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Perspective of Reactive Separation of Levulinic Acid in Conceptual Mixer Settler Reactor

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ABSTRACT

Many industries are using directly biomass as a raw material for the production of valuable biochemicals. These are used different toxic chemicals such as sulphuric acid, hydrochloric acid, nitric acid, etc. as a catalyst during the production of biochemicals and exit downstream waste material and create environmental pollution. Therefore, downstream waste material separation is important for decrease environmental pollution. Levulinic acid is a carboxylic acid which can be present downstream of industrial waste. It is a very important chemical and can be transformed into different important chemicals such as 1-4 pentanediol, aminolevulinic acid, succinic acid, gamma valarolactone, hydroxyvaleric acid, diphenolic acid, etc. It is considered in the top ten important and bio-derived acids. Levulinic acid can be directly produced from biomass through chemical synthesis and fermentation processes at industrial and lab scales. The synthesis process produces the char whereas the fermentation process produces wastes during the production of levulinic acid, thus increasing the production cost and industrial waste downstream. The separation of levulinic acid from the waste is costly and challenging. In this study, reactive extraction was employed with TOA in i-octanol for the separation of levulinic acid. The experimental results have been expressed in various performance parameters like distribution coefficient (0.099-6.14), extraction efficiency (9-86%), loading ratio (0.09-0.7), and equilibrium constant (11.34-1.05). The mass action law model was also been applied and found the predicted value close with the experimental results. The mixer settler extraction in the series was used to achieve more than 98% separations of acid. Further, the conceptual approach for levulinic acid separation using mixer-settler reactor scheme is discussed and presented various design parameters including extraction efficiency, diffusion coefficient, extraction equilibrium constant, and loading ratio. This study decreases the industry downstream material and can be solved environmental pollution problems.

Keywords: Levulinic acid separation, reactive extraction, diffusion coefficient, mixer settler reactor, mass action law

33 1. INTRODUCTION

34 Many industries exit the downstream wastes during the production of their products. These
35 industrial downstream wastes create soil, water, and air pollution in the environment (Tyagi et
36 al. 2014). Some of the valuable chemicals and biochemicals are also present in the industrial
37 downstream waste and fermentation broth (Shen et al. 2018). The separation of these
38 compounds is important due to their harmful effects on the environment. The various
39 carboxylic acids such as levulinic, lactic, glutaric, aspartic, vanillic, photocatalytic acid, etc.
40 can be carried in the fermentation broth and industrial downstream waste. These acids are very
41 important due to their various applications like fuel, medicine, food, plastics, cosmetics,
42 chemicals, fertilizer, etc.

43 Levulinic acid (LA) is a carboxylic acid, used in the manufacture of many daily need items. It
44 can be used as a raw material in a variety of industries including plastics, polymers,
45 pharmaceuticals, cosmetics, food, agriculture, biofuel, chemical solvents, rubber
46 manufacturing, etc.(Andersson-Engels et al. 1995; Rackemann and Doherty 2011; Pasquale et
47 al. 2012; Zhang et al. 2012; Mthembu 2015). It can also be used as a platform chemical for the
48 manufacturing of value-added products such as MTHF (methyltetrahydrofuran), a fuel
49 additive; DALA (δ -aminolevulinic acid), a broad-spectrum herbicide/pesticide; or diphenolic
50 acid (DPA); a substitute for bisphenol A in the polymer industry.

51 Levulinic acid (LA), also known as keto acid ($C_5H_8O_3$), is a ketonic group compound which
52 has largely replaced petroleum-based goods in the chemical and biofuel industries. It is a
53 colorless, small chain fatty acid, soluble in acidic ethanol, diethyl ether, and water. LA is a
54 common substrate in chemical reactions such as condensation, esterification, halogenation,
55 hydrogenation, oxidative dehydrogenation, and salt formation (Zhang et al. 2020). It is a very
56 versatile and potential building block for the synthesis of various organic products (Çelebican
57 et al. 2020). Various fuel and chemical products can be obtained from levulinic acid. Levulinic
58 acid is considered the top twelve organic chemicals by the Energy Department of the USA
59 (Holladay JE, Bozell JJ, White JF 2004). Its permeation enhancers are very safe and effective.
60 Levulinic acid can also be obtained from cellulosic biomass, grass, and wood chips, and has
61 also been regarded as a basic premium material due to its high chemical reactivity. The
62 company GF Biochemicals Ltd. has shared the most levulinic acid manufacture in the world.
63 Hebei Yanuo, Zibo changlin Chemical, Heroy Chemical Industry, Hefei TNJ Chemical, and
64 Langfang Triple well Chemical have started the production of levulinic acid utilising biomass

65 as a raw material in recent times. The rice straw, sugarcane bagasse, rice husk, wheat straw,
66 corn straw, and other agricultural wastes contain sucrose, glucose, xylose, and fructose, which
67 can be converted to levulinic acid (Kumar et al. 2019).

68 According to the industry report, the market of levulinic acid can be predicted to increase at a
69 CAGR of 6% from 2019 to 2024. The increasing demand for levulinic acid in the plasticizer,
70 pharmaceutical, and cosmetic sectors is the primary factor for its larger market. According to
71 economic analysis, the market of levulinic acid market will be worth USD 71.85 million by
72 2027, with the growth at a 14.10% annual rate from 2020 to 2027.

73 To remove and recover carboxylic acids from water, a variety of separation techniques have
74 been used including adsorption, extraction, ion exchange, ultrafiltration, nanofiltration,
75 precipitation, electrodialysis, distillation, membrane separation, and reverse osmosis. (Inci and
76 Aydin 2003; Lalikoğlu et al. 2015). Among these techniques, extraction (Brouwer et al. 2017),
77 nanofiltration, and electrodialysis (Kim et al. 2013), and adsorption (Datta and Uslu 2017) have
78 been employed in the separation of levulinic acid from aqueous solutions. These processes are
79 expensive, cumbersome, and producing waste material during the process. Some advantages
80 and disadvantages of separation process are listed in **Table 1**. As a result, the commercial
81 separation of levulinic acid requires low-cost, simple, and environmentally benign process. In
82 comparison to other methods, reactive extraction is a simple, low-cost, promising, and
83 ecologically beneficial method (Antony and Wasewar 2019) because it produces less waste
84 material in the reject stream. The acid molecules present in aqueous phase form complexes
85 with organic phase molecules in reactive extraction, and facilitate improved acid separation.

86 The purpose of the present study is to separate levulinic acid from industrial downstream
87 material and decreases the problems of environmental pollution. In this study was used
88 promising and environment-friendly method of reactive separation for the recovery of levulinic
89 acid. The partition coefficient (P), distribution coefficient (K_D), dimerization constant (D),
90 extraction efficiency (η), loading ratio (Z), and experimental equilibrium constant (K_E) have
91 been evaluated by conducting the various experimental runs. The mass action law model was
92 used to predict the various parameters and compared them with experimental values.

93 **2. MATERIALS AND METHOD**

94 *2.1 Chemicals*

95 Levulinic acid ($\geq 98\%$ with 1.14 g.cm^{-3}), i-octanol ($\geq 99\%$ with 0.832 g.cm^{-3} density),
96 trioctylamine ($\geq 95\%$ with 0.918 g.cm^{-3} density), sulphuric acid ($\geq 98\%$ with 1.84 specific
97 gravity) were purchased from SIGMA-ALDRICH, Loba Chemie Pvt. Ltd., Spectrochem Pvt.
98 Ltd., and Rankem chemicals India respectively and used without the further purification. The
99 details of all chemicals are listed in **Table 2**.

100 *2.2 Experimental Procedure*

101 The experiments were performed using $0.1\text{-}1.0 \text{ mol.L}^{-1}$ as the initial concentration of levulinic
102 acid in the aqueous phase because the occurrence of lower range of concentration of acid in the
103 fermentation broths and industrial waste streams. The organic phase was prepared using i-
104 octanol with TOA extractant (0-80% v/v). The sample was taken in equal volume of organic
105 phase and aqueous phase solution in 250 ml conical flask and shaken in an orbital shaker (S-
106 24, REMI) for 300 min at a constant temperature of 298.15 K. After 300 min, sample was taken
107 out and centrifuged for 5 min at 4000 rpm using REMI CENTRIFUGE R-4C for the clear
108 separated phases i.e. the aqueous and organic phase.

109 *2.3 Analysis*

110 *2.3.1 HPLC Analysis*

111 After the phase separation, the aqueous phase was filtered by syringe filter (0.45-micron) and
112 diluted 100 times with double distilled water. The aqueous phase samples were analysed by
113 using an Agilent 1200 HPLC (High-Performance Liquid Chromatography). Sample analysis
114 was carried out using a C-18 column with Refractive Index Detector (RID). The analysis was
115 done using, 5 mM H_2SO_4 as the mobile phase, with a flow rate of 0.6 mL/min at a column
116 temperature of 35°C . The HPLC analysis peak is shown in **Figure 1**.

117 *2.3.2 Fourier Transform Infrared (FTIR) Analysis*

118 The spectroscopic techniques used Fourier Transformation Infrared (Shimadzu, IRAffinity-1)
119 were interpreted to interpret the acid: TOA complex production in the organic phase. All
120 measurements were carried out in a potassium bromide window cell. The acid: TOA
121 complexity was observed and examined in levulinic acid reactively extracted with TOA diluted
122 with i-octanol. In the initial aqueous phases, the comparative IR spectrum was obtained and
123 analysed in conjunction with the organic phases of the balance condition concerning
124 stoichiometry in the acid: TOA complex. The vibration peak at 1791 cm^{-1} represents the C=O

125 stretching strong carbonyl group (carboxylic acid); 1153 cm⁻¹ and 1053 cm⁻¹ confirm the
 126 presence of C-N stretching of amine; and 728 cm⁻¹, 1352 cm⁻¹, 2866 cm⁻¹, and 2922 cm⁻¹
 127 confirmed the C-H stretching of alkanes group. FTIR spectra of range 500-4000 cm⁻¹ are shown
 128 in **Figure 2**.

129 3. RESULTS AND DISCUSSION

130 After the production of levulinic acid through the fermentation broth and synthesis process, it
 131 occurs in a lower and very dilute range of concentration in the waste streams. Therefore, the
 132 sample of levulinic acid was prepared with 0.1-1 mol.L⁻¹ as initial concentration of acid in the
 133 aqueous phase. The organic phase containing TOA as reactive solvent and i-octanol as diluent
 134 was used.

135 3.1 Physical Extraction

136 Between the organic and aqueous phases, the distribution of un-dissociated LA molecules are
 137 characterised as follows:



139 In this situation, the partition coefficient (P) can be defined as:

$$140 \quad P = \frac{[LA]_{org}}{[LA]_{aq}} \quad (2)$$

141 The dimerization constant of LA can be represented as:



$$143 \quad D = \frac{[LA]_{2.org}}{[LA_{org}]^2} \quad (4)$$

144 Where $[LA]_{2.org}$ and $[LA_{org}]^2$ are the concentration of levulinic acid in the organic phase and
 145 dimerization form respectively.

146 The overall distribution coefficient is influenced by the concentration of H⁺ ions in the
 147 solution as well as its ionic strength. Overall distribution coefficient can be written as:

$$148 \quad K_D = \frac{[LA]_{org}^{total}}{[LA]_{aq}^{total}} = \frac{[LA]_{org} + 2[LA_2]_{org}}{[LA]_{aq} + [LA^-]} = \frac{P + 2P^2D[HLA]_{aq}}{1 + K_{LA}/[L^+]_{aq}} \quad (5)$$

149 In the present study, the dilute concentration of levulinic acid (0.1-1 mol.L⁻¹) was used.
 150 Therefore, the term $K_{LA}/[L^+]_{aq}$ in denominator of (5) can be considered as negligible. Hence,
 151 equation (5) can be considered as:

$$152 \quad K_D = P + 2P^2D[LA]_{aq} \quad (6)$$

153 Alternatively, equation (6) can be written as:

$$154 \quad [LA]_{org} = P[LA]_{aq} + 2P^2D[LA]_{aq}^2 \quad (7)$$

155

156 The physical extraction and its results are discussed in form of distribution coefficient (0.099-
157 0.681), dimerization coefficient (226), partition coefficient (0.051), and extraction efficiency
158 (9- 40.5 %) respectively. The experiments were performed using initial concentrations (0.1-1
159 mol.L⁻¹) of levulinic acid with i-octanol, and maximum extraction efficiency 40.5% with 0.681
160 distribution coefficient was observed at equilibrium condition in case of physical equilibrium.
161 The values of the dimerization coefficient (D) and partition coefficient (P) initiated the linear
162 regression method using equation 7.

163 *3.2 Chemical Extraction*

164 The physical extraction efficiency is not sufficient for the separation of levulinic acid
165 separation from the industrial downstream waste. To improve K_D values, low-density non-
166 reactive solvents can be used as diluents along with reactive solvents. During the experimental
167 work, trioctylamine was used in organic phase. The trioctylamine (TOA) is less soluble in
168 water and provides a higher separation efficiency of the acid. In TOA, the N-H bond carries
169 more polarity than the C-H bond but is lesser than the O-H bond. On comparing the physical
170 properties of amines, the polarity becomes apparent. Therefore, TOA transferred more
171 molecules of acid from aqueous phase to organic phase and improve the extraction efficiency.
172 The equilibrium isotherms of acid concentration between aqueous and organic phases are
173 shown in **Figure 3**.

174 The values of distribution coefficients were determined in the range of 0.47-6.14 with (20-80
175 vol %) of TOA. The distribution coefficient was found to be decreased with increasing the
176 levulinic acid concentration in aqueous phase. The higher K_D value was obtained at lower
177 concentration of levulinic acid (0.1 mol.L⁻¹). The higher concentration of acid leads to increase
178 the loading ratio in organic phase and the back extraction may be performed for the recovery
179 and regeneration of TOA and levulinic acid. More number of molecules interacted in the
180 extractant phase of chemical extraction results in better mass transfer from the aqueous phase.
181 Figure 3 depicts the chemical equilibria of the aqueous and organic phases. The acid-amine
182 complexes were formed due to the strong interaction between amine and acid that results in
183 high distribution coefficients (Yang et al. 1991). Based on the analysis of K_D values, TOA was

184 found to be a good reactive component in i-octanol for the separation of LA from the aqueous
185 phase.

186 The extraction efficiency (η) was estimated in the range of 32-86%, using TOA with i-octanol.
187 In case of chemical extraction, the extraction efficiency increased with the TOA concentration
188 up to 40% TOA in i-octanol and therefore it decreases with the further increase of TOA (**Figure**
189 **4**). It may be attributed to the governing synergistic effect of hydrogen bonding and polarity of
190 i-octanol with acid molecules (Wasewar et al. 2004). The separation efficiency depends on the
191 physical properties of diluent like solubility, molecular weight, dielectric constant, refractive
192 index, etc(Kumar et al. 2020). The i-octanol was used along with reactive solvents, which leads
193 to the higher separation efficiency of LA.

194 The loading ratio is defined as the ratio of acid concentration in the organic phase at equilibrium
195 to the initial concentration of reactive solvent in the organic phase. The loading ratio (Z) was
196 determined to analyses the complex formation in reactive extraction. The values of Z were
197 found in the range of 0.06–0.7 using 20-80% TOA in i-octanol. The Z values depend on the
198 strength of the acid-extractant interaction and the stoichiometry of the overall extraction
199 equilibrium (Kertes and King 1986; Keshav et al. 2009; Wasewar et al. 2011). The loading
200 ratio decreases with the increase of reactive solvent concentration in the organic phase that
201 enhances a more favorable solvating agent (Yang et al. 1991). The loading fraction was found
202 to be greater than 0.5, hence the acid-extractant complex of 1:1 and 2:1 in the organic phase
203 can be formed.

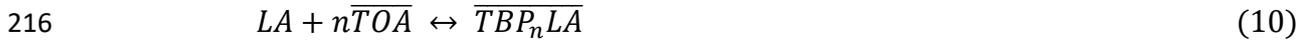
204 The equilibrium constant, K_E is affected by the formation of complexes between levulinic acid
205 and the reactive solvent. It depends on the loading ratio; i.e., the complex can form (1:1) or
206 (2:1) in the organic phase (**Figure 5**). The following equation can be used to calculate the
207 equilibrium complexation constant; K_E :

$$208 \quad \frac{Z}{1-Z} = K_E [LA]_{aq} \quad \text{If } Z < 0.5 \quad (8)$$

$$209 \quad \frac{Z}{2-Z} = K_E [LA]_{aq}^2 \quad \text{If } Z > 0.5 \quad (9)$$

210 The complexation extraction equilibrium constant (K_E) was found in the range of (11.34-1.05)
211 with (0.457-1.83 mol.L⁻¹) TOA in i-octanol. The various estimated value of K_E is listed in Table
212 3.

213 The reaction mechanism can be predicted in the organic phase wherein n molecules of TOA
 214 per molecule of levulinic acid take part in the reaction to form the acid-extractant complex,
 215 given as:



217 Theoretically, the mass action law can be used to estimate the equilibrium extraction constant
 218 (K_E) and the number of extractant molecules per acid molecule (n). As per the definition of
 219 complexation extraction equilibrium constant, K_E can be written as:

$$220 \quad K_E = \frac{\overline{[TOA_nLA]}}{[LA][\overline{TOA}]^n} \quad (11)$$

221 Also, levulinic acid dissociates at equilibrium in the aqueous phase. It can be written as:



$$223 \quad K_a = \frac{[L^+][A^-]}{[LA]} \quad (13)$$

224 Where K_a , is the dissociation constant

225 C_{LA} can be expressed as:

$$226 \quad C_{LA} = [LA][A^-] \quad (14)$$

227 Using equations (13) and (14)

$$228 \quad [LA] = \frac{C_{LA}}{\left(1 + \frac{K_a}{[L^+]}\right)} \quad (15)$$

229 The distribution coefficient and extraction efficiency can be determined using equations (16)
 230 and (17);

$$231 \quad K_D = \frac{\bar{C}_{LA}}{C_{LA}} = \frac{\overline{[TOA_nLA]}}{C_{LA}} \quad (16)$$

$$232 \quad \eta\% = \left(\frac{K_D}{1 + K_D}\right) \times 100 \quad (17)$$

233 Using equations (15) and (16);

234
$$K_D = \frac{K_E [\overline{TOA}]^n}{\left(1 + \frac{K_a}{[L^+]}\right)} \quad (18)$$

235 On taking the logarithm on both sides and rewriting the equation:

236
$$\log K_D + \log \left(1 + \frac{K_a}{[L^+]}\right) = \log K_E + n \log([\overline{TOA}]) \quad (19)$$

237
$$\log \left(\frac{K_D}{\left(1 + \frac{K_a}{[L^+]}\right)}\right) = \log K_E + n \log([\overline{TOA}]) \quad (20)$$

238 Where $[\overline{TOA}] = [\overline{TOA}]_{in} - n[\overline{TOA}_n LA]$

239 Assuming $[\overline{TOA}]_{in} \gg n[\overline{TOA}_n LA]$, and the initial concentration $[\overline{TOA}]_{in}$ can be substituted
240 in equation (20) to determine the value of n and K_E .

241 Eqⁿ (20) represents a straight line if plotted $\log K_D + \log \left(1 + \frac{K_a}{[L^+]}\right)$ vs $\log ([\overline{TOA}]_{in})$. The
242 value of K_E and n can be found using the intercepts and the slope of a linear line (**Figure 6**).

243 The values of n and K_E were calculated with the help of plot between $\log K_D + \log (1 + K_{LA}$
244 $/[L^+])$ vs $\log [TOA]_{in}$ which yields a straight line with a slope of n and an intercept of $\log K_E$.
245 The graphical representation can be used to calculate the values of K_E and n for various
246 extraction systems. The K_E value defines the separation of acid. If $K_E < 1$ means product
247 separation efficiency is low as compared to the reactant. Whereas if $K_E > 1$, it defines the good
248 separation efficiency of the acid. The values of K_E and n were found (12.40-0.99) and (0.35-
249 0.99) with different concentrations of TOA and levulinic acid.

250 The experimental value of K_E is closed to the predicted value by mass action law value.
251 Therefore, the mass action law holds good model represents the understanding of the separation
252 of levulinic acid.

253 **4. Mixer Settler Reactor**

254 *4.1 Mass balance for multiple reactor*

255 According to the experimental results and its understanding, the process needs process
256 intensification-based designing. The mixer settler reactor can be used in series to increase the
257 separation efficiency by more than 98% and decrease the concentration in waste stream. In this

258 study, the best and optimum experimental data was used for design the conceptual mixer settler
259 reactor in series and achieving 98% recovery of levulinic acid.

260 The diagram of stage-to-stage calculation is shown in Fig. 7. The given values of inlet
261 concentrations of levulinic acid $[LA]_{inlet\ 1}$ and $[LA]_{inlet\ 2}$ for reactor first and second. The
262 outlet value defined as Mass balance for mixer settler reactor can be derived as:

$$263 \quad [LA]_{org\ outlet\ 1} = [LA]_{inlet\ 1} - [LA]_{aq\ outlet\ 1} \quad (19)$$

$$264 \quad \text{Distribution coefficient } K_{D1} = \frac{[LA]_{org\ outlet\ 1}}{[LA]_{aq\ outlet\ 1}} \quad (20)$$

$$265 \quad \text{Extraction efficiency } (E) = \frac{K_{D1}}{1+K_{D1}} \times 100 \quad (21)$$

$$266 \quad [LA]_{aq\ outlet\ 1} = [LA]_{inlet\ 1} - (\text{Efficiency} \times [LA]_{inlet\ 1}) \quad (22)$$

267 The calculation for the first mixer settler reactor-

$$268 \quad [LA]_{aq\ outlet\ 1} = 0.1 - (0.86 \times 0.1)$$

$$269 \quad [LA]_{aq\ outlet\ 1} = 0.014 \text{ mol. } L^{-1}$$

270 Calculation of second mixer settler reactor-

271 In this case first reactor aqueous outlet consider inlet for second reactor, then

$$272 \quad [LA]_{aq} = 0.014 - (0.86 \times 0.014)$$

$$273 \quad [LA]_{aq} = 0.00196 \text{ mol. } L^{-1}$$

274 Then overall efficiency:

$$275 \quad \%E = \left(\frac{0.1 - 0.00196}{0.1} \right) \times 100$$

$$276 \quad \%E = 98\% \text{ recovery of levulinic acid}$$

277 The first mixer settler reactor provides the distribution coefficient as 6.14 with extraction
278 efficiency 86%. The overall distribution coefficient and extraction efficiency could be achieved
279 as 58.02 and 98% respectively with the second mixer settler reactor. The conceptual mixer
280 settler reactor and optimized parameter are shown in **Figure 7**. The designing method is
281 increasing the separation efficiency and maybe exit negligible waste downstream.

282

283 *4.2 Environmental issues*

284 Many industries were used toxic acid as a catalyst (H_2SO_4 , HCl , HNO_3 , etc.) for the
285 manufacturing of valuable levulinic acid. During the production of acid, the primary effect of
286 the chemical industry on the environment and the lifestyle as well, is due to the pollution,
287 arising from the industrial activities, resulting in wastewater polluting, gas emissions,
288 underground water and natural ponds, etc. The industrial downstream material required the
289 separation method for controlling these types environmental pollution. The mixer settler
290 reactor designing can be play an important role for preventing the environmental pollution.

291 **4. CONCLUSION**

292 The main obstacles in dealing with industrial waste and fermentation broth aqueous streams
293 can be addressed using the reactive extraction method. The experimental data suggested that
294 reactive separation is an effective and flexible process for recovering the valuable levulinic
295 acid as compared to the other methods like membrane, adsorption, distillation, etc. The overall
296 results conclude the highest separation efficiency as 86% at 40% TOA with initial
297 concentration (0.1 mol.L^{-1}) of levulinic acid. The lower concentration of TOA provides
298 sufficient extraction efficiency. The mass action law applied to experimental results and found
299 the predicted value near to experimental value. Therefore, mass action law can be applied to
300 the experimental results as the predicated values are close found to experimental value.
301 Therefore, mass action law can represent a model for the separation of levulinic acid. To
302 increasing the separation efficiency, the mixer settler reactor was designed in series and could
303 achieve the recovery of levulinic acid as 98%. Moreover, the conceptual mixer settler reactor
304 method carries with zero waste and with minimum energy usage during the recovery process
305 of levulinic acid. This experimental study can be used to decrease industrial waste material and
306 environmental pollution.

307 • **Ethical Approval**

308 Authors are approval that this article presented original work and did not submit in
309 other journals.

310 • **Consent to Participate**

311 Authors are giving consent to participate

312 • **Consent to Publish**

313 Authors are giving consent to publish the present work as per publisher policy.

314 • **Authors Contributions**

315 Anuj Kumar: Conceived and designed the experiments; Performed the experiments;
316 Analysed and interpreted the data; wrote the paper.

317 Anjali Ingle: Analysed the HPLC analysis and interpreted the data

318 Diwakar Z. Shende: Conceived and designed the experiments; Analyzed and interpreted
319 the data; Contributed reagents, materials, analysis tools, or data.

320 Kailas Wasewar: Conceived and designed the experiments; Analyzed and interpreted the
321 data; Contributed reagents, materials, analysis tools, or data.

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323 Not applicable

324 • **Competing Interests**

325 Not applicable

326 • **Availability of data and materials**

327 Data and other materials will be made available on request to the authors.

328

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403 **Table 1** Some advantages and disadvantages of various methods of separation

Method	Advantages	Disadvantages
Distillation	-Simple installation -Products of high purity -Low capital investment -Low risk	-High energy required -High cost -Components are thermally stable
Membrane	-Product of high yield -Low energy required -Reliable	-Membrane fouling
Evaporation	-Low capital investment, -Low-risk operation	-High energy demand
Adsorption	-Easy to install - Relatively high Selectivity	-High costs and energy demand - Low adsorption capacities
Reactive extraction	-Control of the pH in the reactor -Solvents can be used -Higher product concentration	-

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406 **Table 2** The physiochemical properties of various chemicals used

Chemical	Supplier	Purity%	IUPAC name	Viscosity/cP at 25°C	Density/g.cm⁻³
Levulinic acid	SIGMA-ALDRICH	98	4-oxopentanoic acid	–	1.14
i-octanol	Loba Chemie Pvt. Ltd. India	99	2-ethylhexanol	7.36	0.832
Trioctylamine (TOA)	Spectrochem Pvt. Ltd. Mumbai. India	95	Tricaprylamine	7.862	0.8
Sulphuric acid	Rankem chemicals	98	–	26.7	1.83

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409 **Table 3** Define extraction equilibrium constant of experimental and mass action law

TOA (mol.L⁻¹)	Experimental (K_E)	Mass action law (K_E)
0.457	11.34	12.40
0.915	7.41	6.45
1.372	2.91	3.56
1.83	1.05	0.99

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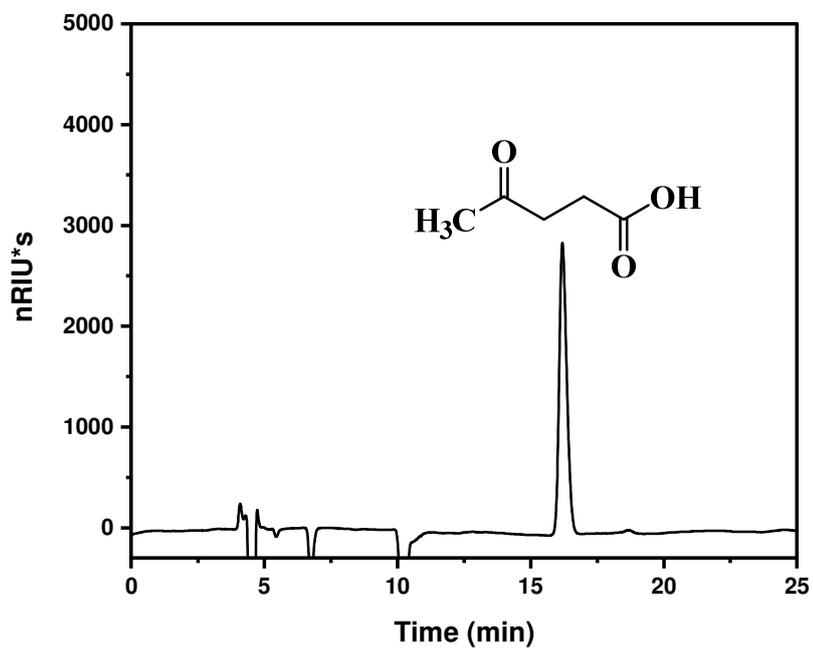
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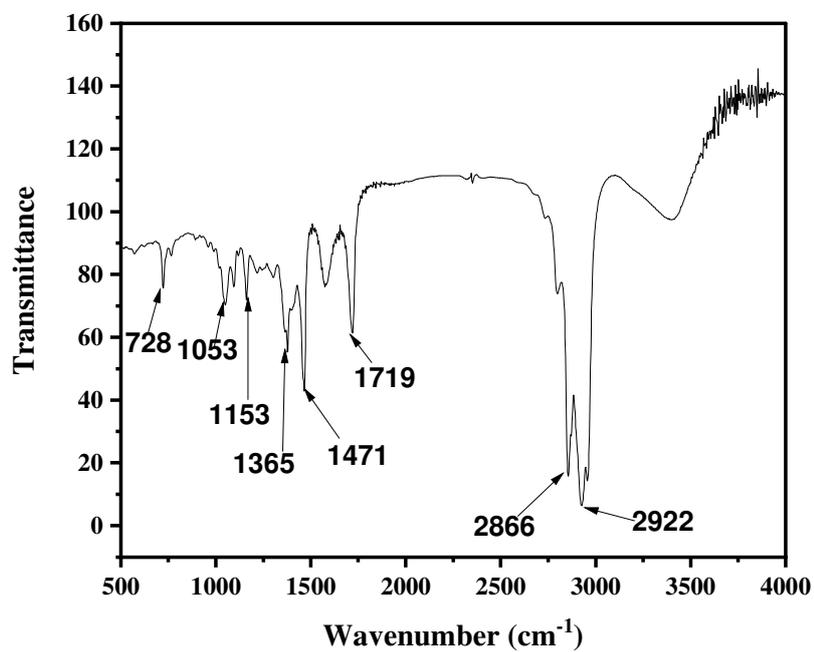
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Figure 1 High-Performance Liquid Chromatography analysis for levulinic acid

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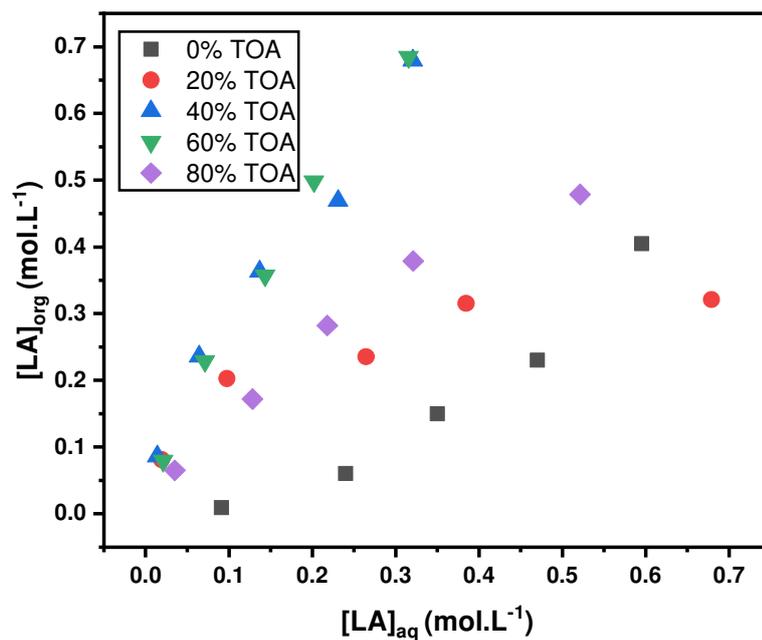
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Figure 2 FTIR Spectra (500-4000 cm⁻¹ range) for levulinic acid

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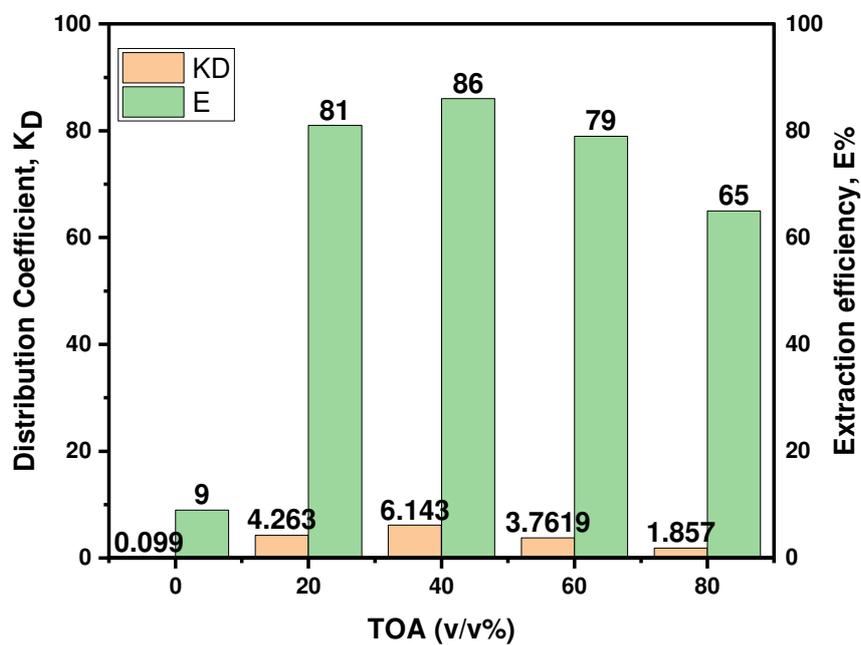
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433 **Figure 3** Equilibrium isotherms of acid concentration between aqueous and organic phase with TOA (0-80
 434 v/v%) in i-octanol.

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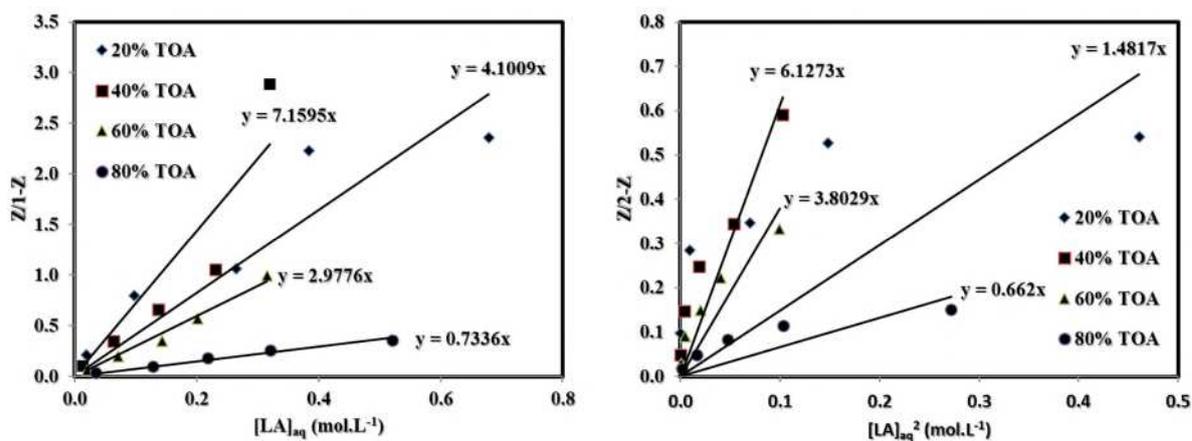
438 **Figure 4** Effect on distribution coefficient (K_D) with the initial concentration of levulinic acid at (0-80 v/v%)
439 TOA varies in i-octanol

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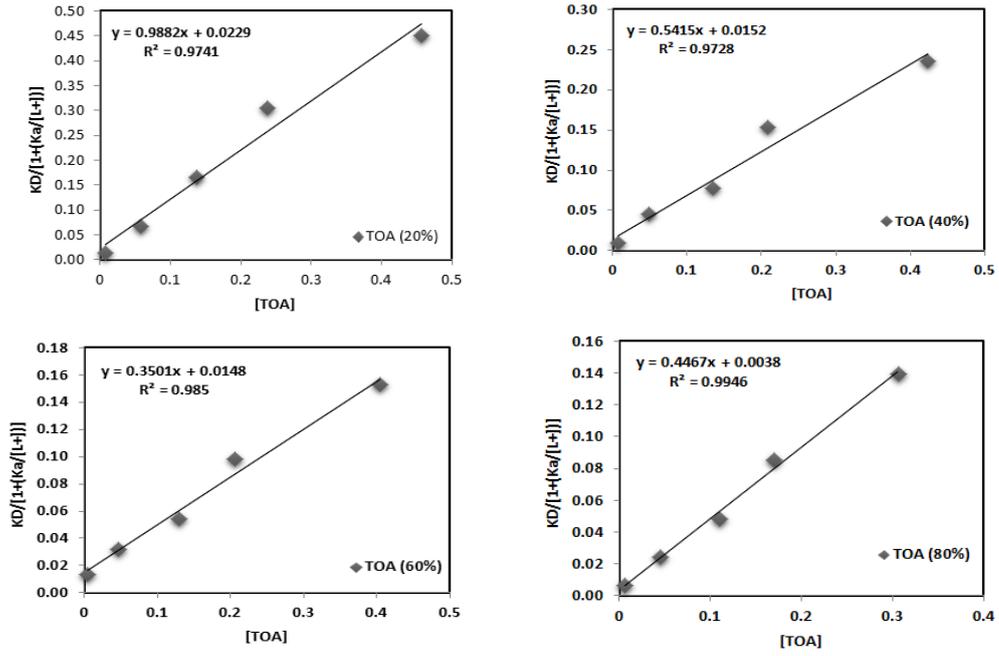
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445 **Figure 5** Plot of $Z/(1-Z)$ vs $[LA]_{aq}$ and $Z/(2-Z)$ vs $[LA]_{aq}^2$ for the estimation of (1:1) and (2:1) levulinic acid-
446 TOA equilibrium complexation constant in i-octanol.

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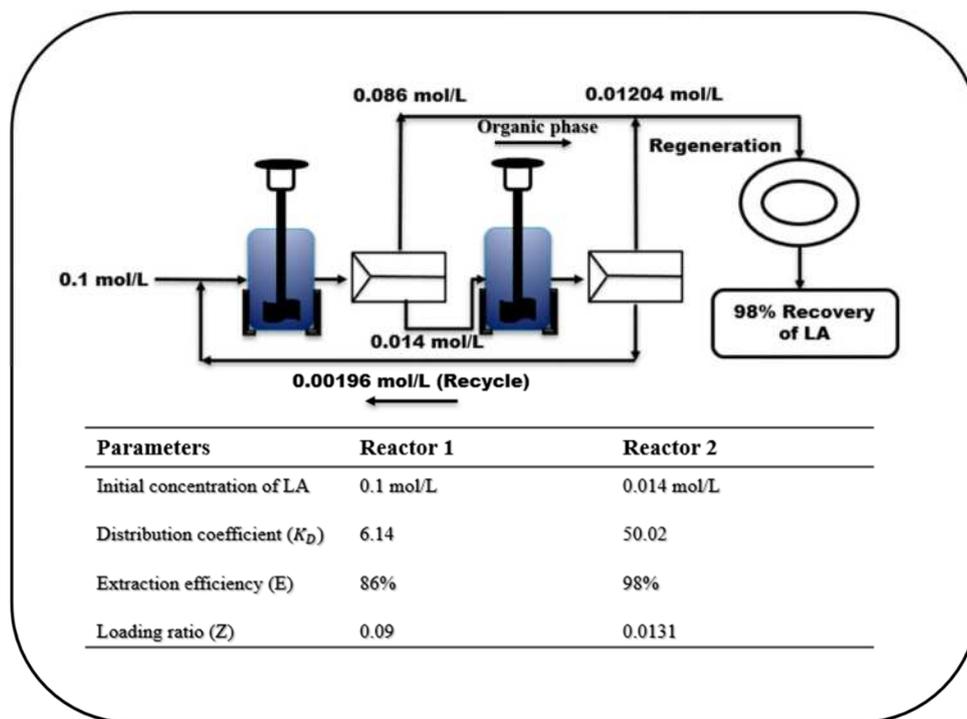
449 **Figure 6** Variation of $K_D/[1+(K_a/[L^+])]$ with various TOA concentrations for the various concentration of
 450 levulinic acid

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Figure 7 Conceptual mixer settler reactor connected in series for achieving 98% recovery of LA.

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