RESEARCH ARTICLE-CHEMICAL ENGINEERING

Succinic Acid Recovery and Enhancement of Emulsion Liquid Membrane Stability using Synergist Aliquat 336/TOA/Palm Oil System Assisted with Nanoparticle

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Abstract

Succinic acid (SA) production from fermentation has drawn great interest owing to its simplicity and environmentally friendly process, but it is constrained by high downstream processing costs. The Pickering emulsion liquid membrane (PELM) process containing synergistic carriers (Aliquat 336 and trioctylamine (TOA)) in palm oil is an attractive technology for SA recovery from fermentation broths. The synergistic extraction mechanism was investigated using reactive extraction and the method of slope analysis. Almost 100% of SA was extracted from a 10 g/L simulated solution with a synergistic coefficient of 640. Based on the individual and mixed carrier investigations, it infers that Aliquat 336 and TOA function as base and synergist carriers, respectively. The stability of water-in-oil-in-water (W/O/W) emulsion was studied by varying the agitation speed, Span 80 concentration, and mixed surfactant concentration (Tween 80 and Span 80). At the best stability condition of 5% w/v (Span 80 + Tween 80), hydrophilic–lipophilic balance 6, 300 rpm agitation speed, 0.1% w/v Fe_2O_3 nanoparticles, 0.1 M Aliquat 336 + 0.1 M TOA, and 1.0 M sodium hydroxide, the emulsion was stable, and almost 100% of SA was extracted and enriched five times in the internal phase. The concentration limit of SA during its recovery by ELM is 10 g/L. Meanwhile, the results from water phase separation and droplet image proved that PELM has the advantage of rapid and efficient demulsification performance, where the demulsification can be completed within 5 min. Hence, synergistic PELM is a new class of ELM for the recovery of SA and it may be extended for downstream and bio-based manufacturing.

Keywords Succinic acid · Enrichment · Pickering emulsion liquid membrane · Synergist · Nanoparticle · Stability

1 Introduction

Succinic acid (SA) is a dicarboxylic acid that is commonly known as butanedioic acid [1]. Recently, the interest in this compound has increased as it could serve as a platform for various commodity chemicals, such as adipic acid, dimethyl/diethyl succinate, 2-pyrrolidinone, succinimide, and maleic anhydride [2]. Besides, SA can be applied in various products, including biodegradable polymers, pharmaceuticals, cosmetics, food ingredients, solvents, and feed additives [1]. Succinic acid is produced commercially from the derivation of maleic anhydride that is obtained from n-butane. After that, maleic anhydride is hydrogenated to succinic anhydride, followed by hydration to SA. Alternatively, SA can also be produced from the hydrolysis of maleic anhydride to maleic acid, followed by hydrogenation [3]. Petrochemically produced SA could lead to environmental pollution and sustainable development concern owing to the use of finite petrochemical feedstock. In addition, those processes involve high temperatures and high-pressure conversion that emit a substantial amount of carbon dioxide and lead to global warming, as well as contribute to a higher subsequent environmental cost.

Recently, due to its simplicity and environmental friendliness, the production of SA by means of fermentation has received quite significant attention [4, 5]. Various natural

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and metabolically engineered microorganisms have been employed for fermentative SA production, such as *Actinobacillus succinogenes*, *Anaerobiospirillum succiniciproducens*, *Mannheimia succiniciproducens*, *Escherichia coli*, *Corynebacterium glutamicum*, and *Saccharomyces cerevisiae* [6]. However, the existence of by-products (e.g., lactic, formic, and acetic acids), protein, and unconsumed carbon sources could decrease SA yield and complicate the purification process. Therefore, an effective and economical separation method is crucial in downstream SA processing from fermentation broths.

Several processes for SA recovery have been studied extensively, including precipitation, solvent extraction, reactive extraction, membrane separation, and crystallization. Excellent reviews by Kumar et al. [7] summarize the merits and demerits of the different conventional unit operations used during the downstream processing of SA. In the classical precipitation process, calcium hydroxide is added in excess to form calcium succinate. After the treatment with sulfuric acid, SA is then obtained. Despite its simplicity and highly selective separation, this process generates a high amount of calcium sulfate by-product and low final product purity [8]. Reactive extraction and solvent extraction are highly efficient processes that give over 95% product yield and low usage of energy; however, a high amount of organic diluent and extractant is required [9]. Meanwhile, a high product yield up to 92% can be obtained through membrane filtration. However, membrane fouling and high equipment costs become the limitation [10]. The required product can be achieved by crystallization without the need for a sophisticated unit operation. However, such a process requires high energy consumption [11]. An energy-intensive electrodialysis process has also been reported for the separation of SA. Unfortunately, this process is costly due to the frequent replacement of the membrane [6]. Chromatography-based methods, such as adsorbent and ion exchange, can be employed to recover SA, but frequent regeneration of saturated resin requires a large quantity of acid/alkali, generating wastewater [12]. Additionally, in situ separation can be easily integrated with an SA fermenter, but the process is rather complex and needs regeneration of the sorbent inhibition [6]. On the other hand, the downstream processing of nanofiltration (NF) membrane for separation of glucose from gluconic acid has been reported [13]. The membrane-based separations can produce products with high purity. However, fouling problem cannot be ignored and it could be enhanced with time of operation.

Emulsion liquid membrane (ELM) is one of the potential technologies for recovering SA. It is a one-of-a-kind method that combines solvent extraction and membrane separation into a single unit operation. The potential to recover substances from dilute solutions, very selective to the target solute, high efficiency (low membrane fouling), fast extraction due to large mass transfer area, and low energy requirement are all benefits of ELM [14–16]. In principle, ELM consists of a very thin liquid barrier (usually organic) that separates two other aqueous liquid phases. The procedure entails dispersing a primary emulsion with internal and organic phases into an external feed phase with the appropriate solute. The solute from the external phase diffuses across the organic phase and reacts chemically with the stripping agent, remaining contained in the internal phase [17].

The right selection of liquid membrane formulation will improve the selectivity of the solute in ELM [14]. The formulation includes a diluent as a base of liquid membrane, a carrier, a stabilizer, and a stripping agent. Normally, a single carrier is used. However, the application provides limited loading capacity and phase separation is slow [18, 19]. A synergistic extraction system might be created in order to increase the efficiency of ion transport and process. Synergism occurs when two or more carriers cooperate or interact, resulting in a larger combined effect than the sum of the individual carrier effects [20]. A mixture of any type of carrier can be used to perform synergistic extraction. Hu et al. [21] used a combination of Cyanex 923 and Cyanex 272 to attempt the recovery of scandium. Another research described the separation of copper from nickel/copper mixture using a synergistic extraction technique of M5640 and TRPO as the carrier [22]. Sulaiman et al. [23] conducted the extraction of reactive dye using a synergistic combination of Aliquat 336 and D2EHPA carriers. Based on the findings, the synergistic carriers are very useful in improving extraction performance and sustaining the process by minimizing the chemical used. Furthermore, the use of costly chemicals could be reduced with the right formulation and process conditions.

Despite its many benefits, ELM's commercial application has been limited due to emulsion instability and the difficulty of demulsification after extraction. During solute extraction, the liquid membrane's stability is described as its capacity to withstand leakage or rupture [24]. There have been a number of studies on the elements that influence emulsion stability, particularly those related to the emulsification procedure, processing conditions, and emulsion formulation. As most emulsions are stabilized by surfactants, demulsification after extraction is very difficult. Chemical demulsification is unacceptable because the organic phase cannot be reused after the process. Physical demulsification methods, such as electrical, ultrasonication, and thermal treatment, have been reported [25–27], but the high energy consumption and low efficiency restricted the commercial application of ELM technology.

A particle-stabilized emulsion or Pickering emulsion has drawn significant interest owing to emulsion stability, less toxicity, and ease to be demulsified [28]. Several particles, such as silica, clay, chitosan, cyclodextrin, carbon nanotube,

and hydroxyapatite, are supplemented in the ELM formulation that adsorbs at the interface and stabilizes emulsion globules against coalescence. Recently, the application of magnetic nanoparticles as a stabilizing material has been widely researched owing to their negligible toxicity and useful magnetic properties. Also, Pickering emulsion liquid membrane (PELM) involves nanoparticle concepts to achieve a more stable emulsion for wastewater treatment [28]. For instance, Lin et al. [29] utilized hydrophobic oleic acid-coated nano-Fe_3O_4 particles to extract 4-methoxyphenol. The study achieved an extraction efficiency of over 86% and the emulsion could be demulsified by magnetic or centrifugation force without causing an obvious change in oil phase chemistry. Mohammed et al. [30] attempted the removal of benzoic acid by PELM stabilized by magnetic Fe_2O_3 and reported 99.74% removal, with emulsion leakage of less than 0.2%. Meanwhile, Mohammed et al. [31] studied membrane stability and extraction of ciprofloxacin using ELM stabilized by magnetic nano-Fe_2O_3 particles, and more than 98% of ciprofloxacin was extracted without significant emulsion breakage.

To the best of our knowledge, no study has been reported regarding the use of synergistic formulation assisted with nanoparticles (magnetic nano-Fe_2O_3) for creating PELM for SA recovery. This study aims to investigate the stability and extraction capacity of PELM for the recovery of SA from a simulated solution. The extraction of SA in this study was performed by using the synergistic formulation proposed by Nurulashikin et al. [32] containing palm oil and a mixture of carriers (Aliquat 336 and trioctylamine (TOA)) as a diluent and a synergistic carrier, respectively. This study was further investigated to determine the effect of relative proportions of different organic phase compositions that comprised the synergistic and base carriers. The results were then used to determine the possible extraction mechanism of SA. The generated formulation was employed in ELM to evaluate SA extraction performance, where a complementary study was performed to investigate the stability of the ELM with the addition of nanoparticles in the PELM formulation. The water phase separation and droplet image from demulsification were also included. In the last subsection, the most effective stripping agent concentration for SA recovery and demulsification of the Pickering emulsion were studied.

2 Methodology

2.1 Materials

Cooking palm oil (BURUH) was produced by Lam Soon Edible Oils Sdn. Bhd. Trioctylamine (TOA, 98% purity) and sodium carbonate powder (Na_2CO_3, 99% purity) were obtained from Merck. Succinic acid (99% purity), polyoxyethylene sorbitan monooleate, Tween 80 ($\geq$ 58% oleic acid), Sorbitan monooleate, Span 80 ($\geq$ 60% oleic acid), and Iron (III) oxide nanoparticle (Fe_2O_3 NPs, < 50 nm particle size) were purchased from Sigma-Aldrich. Tricaprylmethylammonium chloride (Aliquat 336, 99% purity) and sodium hydroxide (NaOH, 98% assay) were procured from Acros Organics and J.T. Baker, respectively. All these reagents and chemicals were of analytical grade and were utilized without additional purification when they arrived.

2.2 Mechanism of Synergistic Succinic Acid Extraction

In order to develop ELM formulation, liquid–liquid extraction (LLE) is employed to find a suitable carrier, diluent, and stripping agent. Based on the formulation obtained from Nurulashikin et al. [32], the synergistic SA extraction mechanism was investigated using a reactive extraction procedure. An equal proportion of the aqueous feed phase (10 g/L simulated SA solution) and organic phase (TOA and Aliquat 336 in palm oil) were mixed in a 25 mL conical flask and agitated using a mechanical shaker (IKA-KS 130 basic, Germany) at 300 rpm for 18 h to attain equilibrium. After that, the solution was allowed to separate into aqueous and organic phases for 30 min in a separation funnel. The leftover SA content in the aqueous phase at the bottom of the funnel was determined using high-performance liquid chromatography (HPLC). The SA extraction performance was determined based on the mass balance principle, as shown in Eq. 1. The procedures were repeated with 0.015–0.1 M concentration of Aliquat 336 and TOA. One-factor-at-a-time method was applied. For instance, TOA concentration was varied while maintaining Aliquat 336 concentration.

$$\text{Extraction}(\%) = \frac{C_{i,aq} - C_{f,aq}}{C_{i,aq}} \times 100 \tag{1}$$

where $C_{i,aq}$ and $C_{f,aq}$ are the succinic acid concentrations (mg/L) in the initial and final aqueous phases, respectively.

For the stripping process, 10 mL of SA-loaded organic solution from the extraction process was mixed with 10 mL of stripping agent solution at 300 rpm for 18 h. Upon completion, the aqueous internal phase and organic phase were left for phase separation within 15–30 min. High-performance liquid chromatography was used to determine the SA content in the aqueous phase at the bottom of the funnel. The procedure was repeated with different types of stripping agents and various concentrations of the selected stripping agent. The performance of the stripping process was evaluated using Eq. 2. The experiment was carried out at room temperature (26 ± 1 °C) and repeated at least three times with less than

5% standard deviation.

$$\text{Stripping (\%)} = \frac{C_{\text{fs,aq}}}{C_{\text{i, org}}} \times 100 = \frac{C_{\text{fs,aq}}}{C_{\text{i,aq}} - C_{\text{f,aq}}} \times 100 \quad (2)$$

where $C_{\text{fs, aq}}$ and $C_{\text{i, org}}$ are the succinic acid concentrations (mg/L) in the aqueous phase after stripping and organic phase after extraction, respectively.

2.3 Emulsion Liquid Membrane Stability Study

The stability of emulsion assisted with nanoparticles (Pickering emulsion) was investigated through a two-step procedure consisting of primary water-in-oil (W/O) emulsion preparation and dispersion. The W/O emulsion was produced by mixing 5 mL of organic membrane solution (Span 80, mixed carrier, and diluent) with 5 mL of stripping agent solution using a motor-driven homogenizer (Heidolph Silent Crusher M, Germany) at 7000 rpm [33]. Accordingly, 0.1% w/v of nanoparticles was added to the organic solution. The freshly prepared W/O was dispersed into 30 mL of external phase (SA solution), forming a double water-in-oil-in-water (W/O/W) emulsion. The system was agitated using a digital mixer system (Cole-Parmer EW-50006–00, Germany) at a speed of 300 rpm for 5 min. Once completed, the emulsion and the aqueous phase were allowed to separate. The volume of the aqueous phase (external feed phase) was measured by placing it into a measuring cylinder. The proportion of emulsion swelling, as given in Eq. 3, was used to represent the emulsion stability. The procedures were repeated by varying Span 80 concentration (1–7%) and mixed surfactant concentration (Span 80 and Tween 80). For the mixed surfactant study, Tween 80 was added to the external phase. Notably, the mixed surfactant was fixed at a hydrophilic–lipophilic balance (HLB) value of 6 [34] and calculated using Eq. 4 [34].

$$\text{Stability (\%swelling/breakage)} = \frac{V_{\text{f,em}} - V_{\text{i,em}}}{V_{\text{i,em}}} \times 100 \quad (3)$$

$$\text{HLB}_{\text{mixture}} = \text{HLB}_{\text{Span80}} \times \%_{\text{Span80}} + \text{HLB}_{\text{Tween80}} \times \%_{\text{Tween80}} \quad (4)$$

where $V_{\text{i, em}}$ and $V_{\text{f, em}}$ are treat ratio (ratio of emulsion to feed phase), initial and final volume of the emulsion, respectively. The positive value obtained from the calculation indicates emulsion swelling, while the negative value indicates emulsion breakage occurs. Meanwhile, the values of $\text{HLB}_{\text{Span80}}$ and $\text{HLB}_{\text{Tween80}}$ were 4.3 and 15, respectively.

At the best stability condition, the concentration of SA in the external phase after ELM separation was analyzed using HPLC, and the extraction performance was determined
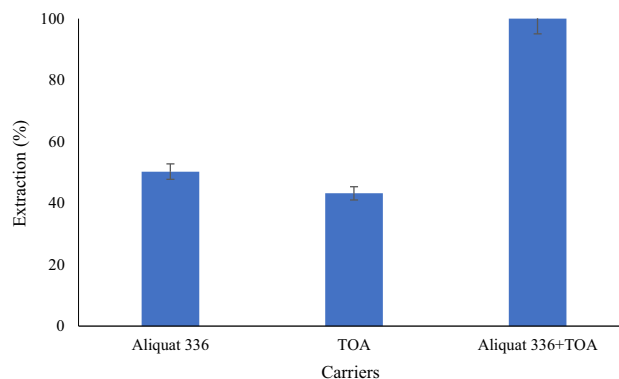
Fig. 1 Effect of single and mixed carriers on succinic acid extraction performances (Experimental conditions: carrier concentration: 0.2 M; aqueous phase volume: 10 mL; organic phase volume: 10 mL; agitation time: 18 h; agitation speed: 300 rpm)

using Eq. 1. To determine the recovery efficiency, the emulsion at the top of the separating funnel was demulsified using heat-induced demulsification method [35]. To begin the demulsification process, the emulsion was immersed in a water bath with ultrasonic vibration (LIR Biotech 020S) for 10 min, followed by heating at 70 °C for 24 h. The aqueous internal phase separated from the emulsion was analyzed using HPLC, and the enrichment ratio was calculated using Eq. 5 [34]. The experiments were repeated at least three times with a maximum standard deviation of 5%.

$$\text{Enrichment ratio (ER)} = \frac{C_{\text{int,aq}}}{C_{\text{i,aq}}} \quad (5)$$

where $C_{\text{int, aq}}$ and $C_{\text{i, aq}}$ are the succinic acid concentrations in the internal and external phase, respectively.

3 Results and Discussion

3.1 Extraction and Recovery of Succinic Acid in LLE Process

3.1.1 Synergistic ELM Formulation

The SA extraction performance using Aliquat 336, TOA, and a mixture of both carriers is illustrated in Fig. 1. The result illustrates that the extraction performance increases in the following order: TOA (43%) < Aliquat 336 (50%) < Aliquat 336 + TOA (100%). It is apparent that a mixture of Aliquat 336 and TOA has shown a synergistic effect on SA extraction performance. This is because SA has been extracted by two carriers simultaneously. Notably, SA can exist in the aqueous phase in dissociated and undissociated forms, depending on the pH of the solution. The molecules of SA will dissociate

at a pH higher than the pKa value, which is reported to be 4.2 and 5.6, respectively [36].

Basically, TOA has long-chain aliphatic tertiary amine, with each alkyl group having seven to nine carbon atoms. It is also reported as an effective and commonly used carrier in various diluents for carboxylic acids [37]. During the process, TOA is not soluble in water and is able to form amine salts that undergo ion exchange reactions with SA. Meanwhile, Aliquat 336 is generally a quaternary amine that has a strong extraction capacity, high enrichment ratio, and wide-ranging pH range [38]. The extraction performance obtained in this study is owing to the anionic exchange reaction between SA and Aliquat 336.

Figure 2 exhibits the Fourier transform infrared spectra analysis of the organic phase with fresh Aliquat 336, the mixture of Aliquat 336 and TOA, and SA loaded with the mixed carrier system. The IR spectra of the organic phases slightly differ from one another in the 400–4000 cm^{-1} range. There are five major absorption bands that can be observed in all organic phases. The broad band between 2800 and 3000 cm^{-1} is due to C–H stretching vibrations [39]. The peak at 1743.65 cm^{-1} results from the vibration of C=C bonds in palm oil that contains fatty acids [40]. The absorption at 1460.11 cm^{-1} indicates the –N–CH$_3$ vibrations in Aliquat 336. Meanwhile, the absorptions at 1157.29 cm^{-1} and 721.38 cm^{-1} are due to the vibrations of the CH$_3$ and CH$_2$ groups, respectively [20]. From the figure, it is apparent that a new band was obtained between 3100 and 3700 cm^{-1} for the loaded organic phase, resulting from O–H vibrations

Table 1 Effect of stripping agent types on succinic acid extraction (Stripping time: 18 h; Agitation speed: 300 rpm; [Stripping agent]: 0.01 M)

Stripping agents	Stripping (%)
NaOH	75
Na$_2$CO$_3$	45

of the extracted SA [20]. In addition, a new band was formed around 1600 cm^{-1} from the C–O–N–C bond as a result of the conjugation of the solute with the carrier molecule.

The effect of stripping agent type on SA extraction from the loaded organic phase is shown in Table 1. The pH difference between the external and internal phases is the driving force for SA extraction due to the nature of the acid. As a result, alkaline solutions like sodium hydroxide (NaOH) and sodium carbonate (Na$_2$CO$_3$) were evaluated in this work as SA stripping agents. The percentage of SA stripped using NaOH is higher, which is 75% compared to Na$_2$CO$_3$, which is only 45%.

The result is likely related to NaOH that creates available spaces for Na$^+$ at the internal phase. Therefore, it rapidly interacts with the acid–amine complex and easily strips the SA [32]. This prevents the accumulation of acid complexes in the liquid membrane, thus improving the efficiency of stripping. The use of NaOH as a stripping agent enables more efficient transport of SA from the organic phase to the internal phase in the reactive extraction system.
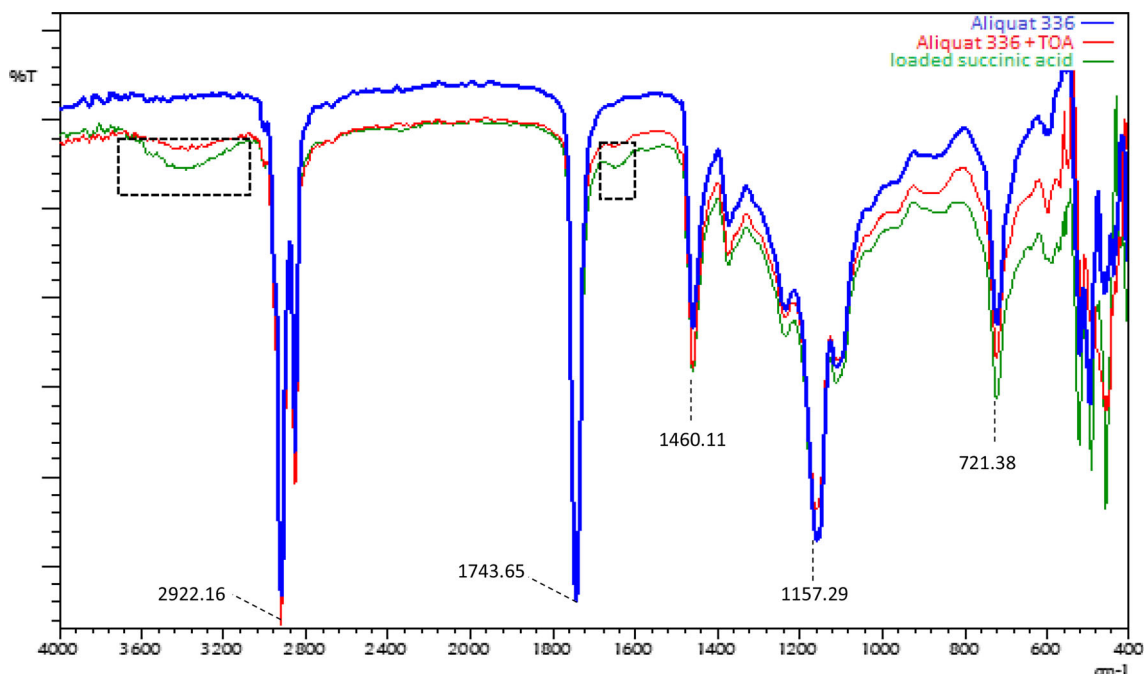

Fig. 2 The FTIR spectra of the organic phase with fresh Aliquat 336, the mixture of Aliquat 336 and TOA, and succinic acid loaded with the mixed carrier system

3.1.2 Succinic Acid Extraction and Stripping Mechanism

To investigate the stoichiometry of succinic acid extraction, the method of slope analysis was used. The possible reactive extraction mechanism between succinic acid with TOA (R_3N) and Aliquat 336 (R_4N) carrier mixture is illustrated in Eq. 6.

$$H_2A\,(aq) + mR_3N\,(org) + nR_4N\,(org)$$
$$\rightarrow H_2A\,(R_3N)_m\,(org) + H_2A\,(R_4N)_n \qquad (6)$$
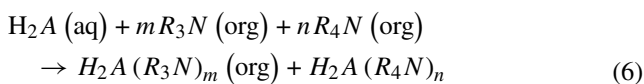
where m and n are stoichiometric constants. To find the values of the constants of reactive extraction reaction stoichiometry by the method of slope analysis, the extraction reaction equilibrium constant K_{ex} is defined in Eq. 7.

$$K_{ex} = \frac{[H_2A(R_3N)_m][H_2A(R_4N)_n]}{[H_2A][R_3N]^m[R_4N]^n} \qquad (7)$$

The distribution ratio of succinic acid is given in Eq. 8.

$$\text{Distribution ratio} = \frac{[H_2A]_{org}}{[H_2A]_{aq}} \qquad (8)$$

By substituting the distribution ratio, D into Eq. 7, Eq. 9 is obtained

$$D_{mix} = K_{ex}[R_3N]^m[R_4N]^n \qquad (9)$$

where D_{mix} is the distribution ratio of succinic acid in the organic phase to the aqueous phase that was obtained using a synergistic extraction system containing a carrier mixture of TOA with Aliquat 336. Taking the logarithm of Eq. 9, the following equation can be obtained.

$$\log D_{mix} = \log K_{ex} + m\log[R_3N] + n\log[R_4N] \qquad (10)$$

The stoichiometry of synergistic reactive extraction in Eq. 6 can be determined by employing Eq. 10 through the method of slope analysis. At a constant Aliquat 336 concentration, the plot of $\log D_{mix}$ against $\log[TOA]$ produced a straight line with a high coefficient of determination value ($R^2 = 0.9895$), as shown in Fig. 3. It can be seen that the slope of the graph is 1.5, indicating that 3 mol of TOA reacted with 2 mol of SA. Meanwhile, Fig. 4 displays the graph of $\log D_{mix}$ versus $\log[Aliquat336]$ concentration at fixed TOA concentration. The slope value of 2 suggests that the molar proportion of Aliquat 336 to SA is 2:1 in the solute-carrier complexes. Therefore, the reaction stoichiometry of SA with the synergistic mixture of TOA and Aliquat 336 can
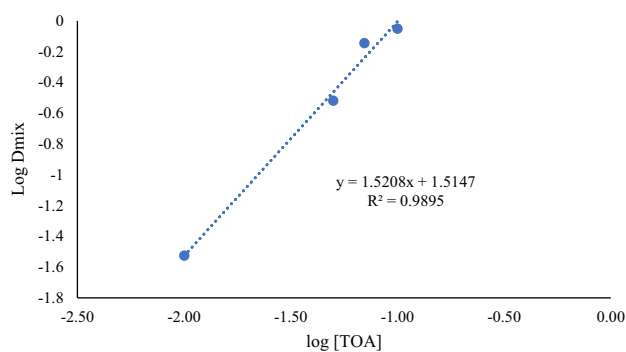

Fig. 3 Stoichiometric study of synergistic succinic acid extraction at fixed Aliquat 336 concentration. (diluent: palm oil; Aliquat 336 concentration: 0.05 M; extraction speed: 300 rpm; extraction time: 18 h; temperature: 26 °C)
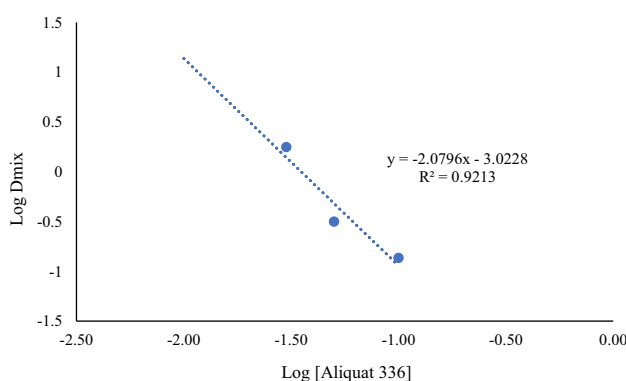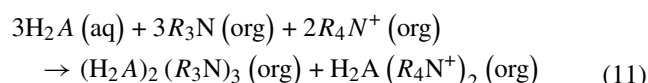

Fig. 4 Stoichiometric study of synergistic succinic acid extraction at fixed TOA concentration. (Diluent: palm oil; TOA concentration: 0.01 M; extraction speed: 300 rpm; extraction time: 18 h; temperature: 26 °C)

be expressed in Eq. 11.

$$3H_2A\,(aq) + 3R_3N\,(org) + 2R_4N^+\,(org)$$
$$\rightarrow (H_2A)_2\,(R_3N)_3\,(org) + H_2A\,(R_4N^+)_2\,(org) \qquad (11)$$

The synergism effect of the mixed carrier extraction system is presented in Fig. 5. The results show that 100% of SA was extracted. Meanwhile, the extraction using an individual carrier of Aliquat 336 and TOA gives low extraction performance, where only 50% and 43% were achieved after 18 h of extraction, respectively, as shown in Fig. 1. In terms of the rate of extraction within 5 min, the results show that a mixture of carriers enhanced the extraction process and the synergism effect existed in the system. In addition, a high synergistic factor of 640 was obtained. The extraction equilibrium of Aliquat 336 and a mixture of Aliquat 336 + TOA was achieved at 5 min. However, the equilibrium for TOA is still inconsistent up to 10 min, which means that the extraction equilibrium was not established. However, after 18 h, as expected for equilibrium achievement, only 43% of SA was
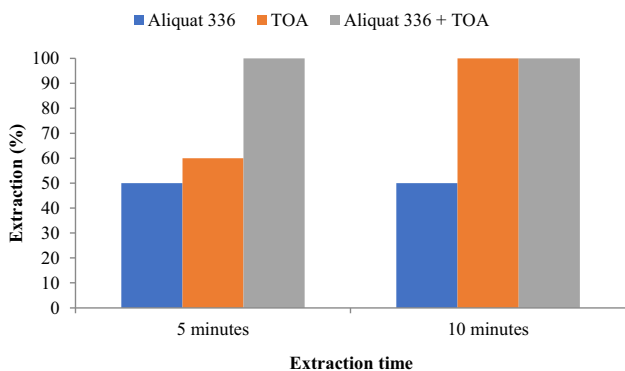
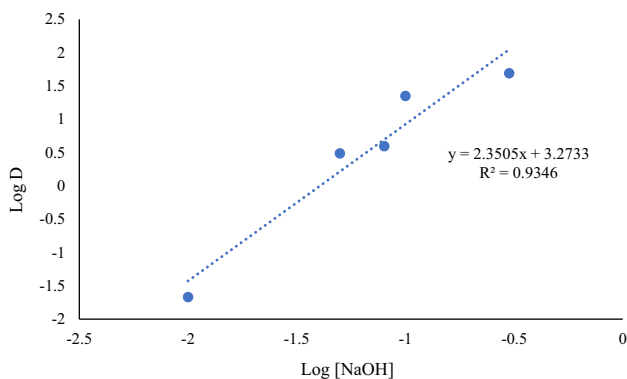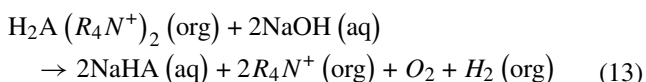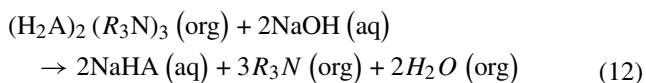**Fig. 5** Synergism effect of Aliquat 336 and TOA

Fig. 6 Stoichiometric plot for the equilibrium of succinic acid stripping

extracted using TOA. Similar results were also observed by Nurulashikin et al. [32], who stated that 18 h is sufficient to achieve equilibrium. According to the basic theory of kinetics, the main carrier typically provides slow kinetics, whereas another carrier, known as the synergist, provides faster kinetics [41]. Based on Fig. 1 and Fig. 5, a single Aliquat 336 gives higher extraction with a slower extraction rate. A higher mole of Aliquat 336 for the extraction compared to TOA is presented in Fig. 6. Hence, it can be deduced from this study that Aliquat 336 serves as a base carrier, while TOA acts as a synergist in SA extraction.

The mechanism of SA stripping was investigated by plotting a graph of log D versus log[NaOH].. The linear plot gives a positive slope of 2.35, which is nearly 2. This implies that the molar ratio of SA complex to NaOH is 1:2. Hence, 2 mol of NaOH reacted with 1 mol of SA-carrier complex for the stripping process, as shown in Eqs. 12 and 13.

$$(H_2A)_2 (R_3N)_3 \, (org) + 2NaOH \, (aq)$$
$$\rightarrow 2NaHA \, (aq) + 3R_3N \, (org) + 2H_2O \, (org) \quad (12)$$

$$H_2A \, (R_4N^+)_2 \, (org) + 2NaOH \, (aq)$$
$$\rightarrow 2NaHA \, (aq) + 2R_4N^+ \, (org) + O_2 + H_2 \, (org) \quad (13)$$

The mechanism of carrier-facilitated transport of SA is exemplified in Fig. 7. Succinic acid in the external phase (H_2A) reacts with TOA $(R_3N.)$ and Aliquat 336 (R_4N^+) to form complexes in the liquid organic phase $(H_2A)_2(R_3N)_3.$ and $H_2A(R_4N^+)_2$. The complexes then diffuse through the liquid organic phase and react with NaOH. At the internal interface, SA is stripped into the internal phase, releasing a free synergistic carrier $R_3N \, and \, R_4N^+$ in the liquid membrane.

3.2 Emulsion Stability Assisted with Nanoparticles iELM process

3.2.1 Characterization of water-in-oil (W/O) emulsion

The stability of W/O/W emulsion containing a synergistic formulation of Aliquat 336/TOA/palm oil for SA recovery was assessed. Previously, Span 80 and Tween 80 were used to stabilize the emulsion in a single carrier system for SA extraction [42]. In this study, nanoparticles were introduced to enhance the stability, as shown in Fig. 8. The existence of these nanoparticles will disturb the stability of the emulsion and simultaneously increase the viscosity, forming more droplets. This result is consistent with Mohammed et al. [43], who reported that the attractive Pickering emulsions are simple and bear strong similarities with the well-known surfactant-based emulsions. The emulsions have high resistance to coalescence due to no amphiphilic character and become a major benefit of the stabilization.

The structure and interaction of Span 80 and Tween 80 assisted with nanoparticles could be arranged at the water–oil interface in a network where the hydrophobic and hydrophilic chains of the surfactants dissolve in the organic liquid membrane and internal phase, respectively. During the dispersion, nanoparticles are adsorbed at the interface between the aqueous and organic phases and serve as a mechanical barrier to prevent the coalescence of emulsion droplets and globules. The protection is based on the energy to expel the particles from the interface to the dispersed droplets. The emulsions become more stable with nano-Fe_2O_3 particles that cover more emulsion interface, hence increasing the extraction efficiency [43]. However, in excess of nano-Fe_2O_3 concentration beyond the droplet coverage, the stability of the ELM will be deteriorated. The extra nano-Fe_2O_3 particles will accumulate in the liquid organic phase [44]. In order to optimize the stability of emulsion in this study, the effect of single and mixed surfactant concentration and also agitation speed was further evaluated.

3.2.2 Effect of Span 80 Concentration

The effect of Span 80 concentration in the range of 1–7% w/v on the stability of a synergistic ELM system was investigated,

Fig. 7 Facilitated transport mechanism of SA through liquid membrane
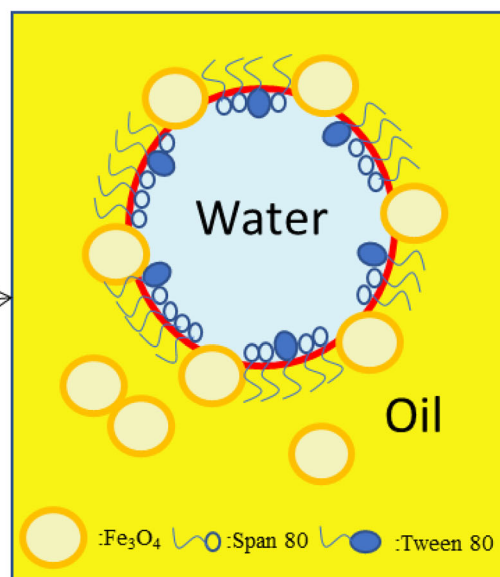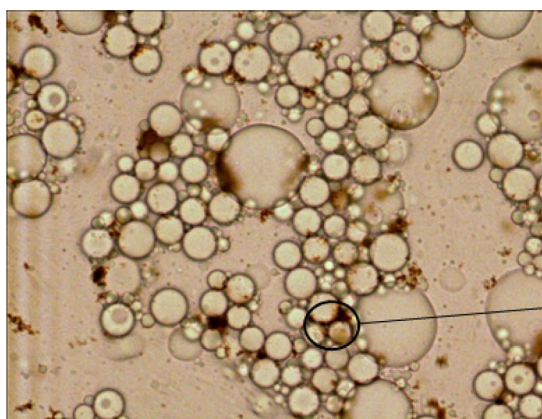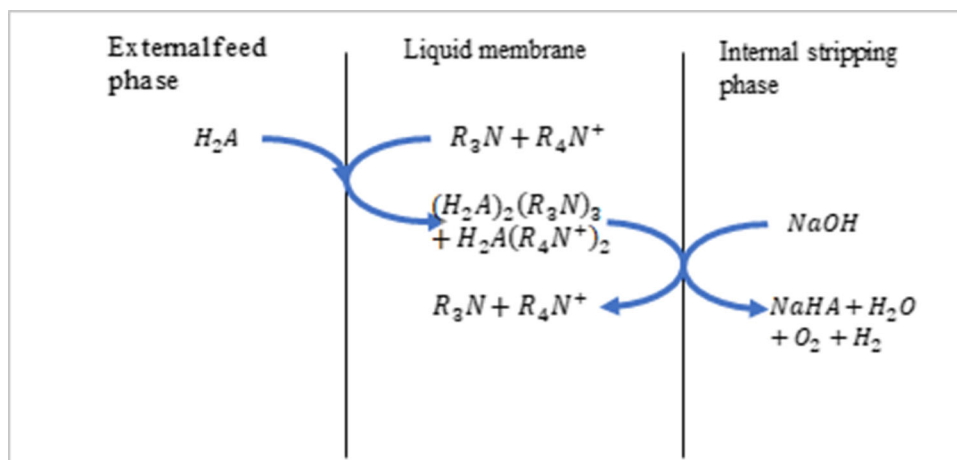
Fig. 8 Adsorption of nanoparticles at the interface to form a stable emulsion

and the results are presented in Table 2. The results show that the emulsion breakage decreased significantly from 80 to 10% with an increment of Span 80 concentration from 1 to 5%. During the dispersion, Span 80 molecules move toward the interface, and the hydrophobic tail of the molecules aligns itself in the less polar liquid organic phase while the hydrophilic head orientates itself toward the polar aqueous phase [45]. The Span 80 molecules break the cohesive interactions between polar and nonpolar molecules, allowing these molecules to replace each other at the interface. The molecular interaction at the interface occurs between the hydrophilic head of Span 80 and the aqueous phase molecules and between the hydrophobic tail of Span 80 and the organic phase molecules [45]. This phenomenon lowers the tension across the interface because the newly developed interactions

are stronger than the interaction between the nonpolar and polar molecules [46].

At low Span 80 concentration, the formation of emulsion droplets and globules is resisted due to insufficient surfactant to reduce interfacial tension. Consequently, the emulsions are unstable and easy to demulsify. This result reflects those of Pratiwi et al. [36], who indicated that lack of surfactant leads to difficulty for emulsion globules to disperse, resulting in rapid coalescence. At a higher concentration, the tendency of Span 80 to adsorb at the interface is significantly increased, providing a denser surfactant packing and resulting in a larger reduction of the interfacial tension.

Meanwhile, further increasing the Span 80 concentration up to 7% (w/v) resulted in poor W/O/W stability, with a 40% emulsion breakup observed. A possible explanation for this

Table 2 Effect of Span 80 concentration on W/O/W emulsion stability (Experimental condition: liquid membrane: palm oil + 0.1 M Aliquat 336 + 0.1 M TOA; stripping agent: 0.01 M NaOH; O/I ratio: 1:3, homogenizer speed: 7000 rpm, emulsification time: 5 min, nanoparticles: 0.1% w/v Fe_2O_3, external phase volume: 30 mL, emulsion volume: 10 mL, agitation speed: 300 rpm)

% Span 80 (w/v)	% Breakage
1	80
3	60
5	10
7	40

Table 3 Effect of Span 80 and Tween 80 at total HLB 6 on W/O/W emulsion stability

Mixed surfactant concentration (% w/v)	% Span 80 (w/v)	% Tween 80 (w/v)	% Breakage
1	0.841	0.159	10
3	2.523	0.477	10
5	4.205	0.795	0
7	5.887	1.113	20

(Experimental condition: O/I ratio: 1:3, homogenizer speed: 7000 rpm, emulsification time: 5 min, nanoparticles: 0.1% w/v Fe_2O_3, external phase volume: 30 mL, emulsion volume: 10 mL, agitation speed: 300 rpm)

is the amount of Span 80 employed in the ELM exceeds the critical micelle concentration, in which the surfactant molecules start to form aggregates known as micelles. These micelles lead to breaking, where the water transport between two aqueous phases is promoted. These results corroborate the ideas of Chanukya et al. [47] and Sulaiman et al. [25], who asserted that the molecules of surfactant might exist as inverse micelles that could transport large quantities of water from the external phase into the internal phase.

3.2.3 Effect of Mixed Surfactant Concentration

A mixture of surfactant concentrations was studied to provide a pronounced effect on emulsion stability. According to Tadros [48], some specific surfactant mixtures provide lower surface tension values compared to either of the two individual surfactants. The efficiency of the surfactant combination was maximum when the blend contained a low HLB surfactant (Span 80, HLB 4.3) and a high HLB surfactant (Tween 80, HLB 15) at a particular proportion (HLB 6) [34]. Table 3 presents the effect of varying mixed surfactant concentrations in the range of 1–5% w/v on the W/O/W emulsion stability. The results show that the mixed surfactant effect on emulsion stability gives a similar trend compared to individual
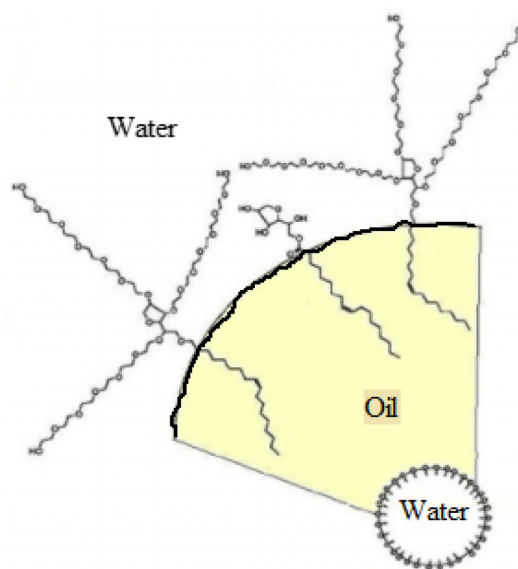

Fig. 9 Schematic representation of the geometrical packing of the mixed surfactants and nanoparticles at the oil–water interface in the emulsion. **a** Water phase separation of emulsion **b** Primary emulsion droplet at 400 × magnification under microscope

Span 80. Besides, it is apparent that the emulsion breakage decreased significantly, where only 0–20% of emulsion breakage was observed. In general, surfactants having HLB values of 3.5–8.0 promote W/O emulsion, whereas surfactants with HLB values of 8.0–16.0 promote O/W emulsions [49]. In the present study, additional Tween 80 migrated to the external O/W interface, further reducing interfacial tension and making the second emulsification easier. Besides, the W/O/W stability has also increased due to the compatibility of the lipophobic surfactant (Tween 80) with the properties of the lipophilic surfactant (Span 80), which promotes interaction at the interfacial area. Due to the similar structure of both surfactants, where Tween 80 is a corresponding ethoxylated ester of Span 80, as shown in Fig. 9, Tween 80 functions to reduce the repulsion of the hydrophilic head group of Span 80, which contributes to a more efficient packing of the surfactants at the interface and promotes better stability.

On the other hand, the most stable emulsion using a combination of Span 80 and Tween 80 as surfactants was also observed at 5% w/v surfactant concentration where 0% breakage was recorded. This implies that the amount of surfactant supplied in the formulation is sufficient. A further increase of mixed surfactant concentration resulted in 20% emulsion breakage, which is likely to be related to the formation of micelles, as discussed in the previous subsection. Besides, according to Karjiban et al. [50], the micelles of Tween 80 may solubilize Span 80, which reduces the concentration of Span 80 in the liquid organic phase. Consequently, emulsion breaking occurred due to an increase in interfacial surface tension. This result is in accordance with Jiao and

Table 4 Effect of agitation speed on emulsion breakage (Experimental condition: O/I ratio: 1:3, homogenizer speed: 7000 rpm, emulsification time: 5 min, nanoparticles: 0.1% w/v Fe_2O_3, external phase volume: 30 mL, emulsion volume: 10 mL, mixed surfactant concentration: 5%)

Agitation speed (rpm)	% Breakage
200	20
300	0
400	20
500	40

Table 5 The extraction and recovery of succinic acid by using different stabilizer

	Extraction (%)	ELM stability	Demulsification process
Span 80 + Tween 80	100	Stable	Difficult (overnight)
Span 80 + Tween 80 + Nanoparticles	100	Stable	Easy (5 min)

(Experimental condition: O/I ratio: 1:3, emulsification time: 5 min, homogenizer speed: 7000 rpm, external phase volume: 30 mL, emulsion volume: 10 mL, mixed surfactant concentration: 5% w/v)

Burgess [51], who observed that a high Tween 80 concentration has a destructive effect on the stability of W/O/W emulsion. Hence, in this study, the mixed surfactant concentration was fixed at 5% (w/v) as it provides the most stable W/O/W emulsion.

3.2.4 Effect of Agitation Speed

In ELM, agitation is applied to disperse the primary W/O emulsion in the external aqueous feed phase. An appropriate speed is required to produce a large amount of emulsion dispersion while maintaining the emulsion stability. Table 4 summarizes the effect of varying the agitation speed from 200 to 500 rpm on W/O/W emulsion stability. At low agitation speed (200 rpm), high breakage of 20% was recorded. This result may be explained by the fact that the energy delivered is inadequate to disperse emulsion in the external phase, resulting in bigger emulsion globules, as demonstrated by Othman et al. [52]. Consequently, the globules formed are easily coalesced, resulting in emulsion breakdown. The results indicate that the stability improved with the increment of agitation speed from 200 to 300 rpm. This observation is due to sufficient shear energy provided to disperse the emulsion. A study by Jusoh et al. [34] indicated that smaller globules are formed with faster agitation, which leads to a more stable emulsion. Besides, there would be a trade-off between the two effects of breakage and swelling phenomena.

Meanwhile, the emulsion breakage increased significantly up to 40% with a further increase of agitation speed from 300 to 500 rpm. A possible explanation for this is a large number of emulsion globules might form when a high agitation speed is applied. Faster agitation can thin the interfacial film, favoring the quick coalescence of emulsion globules. Besides, the observed breakage could be attributed to the exposure of the emulsion to excessive shear, which resulted in globule rupture, leading to the leakage of the internal solution to the external phase. In addition, the turbulent effect in the ELM system, which originated from the impeller blade impact, has a strong influence on the breakage phenomena. These results seem to be consistent with Chaouchi and Hamdaoui [53], who reported unstable emulsion at a high agitation speed in

the ELM extraction of acetaminophen. Accordingly, 300 rpm was chosen in this study as a suitable agitation speed that results in a stable W/O/W.

3.3 Extraction and Recovery of Succinic Acid in PELM Process

Referring to the emulsion stability study, the most stable emulsion was obtained using 5% w/v mixed surfactant concentration and 300 rpm agitation speed. To assess the ELM performance on SA extraction and recovery, the external feed and internal stripping solution were analyzed. The comparison of the ELM systems assisted with and without nanoparticles is shown in Table 5. It can be seen that both systems provide 100% extraction, indicating that the ELM formulation and condition used are favorable for the extraction process. Hence, the emulsion is stable enough for extraction in 5 min. No breakage was observed after the extraction for both processes owing to the small droplet size distribution that promotes emulsion stability. The characteristics of fresh and used ELMs are summarized in Table 6.

In order to recover the SA, demulsification of used emulsion becomes the most significant factor. As in Table 5, the observation results show that the SA recovery using ELM assisted with nanoparticles (PELM) is easier compared to the ELM without nanoparticles, indicating that the internal phase is easier to be separated via heat-assisted ultrasonic vibration. This is supported by Figs. 10a and b, which depict the water phase separation of W/O emulsion and a droplet image of a W/O emulsion with nanoparticles at 1–5 min demulsification time, respectively. Figures 10a) (i) and b (i) show the W/O emulsion after the extraction. As can be seen, the W/O emulsion (used PELM) was uniformly distributed in the organic phase with a diameter of 3.09 μm, indicating consistent emulsion stability of the system.

After 3 min of demulsification, the water–oil emulsion mixture was separated rapidly under strong ultrasonic vibration (Fig. 10a (iii)). For the microscopic observation of the separated water, it was observed that a small amount of water

Table 6 Characteristics of fresh and used ELMs

Condition	ELM		PELM	
	Fresh	Used	Fresh	Used
Component	Palm oil Aliquat 336 TOA Span 80 Tween 80 NaOH	Palm oil Aliquat 336 TOA Span 80 Tween 80 NaOH Succinic Acid	Palm oil Aliquat 336 TOA Span 80 Tween 80 NaOH nano-Fe_2O_3 particles	Palm oil Aliquat 336 TOA Span 80 Tween 80 NaOH nano-Fe_2O_3 particles Succinic acid
Droplet size (μm)	5.41	5.81	3.10	3.09

droplets with a bigger diameter (40.74 μm) was still suspended in the organic phase (Fig. 10b (iii)). This indicates that the nano-Fe_2O_3 particles help to rapidly destroy the protective film at the water–oil interface. Meanwhile, Figs. 10a (iv) and b (iv) show the newly produced organic phase, indicating that demulsification could be completed within 5 min. On the other hand, demulsification without nanoparticles took a much longer time, which is in agreement with Jusoh et al. [34]. Thus, it can be concluded that nano-Fe_2O_3 particles, as a simple and reliable demulsifier, have excellent demulsification efficiency, where demulsification can be completed within a short period of time. These results reflect those of Lin et al. [29], who reported simple demulsification of emulsion containing nano-Fe_2O_3 particles.

In addition, the effect of stripping agent concentration was studied to obtain maximum recovery, as shown in Fig. 11. The results show that at 0.1 M NaOH, the extraction and enrichment performance is 88% and 2 times, respectively. The recovery performance was poor, indicating that there was insufficient stripping agent to strip the SA from the organic phase, hence slowing down the stripping process. By increasing the concentration of NaOH from 0.1 to 1.0 M, the extraction percentage does not change considerably, which means that the carrier is enough for extraction. On the other hand, the enrichment performance increased from two to five times as the concentration of NaOH increased, which further illustrates that greater reactivity between NaOH and SA is achieved at a higher NaOH concentration. A similar result was obtained by Jusoh et al. [42], who indicated that a greater amount of solute within the inner interface could be stripped with a higher concentration of stripping agent. Succinic acid is enriched up to five times compared to the initial external feed phase concentration, indicating that SA was concentrated in the internal phase.

However, the enrichment of SA dropped to four times as the concentration of NaOH increased to 2.0 M. A high concentration of NaOH results in a greater pH gradient between both internal and external phases. The difference in ionic strength acts as a driving force for water to be transported

**Table 7** Effect of NaOH concentration on breakage and final pH of external phase

Stripping agent concentration (M)	Breakage (%)	pH external phase
0.1	0	5.27
0.5	0	5.31
1.0	4	6.42
2.0	20	10.34

into the internal phase, which subsequently dilutes and swells the internal phase [54]. This occurrence thins the membrane layer, which eventually breaks the emulsion and results in a leakage of stripped SA into the external phase [55]. Consequently, low recovery of SA was observed. This is supported by the data, as tabulated in Table 7. The results show that the final pH of the external feed phase increased from 5.27 to 10.34, and 20% of the emulsion broke at 2.0 M NaOH. The significant pH increment is due to the internal phase that leaks to the external phase. According to Jusoh et al. [1], excess NaOH may cause surfactant to hydrolyze, which can negatively influence the emulsion stability. As such, from Fig. 11, the suitable concentration of NaOH in this study was found to be 1.0 M as it gives the highest recovery and enrichment ratio.

Following demulsification, the liquid membrane can be regenerated. Based on Fig. 11, 100% extraction was obtained, indicating that the system is very stable, allowing the recyclability of the liquid membrane. Referring to a previous study [1], the liquid membrane is still in good condition up to the second cycle. The concentration limit of SA in this study is 10 g/L. This limitation is because the recycled liquid membrane is less stable compared to the freshly prepared liquid membrane. Besides, this is likely to be related to the liquid membrane fouling and contamination of complexes inside the liquid membrane. A higher SA concentration in the feed phase can cause an accumulation of complexes, subsequently
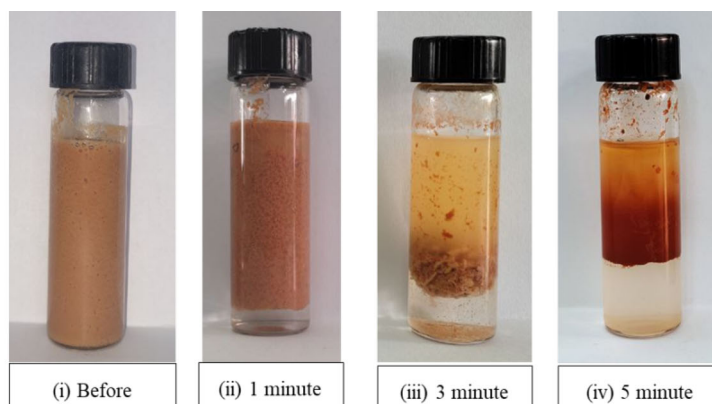
(a) Water phase separation of emulsion
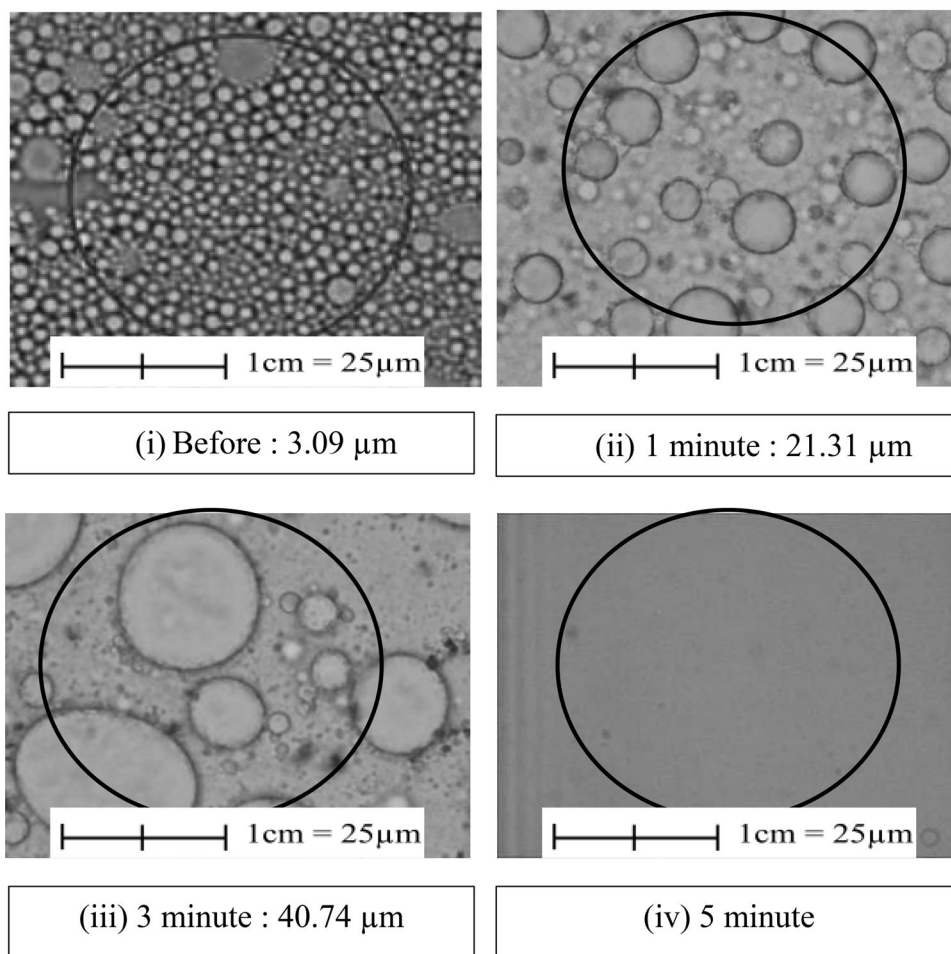
(b) Primary emulsion droplet at 400x magnification under microscope

contaminating the liquid membrane and reducing recycling performance. Better performance is likely to be possible with the regeneration (make-up) of the liquid membrane by an additional carrier, surfactant, or stripping agent.

4 Emulsion Liquid Membrane Prospect in Succinic Acid Recovery

In summary, Table 8 reports some research on SA extraction using ELM. For instance, Jusoh et al. [1] extracted 81%

Fig. 11 Effect of NaOH concentration on the succinic acid extraction and enrichment ratio (Span 80: 4.205%, Tween 80: 0.795%, nanoparticle: 0.1%, pH: 4.32, homogenizer speed: 7000 rpm, emulsifying time: 5 min, agitation speed: 300 rpm; treat ratio: 1:3, extraction time: 3 min)
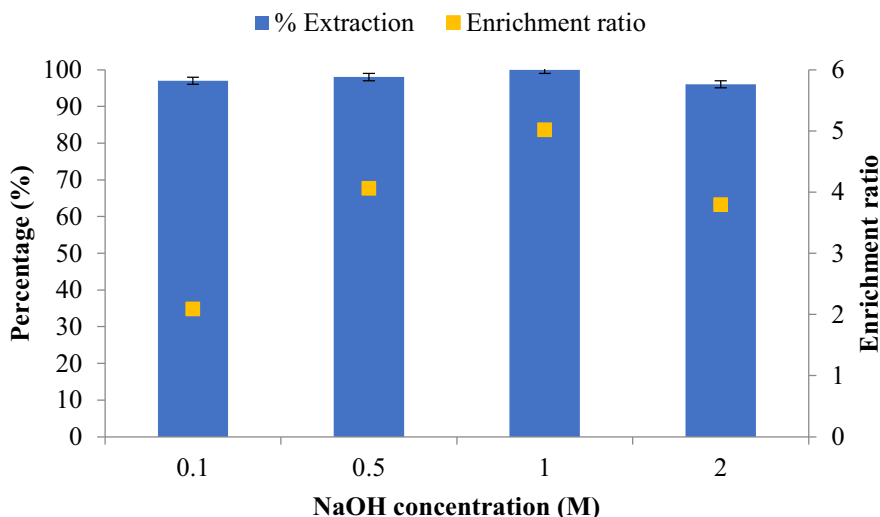

Table 8 The comparison of ELM extraction performance of succinic acid reported in literature

Initial succinic acid concentration	ELM formulation					Total carrier concentration (M)	Extraction (%)	Reference
	Carrier	Diluent	Stripping agent	Surfactant	Modifier			
10 g/L	Amberlite LA2	Palm oil	1.0 M Na_2CO_3	Span 80 + Tween 80	Octanol	0.7	81	[54]
4.72 g/L	Amberlite LA2	Kerosene	0.002 M Na_2CO_3	Span 80	1-octanol	0.05	98	[56]
10 g/L	Aliquat 336 + TOA	Palm oil	0.1 M NaOH	Span 80 + Tween 80	0.1% w/v Fe_2O_3	0.2	100	This study

of SA from an aqueous solution using 0.7 M Amberlite LA2 and 1.0 M Na_2CO_3 as a stripping agent. Meanwhile, 98% of SA was extracted from 4.72 g/L SA solution using 0.05 M Amberlite LA2 and 0.002 M Na_2CO_3 [56]. The results provide high extraction with lower carrier concentration. However, the recovery reported was very low. It is apparent that this study provides the highest extraction (100%), which is likely to be related to the synergistic formulation containing 0.1 M Aliquat 336 and 0.1 M TOA used in the process.

Notably, the optimum conditions must be determined for an efficient ELM process. Several factors must be considered and optimized, including emulsification time, emulsification speed, surfactant concentration, agitation speed, carrier and stripping agent concentration, treatment ratio, and extraction time. The optimization of these parameters is important to obtain excellent extraction and recovery performance, which requires further study.

For instance, the carrier and its concentration significantly influence ELM process efficiency. Essentially, the exploration of the carrier effect in the ELM process is initiated by the screening of suitable carriers and the variation of its concentration. Yet, a study by Sulaiman et al. [23] reported

no significant effect on extraction efficiency was observed after increasing the carrier concentration beyond the optimum level. This is due to the fact that the viscosity of the emulsion was higher and cause a higher mass transfer resistance, thus the extraction performance was affected [57].

Meanwhile, another factor that affects ELM performance is stripping agent concentration. Generally, the capacity of the internal phase for solute recovery increases with stripping agent concentration, consequently increasing the extraction performance [58]. In contrast, ELM performance decreases at a stripping agent concentration beyond a certain limit on account of emulsion instability owing to the swelling of emulsion that occurs due to the osmotic pressure gap between the internal and external phases [49].

Besides, the volume fraction of the emulsion toward the aqueous external phase, also known as the treat ratio, also influences the extraction performance. Basically, the extraction efficiency increases with the treat ratio [59]. According to Ooi et al. [60], the extraction rate is enhanced due to the improvement of solute permeation and stripping. The molar ratio of the internal stripping agents to the solute in the external phase increases with emulsion volume, therefore increasing the capacity of the internal reagent for solute

recovery [61]. On the other hand, Kumbasar [62] found that the increment of the treat ratio beyond a certain level could affect emulsion stability owing to the creation of a viscous emulsion.

Extraction time or agitation time is another parameter affecting ELM. It exemplifies the contact period between the emulsion and the aqueous external phase during ELM. Sufficient time is required for the distribution of a higher number of emulsion globules in the aqueous external phase. In contrast, Kulkarni [63] found that prolonged extraction time induced water transportation from the aqueous external phase toward the emulsion phase, resulting in swelling of the emulsion. Consequently, the accumulation of water in the internal phase will cause emulsion breakage and result in internal phase leakage [64]. Hence, longer extraction time is not recommended, but adequate time is compulsory for emulsion dispersion and extraction.

Meanwhile, in the case of carrier-mediated ELM transport, the pH of the external aqueous phase is critical for solute extraction. This is on account of the carrier being controlled by the pH of the feed phase solution to attain equilibrium during the reaction with the targeted solute. The external phase pH should also be adjusted to prevent emulsion swelling and ensure emulsion stability [65]. Regarding the ELM prospect discussed, it is expected that PELM is a potential method to recover SA. In order to optimize the process, further study should be performed.

5 Conclusion

For the first time, synergistic PELM was used to recover SA from the simulated solution. The experimental results show that almost 100% of SA was extracted with a synergistic coefficient of 640. Further SA extraction and recovery using PELM containing synergistic formulation were investigated in this study. At the condition of 5% w/v of mixture Span 80 + Tween 80 at HLB 6, 300 rpm agitation speed, 0.1% w/v nanoparticles, 0.1 M Aliquat 336 + 0.1 M TOA, and 1.0 M NaOH, the emulsion was stable, and almost 100% of SA was extracted with 5 times enrichment. Pickering emulsion has the advantage of rapid and efficient demulsification performance, where it is easily demulsified using heating and ultrasonic vibration. Therefore, it can be concluded that the synergistic PELM method could be a promising option regarding lower carrier consumption, stable, and high extraction performance.

Authors' Contribution NFMN was involved in investigation, conceptualization, methodology, writing—original draft, writing—review & editing. NO helped in conceptualization, methodology, resources, supervision, writing—review & editing. NJ helped in conceptualization, methodology, resources, writing—review & editing. INSK contributed to investigation. SSS was involved in investigation.

Declarations

Conflict of Interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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