 (v/v); emulsification time: 20 min; Span 80 concentration: 4% (v/v); phase ratio: 1.0; stirring speed: 200 rpm; stripping phase concentration (Na_2CO_3): 0.25 [M]; TOA concentration: 10 % (v/v); diluent: n-hexane]

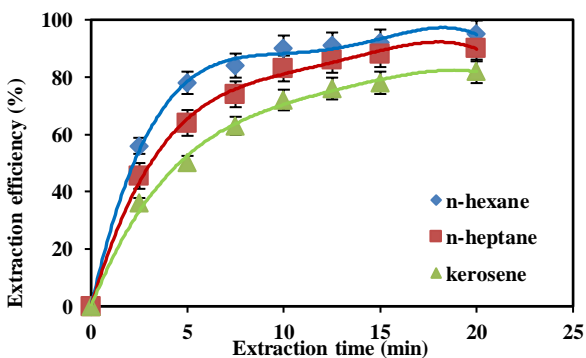


Fig. 4: Effect of diluents on LA extraction efficiency through ELM. [Experimental conditions: LA concentration: 0.05 [M]; emulsion volume: 20 mL; treat ratio: 2 (v/v); emulsification time: 20 min; phase ratio: 1.0; stirring speed: 200 rpm; stripping phase concentration (Na_2CO_3): 0.25 [M]; span 80 concentrations: 4 (% v/v); TOA concentration: 10 % (v/v)]

the interacted product. Till date, various organic diluents (such as toluene, n-heptane, n-hexane, kerosene, and Escaid 100) were used as diluents [34]. The presence of the diluent may affect significantly the extraction ability of the tertiary amines based extractant due to polar nature of diluents favoring the formation of hydrogen bonds and ion-pairs which further increases the diffusion rate of the complex [36]. To evaluate the extraction efficiency of these organic diluents, experiments were performed at optimum conditions of various process parameters and the results are shown in Fig. 4. n-Hexane as diluent in the membrane phase had shown better LA extraction efficiency than n-heptane and kerosene (Fig. 4). The viscosity of individual diluent is a major contributor towards the overall viscosity of the membrane phase. The order of viscosity of used diluents is n-hexane (0.202 ± 0.012 mPa s) < n-heptane (0.386 ± 0.025 mPa s) < kerosene (1.381 ± 0.033 mPa s). The large viscosity of the membrane phase causes increase in the thickness of the membrane phase and further decreases the permeability of the membrane for the solute [37]. It was observed that the different diluents had shown different LA extraction efficiency after 20 min experimental extraction time as: n-hexane ($95 \pm 1.5\%$) > kerosene ($90 \pm 1.4\%$) > n-heptane ($82 \pm 1.1\%$). Hence, for this current LA extraction through ELM, n-hexane was selected as the most convenient diluent.

Effect of sodium carbonate concentration

Stripping phase concentration plays a vital role in the transport of solute from external phase to stripping phase through ELM [22]. The effect of sodium carbonate concentration was determined to know about the reaction

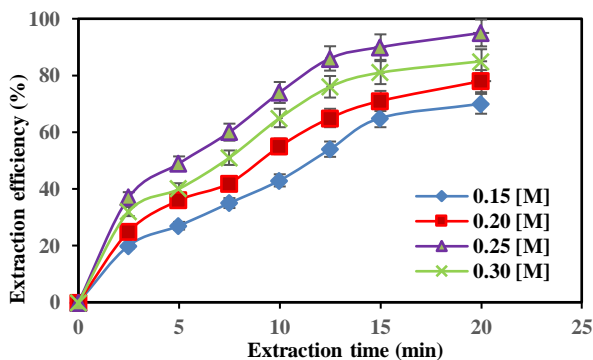


Fig. 5: Effect of stripping reagent concentration in stripping phase LA extraction efficiency through ELM. [Experimental conditions: LA concentration: 0.05 [M]; emulsion volume: 20 mL; treat ratio: 2 (v/v); emulsification time: 20 min; Span 80 concentration: 4 % (v/v); phase ratio: 0.5; experimental extraction time, 10 min; stirring speed: 200 rpm; TOA concentration: 10 %(v/v); diluent: n-hexane]

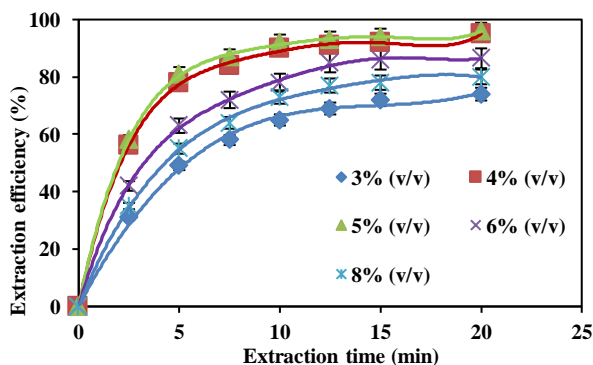


Fig. 6: Effect of surfactant span 80 concentrations on LA extraction efficiency through ELM. [Experimental conditions: LA concentration: 0.05 [M]; emulsion volume: 20 mL; treat ratio: 2 (v/v); emulsification time: 20 min; phase ratio: 1.0; stirring speed: 200 rpm; stripping phase concentration (Na₂CO₃): 0.25 [M]; TOA concentration: 10 % (v/v); diluent: n-hexane]

capacity between the stripping agent and LA-TOA complexes. Na₂CO₃ concentration of the stripping solution for the LA extraction was varied at different concentration levels from 0.15 to 0.3 [M] as described in Fig.5. LA extraction efficiency increases with an increase in stripping reagent concentration (<0.25 [M]). It may be due to the larger reaction potential of Na₂CO₃ at higher initial concentration with the LA. It causes a higher hydrogen ion difference to re-extract the LA from the LA-organic complexes due to the differences of sodium ion concentration in the feed phase and external phase. The other feasible reason is that

the high stripping concentration tends to yield large number of internal molecules which further improves the degree of the decomplexation of LA-extractant [32]. The hydrogen ion difference will be higher for minimum LA concentration [38]. For higher Na₂CO₃ concentration (>0.25 [M]), LA extraction efficiency tends to decrease irrespective of LA concentration. This may be attributed to the reason that the increased amount of Na₂CO₃ in the stripping phase decreases the difference of densities and increases the emulsion viscosity which further creates a hinderance to mass transfer process [37].

Moreover, high Na₂CO₃ concentration increases the pH of stripping phase due to which the problem of osmotic swelling may occur under a high pH difference between the external phase and the stripping phase. This process of osmotic swelling further leads to the transportation of water from the external phase to the internal phase causing an increase in the internal emulsion volume, which in turn decreases the area for mass transfer for LA extraction [39]. In addition, difference in ionic strength between external to internal phase led to internal phase volume increasing which further promotes excess emulsion leakage [37]. There are also the chances that sodium carbonate may start reacting with the surfactant causing thus decrease in the emulsion stability [40].

Effect of surfactant concentration

A stable ELM needs an appropriate amount of surfactant. Both small concentration (renders the membrane weak) as well as large concentration (creates larger diffusional resistance) of surfactant have a problem in emulsion stability. ELMs are normally unstable in nature and to make them stable and to avoid coalescence of dispersed drops, a certain amount of surfactant must be added [34, 40]. The variation in the extraction efficiency during the extraction of LA from aqueous external phase for various non-ionic surfactant i.e., span 80 (sorbitan monooleate) concentrations (3% - 8%, v/v) has been depicted in Fig.6. An increase in extraction efficiency had been found with the increase in the surfactant concentration (3% - 5%, v/v). The membrane breakage ratio usually declines with the rise in span 80 concentration. The extraction efficiency was reduced at low surfactant concentration due to this small amount of span 80 may not be able to cover the membrane interface completely. The insufficient surfactant also promotes the formation of bigger

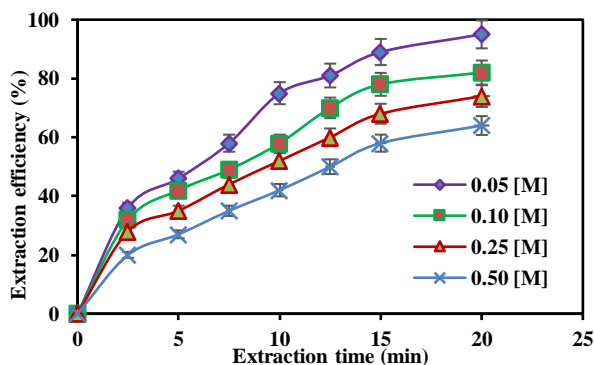


Fig.7: Effect of LA concentration on LA extraction efficiency through ELM. [Experimental conditions: Emulsion volume: 20 mL; treat ratio: 2 (v/v); emulsification time: 20 min; Span 80 concentration: 4% (v/v); phase ratio: 1.0; stirring speed: 200 rpm; stripping phase concentration (Na_2CO_3): 0.25 [M]; TOA concentration: 10 % (v/v); diluent: n-hexane]

emulsion droplets, as high surface tension hinders adequate emulsion droplets dispersion [42, 43].

Though the stability of the emulsion has been observed to be increasing with the increase in surfactant concentration (> 5% v/v), but a negative effect on LA extraction efficiency (%) had been observed. This may be due to the fact that high surfactant concentration results in high interfacial occupancy of the surfactant generating higher interfacial resistance leading to a decrease in the LA extraction at the external phase-membrane phase interface [41]. Moreover, it also increases the interfacial viscosity causing a decrease in the movement of inner droplets within the emulsion globule [37]. This means that the span 80 concentration in the membrane phase is a key parameter affecting both the stability of W/O emulsion and LA extraction efficiency of W/O/W emulsion. Based on the above observations and the results obtained as presented in Fig.6, 4% (v/v) of span 80 concentration has been accepted as the appropriate surfactant concentration to form the stable W/O emulsion and effective extraction efficiency in total harmony with each other.

Effect of lactic acid concentration

The effect of LA concentration, in the range of 0.05 [M] to 0.5 [M], was examined. In Fig. 7, the results have been elucidated. At a low LA concentration of 0.05 [M] in the feed phase, it was observed that the LA extraction efficiency was high i.e., 95 % whereas ahead of 0.05 [M] of LA concentration, it had resulted in decrement in LA extraction efficiency. The plausible fact was that the region

of outer interface becomes saturated more quickly with the solute molecules. So, the LA complex compounds permeate very gradually through the membrane phase, and this occurs due to large mass transfer resistance developed by high LA concentration [18].

The extraction efficiency was found to decrease with the increase in LA concentration. This can be explained with the reference to consideration of advancing front model for ELM such that as the LA concentration in the feed 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, generating the necessity of more stripping reagent [44, 45]. Hence, mass transfer resistance in the membrane phase becomes important for high values of LA concentration whereas, for low values of LA concentration, external mass transfer is rate controlling. Therefore, it is clear that the LA extraction efficiency was dependent on the molecular diffusion in the system. The LA extraction efficiency was found to 95 ± 1.5 % as observed from the above Fig.. This result indicates the effectiveness of ELM based separation technique.

Effect of extractant concentration

Extractant concentration has a great impact on ELM and acts as a vehicle to separate the solute ions across the ELM [18]. It affects the ELM performance by promoting the rate of diffusion of solute ions. The extractant (tri-n- octyl amine (TOA)) used in this present work makes a LA-carrier complex (as described in reaction mechanism, Fig. 2) at the outer interface (as discussed in Fig. 2) and efficiently encouraged the diffusion of solute ions through the ELM. This phenomenon was then followed by the release of LA ions at the inner interface (as discussed in Fig.2) in the internal phase [18, 46]. The effect of carrier concentration (0-15% v/v) on the LA extraction percentage has been shown in Fig.8. During this set of experiments, extraction efficiency had been observed to increase with the increase in extractant concentration in the membrane phase.

Since extractants provide high distribution coefficient due to their tendency to form ion pair association of the alkyl ammonium cation with the acid anion [47]. It may be also due to increase in number of extractant molecules taking part in the transportation of LA ion in the ELM process. Increasing the extractant concentration in membrane phase had led to enhancement

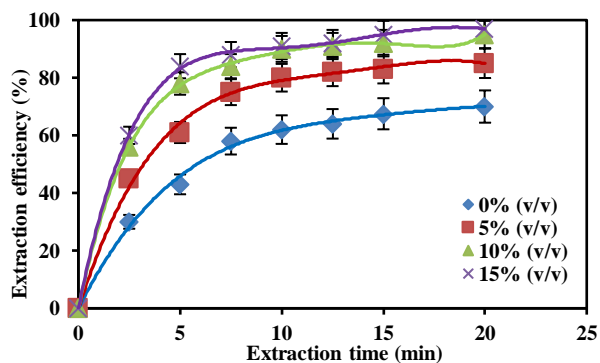


Fig.8: Effect of extractant (TOA) concentration on LA extraction efficiency through ELM. [Experimental conditions: LA concentration: 0.05 [M]; emulsion volume: 20 mL; treat ratio: 2 (v/v); emulsification time: 20 min; Span 80 concentration: 4% (v/v); phase ratio: 1.0; stirring speed: 200 rpm; stripping phase concentration (Na_2CO_3): 0.25 [M]; TOA concentration: 10 % (v/v); diluent: n-hexane]

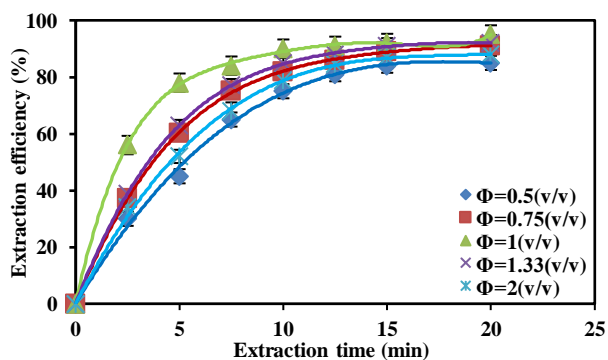


Fig. 9: Effect of phase ratio on LA extraction efficiency through ELM. [Experimental conditions: LA concentration: 0.05 [M]; emulsion volume: 20 mL; treat ratio: 2 (v/v); emulsification time: 20 min; stirring speed: 200rpm; stripping phase concentration (Na_2CO_3): 0.25 [M]; span 80 concentration: 4 % (v/v); TOA concentration: 10 % (v/v); diluent: n-hexane]

in extraction efficiency but the rate of enhancement was declined when the extractant concentration was above the threshold limit (>10%, v/v). Another possible reason is that with the increase in carrier concentration, membrane wall thickness increases causing a decrease in diffusion coefficient due to more diffusional resistance to LA ion diffusion [36, 48]. Higher content of extractant also increases viscosity leading to the formation of larger globules causing a decrement in mass transfer area and also supporting permeation swelling causing dilution of the aqueous stripping phase resulting in a reduction in driving force which affects negatively the extraction efficiency [43].

Recently published work reported that the excess of free carrier was not given any improvement in LA extraction efficiency [45].

Effect of phase ratio

The volume ratio of stripping solution to membrane solution is known as phase ratio. It plays an imperative role in ELM process. The variation in the stripping solution volume fraction not only changes the emulsion properties but also leads to an increment in the extraction capacity of the emulsion. In order to get a stable emulsion, homogeneous distribution of emulsion droplets in the aqueous phase, the phase ratio must be optimized [18, 43]. LA extraction efficiency increases with an increase in phase ratio from low level [0.5-1 (v/v)] because more proportion of internal stripping phase was available for encapsulation of large no. of LA molecules.

Moreover, the membrane thickness also got reduced causing a reduction in mass transfer resistance in membrane phase. Further, increase in the phase ratio causes a decrease in the LA extraction efficiency [23]. This may be owing to the fact that there may be an increase in the internal droplets size causing a reduction in the interfacial contact area between the emulsion and feed solution. Further, it started dominating the effect on mass transport with respect to the thinning of membrane phase which continues with the increase of phase ratio. Low value of phase ratio causes a reduction in the hold-up of the stripping phase, i.e., the emulsion globules which decreases the interfacial area of mass transfer and also decreases the capacity of the stripping phase for trapping LA simultaneously [28, 29]. From the literature it was reported that the phase ratio less than 1 gives poor results. As a result, the phase ratio of 1.0 (v/v) was selected as the best one for further study.

Effect of treat ratio

Treat ratio (volume ratio of external phase to emulsion phase) is known as one of the key process parameters in ELM based separation process. It controls the interfacial mass transfer of LA ions. In general, a high treat ratio was suggested for ELM process aiming to minimize the size of the equipment and economy of the ELM process. The effect of treat ratio on LA ion extraction has been elucidated in Fig.10, which illustrates a negative effect on the LA extraction efficiency as the distribution of the emulsion globules becomes broader hence leading

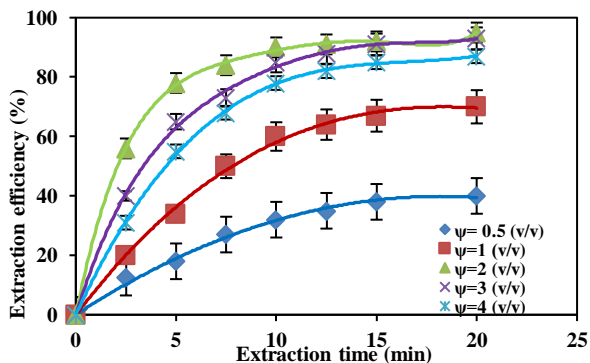


Fig. 10: Effect of treat ratio (ψ) on LA extraction efficiency through ELM. [Experimental conditions: LA concentration: 0.05 [M]; emulsion volume: 20 mL; treat ratio: 2 (v/v); emulsification time: 20 min; span 80 concentration: 4% (v/v); phase ratio: 1.0; stirring speed: 200 rpm; stripping phase concentration (Na_2CO_3): 0.25 [M]; TOA concentration: 10 % (v/v); diluent: n-hexane]

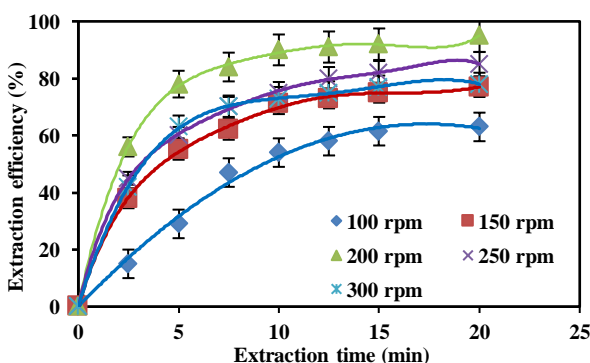


Fig. 11: Effect of w/o/w stirring speed on LA extraction efficiency through ELM. [Experimental conditions: LA concentration: 0.05 [M]; emulsion volume: 20 mL; treat ratio: 2 (v/v); emulsification time: 20 min; Span 80 concentration: 4% (v/v); phase ratio: 1.0; stripping phase concentration (Na_2CO_3): 0.25 [M]; TOA concentration: 10 % (v/v); TOA concentration: 10 % (v/v); diluent: n-hexane]

to increment in the distance between the emulsion globules [49]. With the increase in treat ratio up to 2 (v/v) had resulted in an increase in LA extraction efficiency. It may be due to an increase in the number of emulsion globules per unit external phase volume causing an increment in the membrane surface area as well as in ELM transport capacity [28, 50]. At the treat ratio <2 (v/v), the removal of LA per unit emulsion volume is somewhat low due to improper mixing of phases because of a higher proportion of the viscous emulsion phase. This has also caused an increase in emulsion total viscosity leading

to increase in the globules size resulting in the membrane thickening which resists the LA transportation [42, 24]. Hence, it is not preferred from an economical view [38]. The other plausible reason may be due to the presence of lesser number of emulsion globules (i.e., reduction in surface area) for LA encapsulation [24]. Consequently, poor extraction efficiency (%) was recorded due to less availability of membrane surface.

It may be due to the large space between the emulsion globules which means a decrement in the available interfacial area per unit volume of the feed solution [49]. Hence to conclude, according to Fig.10, maximum extraction efficiency ($95 \pm 1.5\%$) after 20 min of extraction has been yielded at treat ratio of 2 (v/v). So, it is worth mentioning that membrane phase volume holds the key to control the extraction efficiency of emulsion system over the external aqueous phase volume [40].

Effect of stirring speed

In a mechanically mixed batch extractor, a high mixing speed encourages high mass transfer rate though, shear exerted may break the ELM during the extraction process [28]. Therefore, there is a pertinent need to find out the optimum mixing speed which provides uniform distribution of globules in the external feed phase as well as large LA extraction efficiency. The effect of stirring speed was examined in the range of 200 to 300 rpm. The results were presented in Fig 11. This Fig. illustrates that the LA extraction efficiency increases significantly with the increase in the agitation speed from 100 rpm to 200 rpm. Since the LA extraction efficiency depends upon the surface area of the globules available for mass transfer which increases with the increase in speed. The increase in agitation speed decreases the size of emulsion globules and hence results in increment in reaction surface [51]. With the further increase in the agitation speed (beyond 200 rpm), the extraction efficiency was found to decrease. This may be attributed to the hydrodynamic instability of the emulsion at the higher speed.

At higher agitation speed, the osmotic swelling increases due to water co-transport causing emulsion breakage and consequently results in poor extraction. The emulsion breakage also got induced due to an increase in shear on the emulsion phase with the increase in the agitation speed [29, 52]. The best ELM performance was obtained at 200 rpm along with the uniform distribution of globules in the external phase.

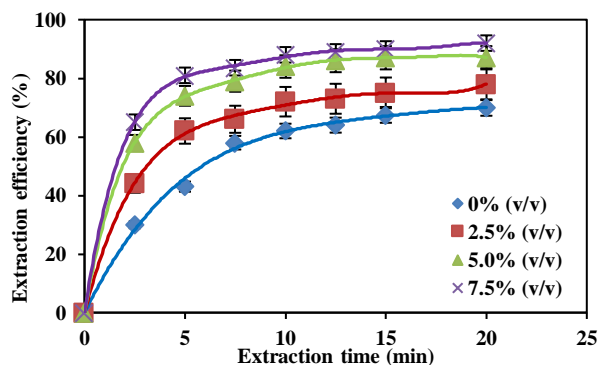


Fig. 12: Effect of oleyl alcohol as the membrane additive on LA extraction efficiency through ELM. [Experimental conditions: LA concentration: 0.05 [M]; emulsion volume: 20 mL; treat ratio: 2 (v/v); emulsification time: 20 min; Span 80 concentration: 5% (v/v); phase ratio: 1.0; stirring speed: 200 rpm; stripping phase concentration (Na_2CO_3): 0.25 [M]; TOA concentration: 10 % (v/v); diluent: n-hexane]

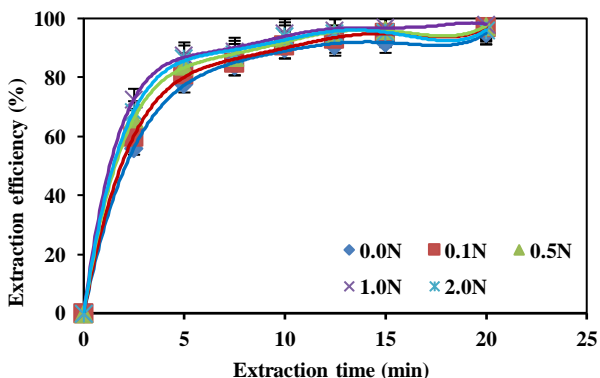


Fig. 13: Effect of H_2SO_4 concentration on LA extraction efficiency through ELM. [Experimental conditions: LA concentration: 0.05 [M]; emulsification time: 20 min; emulsification speed: 2000 rpm; emulsion volume: 20 mL; treat ratio: 2 (v/v); Span 80 concentration: 4% (v/v); phase ratio: 1.0; stirring speed: 200 rpm; stripping phase concentration (Na_2CO_3): 0.25 [M]; TOA concentration: 10 % (v/v); diluent: n-hexane]

Effect of oleyl alcohol concentration in the membrane phase

Oleyl alcohol as the solvent or diluent frequently used during the extraction of carboxylic acids [53]. LA had been partitioned favorably into oleyl alcohol because of their high physical solubility in amphiprotic organic solvent. While LA was found little solubilized in a polar aprotic inert organic solvent such as n-hexane [37]. The oleyl alcohol concentration was varied from 0 to 7.5 % (v/v) to examine the effect on LA extraction efficiency and the results have been presented in Fig. 12. In order to improve the LA extraction efficiency, oleyl alcohol was used

Table 2: Optimized values of various process parameters of LA extraction using ELM

S.No.	Process Parameters	Optimum Values
1	LA concentration	0.05, [M]
2	Na_2CO_3 concentration	0.25 [M]
3	Span 80 concentration	4% (v/v)
4	TOA concentration	10 % (v/v)
5	Phase ratio	1, v/v
6	Treat ratio	2, v/v
7	Stirring speed	200 rpm
8	Internal phase reagent	Sodium carbonate
9	Diluent	n-hexane
	LA extraction efficiency (%)	95±1.5%

as the membrane phase additive so as to improve partitioning of LA into the membrane phase. The extraction efficiency increases with the increase in oleyl alcohol concentration in the membrane phase. But keeping in view the emulsion stability aspect, it had been found that < 7.5% (v/v) is the best option for the use of oleyl alcohol in the membrane phase to achieve the enhanced extraction as elucidated in Fig 12.

Effect of sulphuric acid concentration in external phase

The extraction efficiency increases marginally with an increase in sulphuric acid concentration from 0.1 to 1.0 [N] (Fig. 13) due to with the increase of sulfuric acid concentration, pH of aqueous solution decreases which further increases the rate of the complex (tri-octyl amine-lactic acid) formation, depends on the H^+ concentration in the external phase. However, slight reduction in the extraction efficiency was recorded as the H_2SO_4 concentration increases to 2.0 [N]. Higher H_2SO_4 concentration may cause osmotic pressure gradient between the phases across the membrane phase leading to emulsion swelling which may results enhancement in dilution of internal loaded reagent droplets [19]. The surfactant properties as a stabilizer got badly affected due to highly acidic pH causes destabilization of the w/o emulsion and hence, the greater chances of emulsion breakage [54]. The obtained results for LA extraction efficiency (%) under optimized values of the various process parameters for LA extraction using ELM have been shown in Table 2.

CONCLUSIONS

This current research work mainly focuses on attaining the high LA extraction through ELM from the aqueous solution. The appropriate selection of diluent and stripping agent played an important role during the LA extraction through ELM. It is evident that the application of hexane and sodium carbonate during ELM formulation appropriately succeeded in extracting LA from the aqueous solution. LA extraction efficiency strongly depends on the various process parameters which have been elucidated in detail in this study. Various process parameters that are optimized through which maximum extraction (%) of LA was attained are: LA concentration: 0.05 [M], span 80 concentration: 4% (v/v), phase ratio: 1.0 (v/v), treat ratio: 2 (v/v), stirring speed: 200 rpm, TOA concentration: 10 % (v/v), Na₂CO₃ concentration: 0.25 [M], 2% (v/v) cyclohexanone, and diluent: n-hexane. Under optimal process conditions of various process parameters, % LA extraction efficiency reached the maximum i.e., 95±1.5% using the ELM-based separation technique. It should be concluded that the ELM process having hexane as diluent, TOA as extractant, and sodium carbonate as stripping agent has shown a high potential application for the LA extraction from aqueous solution.

Acknowledgments

The authors are grateful to Sant Longowal Institute of Engineering and Technology for providing the lab facilities and all the necessary help to perform this research work.

Received : Feb. 15, 2023 ; Accepted : Jun. 26, 2023

REFERENCES

- [1] Komesu A., Oliveira J.A.R.D., Martins L.H.D.S., Maciel M.R.W., Maciel F.R., [Lactic Acid Production to Purification: A Review](#), *Bio. Res.*, **12**: 4364-4383 (2017).
- [2] Kumar A., Thakur A., Panesar P.S., [Lactic Acid and Its Separation and Purification Techniques: A Review](#), *Rev. Environ. Sci. Biotechnol.*, **18**: 823-853 (2019).
- [3] Camesasca L., Andrésde Mattos J., Vila E., Cebreiros F., Lareo C., [Lactic Acid Production by Carnobacterium Sp. Isolated from A Maritime Antarctic Lake Using Eucalyptus Enzymatic Hydrolysate](#), *Biotechnol. Rep.*, **31**:e00643 (2021).
- [4] Daful A.G., Haigh K., Vaskan P., Gorgens J.F., [Environmental Impact Assessment of Lignocellulosic Lactic Acid Production: Integrated with Existing Sugar Mills](#), *Food Bio. Prod. Process*, **99**: 58-70 (2016).
- [5] Thummarungsan N., Pattavarakorn D., Sirivat A., [Softened and Flexible Biodegradable Poly \(Lactic Acid\) and Its Electromechanical Properties for Actuator Application](#), *J. Mech. Beh. Biomed. Mate.*, **64**: 31-42 (2016).
- [6] Pradhan N., Giuliana d'Ippolito Dipasquale L., Esposito G., Panico A., Lens P.N.L., Fontana A., [Simultaneous Synthesis of Lactic Acid and Hydrogen from Sugars Via Capnophilic Lactic Fermentation by Thermotoga Neapolitana Cf Capnolactica](#), *Biomass Bioene.*, **125C**: 17-22 (2019).
- [7] Vasmara C., Marchetti R., Carminati D., [Wastewater from The Production of Lactic Acid Bacteria as Feedstock in Anaerobic Digestion](#), *Energy*, **229**: 120740 (2021).
- [8] Edwin C., Van der Poll, Eggink G., Weusthuis R.A., [Production of L \(+\) -Lactic Acid from Acid Pre-Treated Sugarcane Bagasse Using Bacillus Coagulans DSM2314 in a Simultaneous Saccharification and Fermentation Strategy](#), *Biotechnol. Biofuels*, **9**: 248-259 (2016).
- [9] Campos J., Bao J., Lidén G., [Optically Pure Lactic Acid Production from Softwood-Derived Mannose by Pediococcus Acidilactici](#), *J. Biotechnol.*, **335**: 1-8 (2021).
- [10] Liaud N., Rosso M.N., Fabre N., Crapart S., Herpoël-Gimbert I., Sigoillot J.C., Raouche S., Levasseur A., [L-lactic Acid Production by Aspergillus Brasiliensis Overexpressing The Heterologous Ldha Gene from Rhizopus Oryzae](#), *Microbial Cell Factories*, **14(66)**: 1-9 (2015).
- [11] Jiang F., Yan D., Lin J., Kong H., Yao Q., [Implantation of Multiscale Silk Fibers on Poly \(Lactic Acid\) Fibrous Membrane for Biomedical Applications](#), *Materi. Today Chem.*, **21**: 100494 (2021).
- [12] Garzon C.S.L., Straathof A.J.J., [Recovery of Carboxylic Acids Produced by Fermentation](#), *Biotechnol. Adv.*, **32**: 873-904 (2014).
- [13] Tang J., Wanga X., Hua Y., Zhang Y., Li Y., [Lactic Acid Fermentation from Food Waste with Indigenous Microbiota: Effects of Ph, Temperature and High OLR](#), *Waste Manag.*, **52**: 278-285 (2016).

- [14] Min D.J., Choi K.H., Chang Y.K., Kim J.H., [Effect of Operating Parameters on Precipitation for Recovery of Lactic Acid from Calcium Lactate Fermentation Broth](#), *Kor. J. Chem. Eng.*, **28**: 1969-1974 (2011).
- [15] Delgado J.A., Águeda V.I., Uguina M.A., García A., Matarredona J., Moral R., [Modeling of The Separation of Lactic Acid from an Aqueous Mixture by Adsorption on Polyvinylpyridine Resin and Desorption with Methanol](#), *Sep. Purif. Technol.*, **200**: 307-317 (2018).
- [16] Roque L., Escudero I., Benito J.M., [Lactic Acid Recovery by Microfiltration Using Niosomes as Extraction Agents](#), *Sep. Purif. Technol.*, **151**: 1-13 (2015).
- [17] Baral P., Pundir A., Kurmi A., Singh R., Kumar V., Agrawal D., [Salting-out Assisted Solvent Extraction of L \(+\) Lactic Acid Obtained After Fermentation of Sugarcane Bagasse Hydrolysate](#), *Sep. Purif. Technol.*, **269**: 118788 (2021).
- [18] Sujatha S., Rajasimman M., [Development of a Green Emulsion Liquid Membrane Using Waste Cooking Oil as Diluent for the Extraction of Arsenic from Aqueous Solution-Screening, Optimization, Kinetics and Thermodynamics Studies](#), *J. Water Process Eng.*, **41**: 102055 (2021).
- [19] Ma H., Kokkiliç O., Waters K.E., [The Use of the Emulsion Liquid Membrane Technique to Remove Copper Ions from Aqueous Systems Using Statistical Experimental Design](#), *Min. Eng.*, **107**: 88-99 (2017).
- [20] Abbassian K., Kargari A., [Modification of Membrane Formulation for Stabilization of Emulsion Liquid Membrane for Extraction of Phenol from Aqueous Solutions](#), *J. Environ. Chem. Eng.*, **4**: 3926-3933 (2016).
- [21] Mishra B.B., Devi N., [Solvent Extraction and Separation of Europium \(III\) Using A Phosphonium Ionic Liquid and an Organophosphorus Extractant-A Comparative Study](#), *J. Mol. Liq.*, **271**: 389-396 (2018).
- [22] Anarakdim K., Matos M., Cambiella A., Senhadji-Keblache O., Gutierrez G., [Effect of Temperature on The Heat Treatment to Recover Green Solvent from Emulsion Liquid Membranes Used in The Extraction of Cr \(VI\)](#), *Chem. Eng. Processing: Process Intensif.*, **158**: 108178 (2020).
- [23] Zereszki S., Shokri A., Karimi A., [Application of a Green Emulsion Liquid Membrane for Removing Copper from Contaminated Aqueous Solution: Extraction, Stability, and Breakage Study Using Response Surface Methodology](#), *J. Mol. Liq.*, **325**: 115251 (2021).
- [24] Ahmad A.L., Buddin M.M.H.S., Ooi B.S., Kusumastuti A., [Utilization of Environmentally Benign Emulsion Liquid Membrane \(ELM\) for Cadmium Extraction from Aqueous Solution](#), *J. Water Process Eng.*, **15**: 26-30 (2017).
- [25] Kumar A., Thakur A., Panesar P.S., [A Review on Emulsion Liquid Membrane \(ELM\) for the Treatment of Various Industrial Effluent Streams](#), *Rev. Environ. Sci. Biotechnol.*, **18**: 153-182 (2019).
- [26] Daraei P., Zereszki S., Shokri A., [Application of Nontoxic Green Emulsion Liquid Membrane Prepared by Sunflower Oil for Water Decolorization: Process Optimization by Response Surface Methodology](#), *J. Ind. Eng. Chem.*, **77**: 215-222 (2019).
- [27] Anitha M., Ambare D.N., Singh D.K., Singh H., Mohapatra P.K., [Extraction of Neodymium from Nitric Acid Feed Solutions Using an Emulsion Liquid Membrane Containing TOPO and DNPPA as the Carrier Extractants](#), *Chem. Eng. Res. Des.*, **98**: 89-95 (2015).
- [28] Khadivi M., Javanbakht V., [Emulsion Ionic Liquid Membrane Using Edible Paraffin Oil for Lead Removal from Aqueous Solutions](#), *J. Mol. Liq.*, **319**: 114137 (2020).
- [29] Kumar A., Thakur A., Panesar P.S., [Role of Operating Process Parameters on Stability Performance of Green Emulsion Liquid Membrane Based on Rice Bran Oil](#), *Theor. Found. Chem. Eng.*, **55**: 534-544 (2021).
- [30] Kishore G., Karthik A., Gopal S.V., Kumar A.R., Bhat M., Udupa N., [Development of RP-HPLC Method for Simultaneous Estimation of Lactic Acid and Glycolic Acid](#), *Der Pharma Chem.*, **5**: 335-340 (2013).
- [31] Yildiz Y., Manzak A., Tutkun O., [Synergistic Extraction of Cobalt and Nickel Ions by Supported Liquid Membranes with A Mixture of TIOA and TBP](#), *Desalini. Water Treat.*, **53(5)**: 1246-1253 (2015).

- [32] Rahman H.A., Jusoh N., Othman N., Rosly M.B., Sulaiman R.N.R., Noah N.F.M., [Green Formulation for Synthetic Dye Extraction Using Synergistic Mixture of Acid-Base Extractant](#), *Sep. Purif. Technol.*, **209**: 293-300 (2019).
- [33] Daas A., Hamadaoui Q., [Extraction of Anionic Dye from Aqueous Solutions by Emulsion Liquid Membrane](#), *J. Hazard. Mater.*, **178**: 973-981 (2010).
- [34] Manzak A., Tutkun, O., [The Extraction of Lactic Acid by Emulsion Type of Liquid Membranes Using Alamine336 in Escaid 100](#), *Can. J. Chem. Eng.*, **89**: 1458-1463 (2011).
- [35] Chanukya B.S., Kumar M., Rastogi N.K., [Optimization of Lactic Acid Pertraction Using Liquid Emulsion Membranes by Response Surface Methodology](#), *Sep. Purif. Technol.*, **111**: 1-8 (2013).
- [36] Yankov D., Molinier J., Albet J., Malmay G., Kyuchoukov G., [Lactic Acid Extraction from Aqueous Solutions with Tri-N-Octylamine Dissolved in Decanol and Dodecane](#), *Biochem. Eng. J.*, **21**: 63-71 (2004).
- [37] Dâas A., Hamdaoui, Q., [Removal of Non-Steroidal Anti-Inflammatory Drugs Ibuprofen and Ketoprofen from Water by Emulsion Liquid Membrane](#), *Environ. Sci. Pollut. Res. Int.*, **21**:2154-2164 (2014).
- [38] Lee S.C., [Extraction of Succinic Acid from Simulated Media by Emulsion Liquid Membranes](#), *J. Membr. Sci.*, **381**: 237-243 (2011).
- [39] Ng Y.S., Jayakumar N.S., Hashim M.A., [Performance Evaluation of Organic Emulsion Liquid Membrane on Phenol Removal](#), *J. Hazard. Mater.*, **184**: 255-260 (2010).
- [40] Srivastava A., Bhagat A., Sharma U., Dohare R.J., Singh K., Upadhyaya S., [Comparative Study of Arsenic \(V\) Removal from Aqueous Solution Using Aliquat-336 and 2-Ethyl Hexanol through Emulsion Liquid Membrane](#), *J. Water Process Eng.*, **16**: 64-68 (2017).
- [41] Eyupoglu V., Kumbasar, R.A., [Extraction of Ni \(II\) From Spent Cr-Ni Electroplating Bath Solutions Using LIX 63 and 2BDA as Carriers by Emulsion Liquid Membrane Technique](#), *J. Ind. Eng. Chem.*, **21**: 303-310 (2015).
- [42] Chaouchi S., Hamdaoui O., [Extraction of Priority Pollutant 4-Nitrophenol from Water by Emulsion Liquid Membrane: Emulsion Stability, Effect of Operational Conditions and Membrane Reuse](#), *J. Dispers. Sci. Technol.*, **35**(9): 1278-1288 (2014).
- [43] Malik M.A., Hashim M.A., Nabi F., [Extraction of Metal Ions by ELM Separation Technology](#), *J. Disper. Sci. Technol.*, **33**: 346-356 (2012).
- [44] Teresa A.M.R., Ondina M.F.F., Shiva A., Ferreira M.L., Rosinda M.C.I., Remigio M., Jorge M.R.C., [Removal of Phenols from aqueous Solutions by Emulsion Liquid Membranes](#), *J. Hazard Mater.*, **192**: 986-994 (2011).
- [45] Kumar A., Thakur A., Panesar P.S., [Lactic Acid Extraction Using Environmentally Benign Green Emulsion Ionic Liquid Membrane](#), *J. Clean. Prod.*, **181**: 574-583 (2018).
- [46] Jusoh N., Othman N., Rosly M.B., [Extraction and Recovery of Organic Compounds from Aqueous Solution Using Emulsion Liquid Membrane Process](#), *Materials Today Proceed.*, 1-6 (2021).
- [47] Keshav A., Norge P., Wasewar K.L., [Reactive Extraction of Citric Acid Using Tri-N-Octylamine in Nontoxic Natural Diluents: Part 1-Equilibrium Studies from Aqueous Solutions](#), *Appl. Biochem. Biotechnol.*, **167**: 197-213 (2012).
- [48] Sujatha S., Rajamohan N., Anbazhagan S., Vanithasri M., Rajasimman M., [Extraction of Nickel Using a Green Emulsion Liquid Membrane - Process Intensification, Parameter Optimization and Artificial Neural Network Modeling](#), *Chem. Eng. Process: Process Intensif.*, **165**: 108444 (2021).
- [49] Naoh N.F.M., Othman N. Jusoh N., [Highly Selective Transport of Palladium from Electroplating Wastewater Using Emulsion Liquid Membrane Process](#), *J. Taiwan Inst. Chem. Eng.*, **64**: 134-141 (2016).
- [50] Garavand F., Razavi S.H., Cacciotti I., [Synchronized Extraction and Purification of L-Lactic Acid from Fermentation Broth by Emulsion Liquid Membrane Technique](#), *J. Disper. Sci. Technol.*, **39**: 1291-1299 (2018).
- [51] Goyal R.K., Jayakumar N.S., Hashim M.A., [Chromium Removal by Emulsion Liquid Membrane Using \[BMIM\]⁺ \[Ntf2\]⁻ as Stabilizer and TOMAC as Extractant](#), *Desalination*, **278**: 50-56 (2011).
- [52] Benderrag A., Haddou B., Daaou M., Benkhedja H., Bounaceur B., Kameche M., [Experimental and Modeling Studies on Cd \(II\) Ions Extraction by Emulsion Liquid Membrane Using Triton X-100 as Biodegradable Surfactant](#), *J. Environ. Chem. Eng.*, **7**: 103166 (2019).

- [53] Blahusiak M., Martak J., Miranda F., Schlosser S., Teixeira J.A., [Effect of Viscosity of a Liquid Membrane Containing Oleyl Alcohol on the Pertraction of Butyric Acid](#), *Chem. Pap.*, **67**: 1560-1568 (2013).
- [54] Lende A.B., Kulkarni P.S., [Selective Recovery of Tungsten from Printed Circuit Board Recycling Unit Wastewater by Using Emulsion Liquid Membrane Process](#), *J. Water Process Eng.*, **8**: 75-81 (2015).