The Feasibility of Emulsion Liquid Membrane for the Extraction of Organic Acids from Wastewater

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Abstract. The separation of hazardous organic acid pollutants such as phenol and carboxylic acids from aqueous waste streams released from industries is important and essential for environmental pollution. Acetic acid, benzoic acid, and phenol individually extracted from their aqueous solutions using emulsion liquid membranes prepared with kerosene as a membrane phase, Span 80 as a surfactant and NaOH as a stripping agent in the inner phase of W/O emulsions. Experiments have been performed to study the effect of volume ratio of membrane phase to internal phase ($V_M/V_I$), stripping phase concentration in the internal phase, agitation speed of feed solution, and volume ratio of emulsion phase to feed phase ($V_E/V_F$) on the organic acid extraction rates. More than 98% of benzoic acid and phenol can be extracted in less than 5 minutes, acetic can also be extracted but at much slower rates. Comparison of the extraction rates of organic acid indicates that benzoic acid and phenol are extracted more rapidly than that of acetic acid because the distribution coefficient ($m$) of benzoic acid and phenol is much larger than that of acetic acid due to their ability to dissolve in the membrane phase. The effective diffusivities indicate that the mobility of these compounds in the membrane phase obeys the following order: benzoic acid > acetic acid > phenol.

Keywords: Wastewater; Organic acids; Extraction; Emulsion Liquid Membrane

1. Introduction
Wastewater sources with low acid concentrations are invariably found in plants of acid production, industries that use acids as raw materials or catalysts, metal plating industries, processes of fermentation, etc. The concentration ranges of those compounds in wastewater range from 0.5 to 4%, depending on the generation source. Since large volumes with low acid concentrations are to be treated, the primary objective in such situations is to extract acids from the solution and not to separate them with objective being reduction in the Chemical Oxygen Demand (COD) of wastewater to meet prescribed limits[1].
Benzoic acid is used as a preservative in many food products, such as orange juice, sauces, jams, and jellies. A major source of benzoic acid and its derivatives released into the aquatic environment are coal, paper and pulp mill effluents and agricultural runoff. Benzoic acid concentrations in groundwater ranged from 10 to 27500 µg/L [2]. In some countries, the usage of benzoic acid as an additive for food was discontinued; even in small amounts. The World Health Organization (WHO) advises a maximum allowable daily human benzoic acid intake of 5 mg / kg body weight [3].
Acetic acid is one of the major organic pollutants released from industrial sources. Acetic acid's primary sources include the production of cellulose acetate, aspirin, and other processes using acetic acid as a raw material or solvent and petrochemical waste. Depending on the process of nature, the concentration of acetic acid ranges from 0.1% to 5% by weight in wastewater. When high concentrations of acetic acid released into water bodies, this waste would increase the demand for oxygen. It was found to be fatal at 320 ppm and above, with all fish dead at 24 hours [4]. Phenolic compounds are important organic intermediates: they have been largely used in plastics, pharmaceutical, paint, pulp and paper industries, and wood products. A large amount of phenol-contaminated water is therefore produced, which needs to be treated before it is discharged. This is because of their toxicity and contribution to health problems. Phenolic compounds are considered as pollutants of high-priority concerns. According to the US Environmental Protection Agency, phenol is classified as an important pollutant and the total phenols in drinking water are regulated to be below 0.5 μg / L [5].

Wastewaters containing acids, both inorganic and organic acids (carboxylic and phenolics) are often encountered and this has been a hard problem for years. Removal of these pollutants require strategies involving, ion exchange, membrane-based solvent extraction, adsorption, extraction, separation using membranes, reactive extraction, reactive distillation, separation by emulsion liquid membrane, etc. Since the patent of Li in 1968 [6], Separations of the emulsion liquid membrane (ELM) is suggested for various industrial applications. ELM is prepared by forming an emulsion of two immiscible phases and then dispersing the emulsion into a third phase (the phase of continuous or "feed"). In the extraction of dilute organic acids from aqueous solutions by emulsion liquid membrane, the acid solute distributes into and diffuses across the oil membrane phase to react with encapsulated droplets of aqueous sodium hydroxide (or other bases). Emulsion liquid membranes can be considered as double emulsions, water/oil/water (W/O/W) systems or oil/water/oil (O/W/O) systems. The oil phase which is the membrane phase operates as a selective barrier which separates the internal droplets encapsulated in the emulsion from the continuous external phase. The size of emulsion globule depends on the nature and concentration of the surfactants in the emulsion, the viscosity of the emulsion, and the mixing mode and strength. The size is usually controlled in the range between 0.2 and 2 mm diameter. Every emulsion globule has many small encapsulated droplets with a typical diameter of 1–10 μm. The solute to be separated is specifically transferred from the continuous external phase to the encapsulated internal phase droplets. The emulsion is separated by settling or heating at the end of an extraction process and can recover the encapsulated phase by breaking the emulsion [7]. ELM process has gained significant application due to its possible advantages compared to other separation processes, especially over extraction by solvent, distillation, and separation using solid membrane [8]. ELM achieves the advantage of achieving high separation efficiencies due to high available interfacial area for mass transfer, low energy consumption, economical, efficient for low solute concentration, low solvent requirement, and extraction and stripping taking place in a single stage.

The main aim of the present work is to investigate the performance of emulsion liquid membrane for the removal of organic acids and phenol to evaluate the efficacy of treatment methodology in a reduction of their concentration to a minimum in wastewaters. Experiments have been performed to study the effect of two variables of emulsion composition, namely; volume ratio of the membrane phase to internal phase \(V_M/V_I\), and stripping phase concentration in the internal phase, and two parameters of the process; agitation speed of feed phase on the organic acid extraction rates, and volume ratio of emulsion phase to feed phase \(V_E/V_F\). A comparative study for the extraction of the three organic acids by the ELM system was also achieved.

2. Experimental

Kerosene of boiling point ranging from 175 to 325 ° C, pellets of sodium hydroxide, Span 80 (Sorbitan monooleate), phenol, benzoic acid, and acetic acid were A. R. Grade and obtained from
Sigma-Aldrich. The required concentration and solutions of organic acid and sodium hydroxide (NaOH) were prepared by dissolving them in deionized water with appropriate weight or volume.

2.1. ELM extraction experiments

The emulsion type Water-in-oil (W/O) was prepared by gradually adding the internal stripping phase NaOH with concentrations, Cio of (0.3, 0.5, 0.7, 1, 2, 3) M to the oil membrane phase which contains kerosene and 2% (w/v)) Span-80 with efficient mixing supplied by a high-speed homogenizer of type Ultra Turrax IKA-T45 (Germany) at 10,000 rpm speed for 1 min to obtain a milky white liquid membrane. Before the extraction procedure, the emulsion must be freshly prepared. Volume ratios of the membrane phase to the internal stripping phase (V_m/V_i) were (2/1, 3/1, 4/1, 5/1, 9/1). The prepared W/O emulsion was then dispersed in the aqueous feed phase containing organic acids (phenol, benzoic acid, and acetic acid) with initial concentrations (30, 500, and 600) ppm respectively in a ratio of emulsion phase to external aqueous feed phase ratio (V_E/V_F) as (1/1, 1/3, 1/4, 1/5, 1/6) by volume and stirred by Heidolph RZR 2041 (Germany) digital overhead stirrer with an agitation speed of (200, 300, and 400 rpm). Ohaus Corporation (USA) pH meter was used to measure the pH of the feed phase. Figure 1 shows the schematic diagram of the emulsion liquid membrane process.

![Figure 1. Schematic representation of the removal of organic acids by ELM](image)

Samples were taken at different intervals from the agitated solution (from feed phase at 10 cm depth from the beaker) by a micropipette. The taken samples were isolated by filtration from the emulsion phase using a 0.2 μm nominal pore syringe filter. (Simsii, Inc. the USA).

To determine average emulsion globule sizes, enlarged photographs of the emulsion solution were analyzed. In order to get a credible impression of globule sizes, the diameters of more than 250 randomly selected emulsion globules were measured with a microscope (model N117M with fitted 7Mp Digital Camera, Beijing Novel Optics Co., Ltd/China) connected to a desktop computer and the Sauter mean diameter (i.e. area-averaged diameter) was calculated. The sample is taken at best time for pollutants extraction process to occur, and it is placed on the slide of microscope which an image is taken at few minutes before coalescence occurs. The digital camera of the microscope was connected to computer to determine drop size by computer program software (AmScope, version 3.2) as shown in Figure 2.
The concentration of phenol and benzoic acid in the external aqueous phase decreases with time during the ELM extraction as reflected by the decrease in light absorbance determined by Thermo Genesys 10 UV Spectrophotometer (USA). To find concentrations of phenol and benzoic acid at any time during the process in the external phase, calibration curves for absorbance vs. concentration were prepared by measuring the absorbance of different known concentration samples before the experiments. The measurement of maximum absorbance took place at the following wavelengths: phenol, 272 nm; benzoic acid, 287 nm. Because acetic acid does not absorb in the UV light range, its concentration was determined by a conductivity meter (HM digital, COM-100 EC/TDS meter, Korea). Before the test, the relation between the concentration of acetic acid and electrical conductivity was plotted in order to find the acetic acid concentration in the external feed phase at any time during the extraction process.

2.2 Measurement of the partition coefficients
The coefficients of the phase partition were determined for all three organic acids. The viscosity of the membrane phase was measured using a rotational viscometer (Fungilab, Spain) to be used in correlations to estimate the diffusivity of the solute in the membrane. Coefficients of the phase partition were determined by equilibrating 30 mL of an aqueous solution containing 600, 500, 30 ppm of acetic acid, benzoic acid, and phenol respectively, with 30 mL of kerosene containing 3% (w/v) Span-80 at 25°C. Solutions were agitated using a shaker (Karl Kolb D-6072, Germany) for at least 20 minutes (this time determine by experimental). Samples of aqueous phase were then analyzed to find the concentration of the solute in the aqueous phase, and the concentration of solute in the membrane phase was calculated from the mass balance. The partition coefficient was determined from the ratio of organic acid concentration in the membrane phase (kerosene) to its concentration in the aqueous phase.

3. Results and discussion
3.1. Measurement of the partition coefficients
The W/O emulsions containing NaOH as its internal phase when dispersed in the feed solution by agitation break down and form a large number of tiny globules. Each globule of emulsion contains numerous tiny internal aqueous phase encapsulated droplets of sizes ranging from 1–10 μm in diameter[9]. The effectiveness of the ELMs is never constrained by the inner surface areas. It is rather the external surface of dispersed emulsion (organic with a tiny droplet of aqueous internal phase) globules that often dictates the rates of mass transfer. To ensure rapid mass transfer, it is necessary to disperse the emulsion appropriately in the continuous phase. Generally, the size of the emulsion globule depends on the viscosity of the emulsion, concentration and dispersion characteristics of the stripping reagent in the emulsion, and intensity and mixing mode [10].
The globule size and the globule size distribution of emulsion are of the same importance as drop size and drop size distribution in processes of solvent extraction. They are indicative of the interfacial area available between the emulsion and the continuous external phase and have a significant effect on mass transfer, emulsions stability, and hence ELM extraction efficiency [11]. Hence, the determination of the emulsion globules size in an external phase is very important in order to approach a successful design, scale-up, and to study ELM systems performance.

The emulsion globule diameter can be defined as Sauter mean diameter ($d_{32}$) which demonstrates the mean surface diameter as follows [9]:

$$d_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i} = \frac{V}{A}$$

(1)

Where $d_i$, $n_i$: are the globule diameter and number relating to the ith class (the globule diameter was detriment by the analysis of the microscope photographs using computer software AmScope).

$V$, $A$: are the dispersed phase total volume and area, respectively.

The emulsion globule Sauter mean diameters for the three organic acids measured at time in which maximum extraction efficiency was obtained are given in Table 1.

**Table 1. Emulsion globule diameter**

| Organic Acid | Solute concentration (ppm) | $d_{32}$ (µm) |
|--------------|-----------------------------|---------------|
| Acetic acid  | 600                         | 88.3231       |
| Benzoic acid | 500                         | 90.0998       |
| Phenol       | 30                          | 147.9751      |

The size of the globule depends on how much and which extractable solute has been added into the feed phase. Acetic acid with higher feed concentration shows the smaller globule size. This could be due to alteration in interfacial tension resulting from solute concentration [12].

The globule size distribution of the emulsion can be seen in Figure 3. It can be observed that the dominant droplet diameter was 15 µm for acetic acid having a frequency of 68%, 25µm for benzoic acid having a frequency of 27%, and 115 µm for phenol having a frequency of 28%.

**Figure 3.** Emulsion globule size distribution for (a) Acetic acid, (b) Benzoic acid, (c) Phenol

Figure 4 shows optical microscope images of emulsion globule at the time required for maximum removal efficiency viz. 50, 5, 4 min for acetic acid, benzoic acid and phenol respectively. It can be seen from the Figure that the samples of dispersed emulsion globules in the feed phase for acetic and benzoic acids contain relatively fewer globules than of phenol, this explains the reason why phenol is extracted more rapidly than of acetic acid and benzoic acid.
3.2. Distribution coefficients of organic acids between kerosene and water

The distribution coefficients for acetic acid, benzoic acid, and phenol were experimentally determined by equilibrating equal volumes of aqueous phase containing organic acids with kerosene phase containing 3% (w/v) Span-80 at 25˚C.

The distribution coefficient, \( m \), is defined as the ratio of the solute concentration in the organic phase (kerosene) to the solute concentration in the aqueous phase. In certain processes such as partition chromatography, zone refining, and solvent extraction, the distribution coefficient is significant. It also plays an important role in chemistry of surface and can be used to represent different physicochemical equilibrium. The mean values of the measured distribution coefficient of the three organic acids are given in Table 2. Based on these values, the rate of benzoic acid extracted by ELM is much larger than acetic acid and phenol. This behavior stems out from the fact that benzoic acid has a very favorable distribution coefficient towards kerosene over water.

The value of the distribution coefficient is a measure of hydrophobicity and hydrophilicity of the solute. HLB for solute can be calculated from:

\[
H.L.B = \sum (\text{hydrophilic group numbers}) - n (\text{group number per } \text{CH}_2 \text{ group}) + 7
\]  

(2)

where \( n \) is the number of carbon atoms [13].

For a given homologous series, the HLB decreases as the number of C atoms in the chain increases. The hydrophilic-lipophilic balance (HLB) of nonionic surfactants has been correlated with many of their physical properties such as heats of hydration, dielectric constants, concentration of critical micelle, phase inversion temperatures of emulsions, cloud points, spreading coefficients of water on oil or of oil on water, and oil-water interface interfacial tension. Within a given homologous sequence of surfactants, strong correlations were found between the HLB and these properties. To date, the search for a particular correlation between the value of HLB and another surfactant property, which could be determined more easily than the HLB, has not been found.

Apparently, the solute partitioning coefficient between water and oil, \( m \), would appear to be very suitable for correlation with the balance between their hydrophilic and lipophilic tendencies. Davies and Rideal [13] studied the combination of the kinetic treatment of coalescence of the emulsion with the transferring free energy change of a molecule of surfactant from water phase to oil phase and found the following correlation:

\[
HLB = 7 - 0.829 \log(m)
\]  

(3)

Equation (3) can be used for the calculation of HLB values from \( m \) values and vice versa if required [14]. These values of HLB calculated from Eq. 2 are compared in Table 2 with the values calculated from the distribution coefficients according to Eq. 3 for the three organic acids. The correct HLB
values (calculated by Equation (2), are plotted in Figure 5 versus the logarithms of the distribution coefficients to obtain a straight line.

Table (2) Comparison between HLB values from Equation (2) and values derived from distribution coefficients of organic acids Equation (3) between water and (kerosene+ span80)

| Solute      | m  | HLB<sub>Eq(2)</sub> | HLB<sub>Eq(3)</sub> |
|-------------|----|----------------------|----------------------|
| Acetic acid | 0.11 | 8.625                | 7.795                |
| Benzoic acid| 0.99 | 6.250                | 7.00                 |
| phenol      | 0.56 | 6.050                | 7.208                |

The agreement between HLB values of organic acids calculated from Equation (2) and the values estimated by Equation (3) was good with correlation coefficient (R2) value of 0.9.

Figure 5. Relationship between correct HLB values obtained from (Equation (2)) and logarithms of water-kerosene distribution coefficients

3.3 Measurement of the partition coefficients

In order to predict the effective diffusivities (D<sub>eff</sub>) of the individual solutes (acetic acid, benzoic acid, and phenol) within the emulsion globules; (i.e. inside the organic phase toward the tiny internal aqueous droplets) it is necessary first of all to estimate the diffusion coefficients of these solutes in both water and kerosene phase. The Wilke- Chang Equation (4) was used to evaluate the diffusion coefficients (D<sub>AB</sub>) of the various unreacted solutes in both water and kerosene.

\[
D_{AB} = 1.17 \times 10^{-16} \frac{T(\psi M)^{0.5}}{\mu V_A} \tag{4}
\]

where, \( \psi \) is the association factor of solvent, for the aqueous phase and oil phases, which have the values of 2.6 and 1.0, respectively; \( V_A \) is the molar volume of solute (m<sup>3</sup>/kg mol); \( \mu \) is the solvent viscosity (kg/m. s) and \( M \) is the molecular mass of solvent (kg/kg mol) [15]. Then the effective diffusion coefficients were estimated using the Jefferson- Witzell – Sibbett equation (Equation (5)) [16], following the lead of Ho et al.[17], who were the first investigators to conveniently use this equation that had been originally proposed for conductive heat transfer in dispersed systems for estimation of D<sub>eff</sub> in ELMs.

\[
D_{eff} = A_A \left[ 0.5 + n \right] D_A D_w + D_w \frac{A_y}{A_A} \tag{5}
\]

\[
D_A = 2mD_w D_A \left[ \frac{mD_w D_A}{D_w - mD_A} \right] \log \left( \frac{mD_w D_A}{D_w} \right) \frac{1}{(mD_w - D_A)} \tag{6}
\]
\[ A_\alpha = \pi/4 \]
\[ A_r = (1+2n)^2 - \frac{\pi}{4} \]
\[ A_s = (1+2n)^3 \]
\[ n = 0.403 (V_M/V_I)^{1/3} - 0.5 \]

\( m \) is the solute distribution coefficient between membrane phase and aqueous phase, \( V_M/V_I \) is the membrane to internal phase volume fraction (micro drop holdup). \( D_W \) is the diffusion coefficient of the solute in water, and \( D_M \) is the diffusion coefficient of solute in membrane calculated from Equation (4). The calculated values of the diffusion coefficients for various organic acids are given in Table 3.

The Jefferson - Witzell - Sibbett equation was used to estimate the effective diffusivity of organic acids in the mixture of emulsion predicted on the concentration driving force determined in terms of concentration of membrane phase. The only emulsion parameter that influences the effective diffusivities is \( V_M/V_I \). The calculated values of the effective diffusivities for various solutes used in this investigation are presented in Table 4.

Table 3. Diffusion coefficients of organic acids in aqueous and membrane phases

| solute  | Acetic acid | Benzoic acid | phenol |
|---------|-------------|--------------|--------|
| \( D_W \) (cm\(^2\)/s) | 1.33 \( \times \) 10\(^{-7}\) | 9.73 \( \times \) 10\(^{-8}\) | 1.02 \( \times \) 10\(^{-7}\) |
| \( D_M \) (cm\(^2\)/s) | 1.50 \( \times \) 10\(^{-7}\) | 1.14 \( \times \) 10\(^{-7}\) | 1.22 \( \times \) 10\(^{-7}\) |

Table 4. Effective diffusivities (\( D_{eff} \)) and solute reaction equilibrium constant (\( K \)) of organic acids in ELM

| solute       | \( D_{eff} \) (cm\(^2\)/s) | \( K \) (-) |
|--------------|-----------------|----------|
| Acetic acid  | 1.14 \( \times \) 10\(^{-7}\) | 1.8 \( \times \) 10\(^9\) |
| Benzoic acid | 4.67 \( \times \) 10\(^{-7}\) | 6.3 \( \times \) 10\(^9\) |
| phenol       | 1.48 \( \times \) 10\(^{-7}\) | 1.0 \( \times \) 10\(^4\) |

The effective diffusivity represents the diffusivity of organic acids in the membrane phase (diffusion of solutes moving inside the organic phase toward the tiny aqueous internal phase droplets). The effective diffusivities indicate that the mobility of these compounds in the membrane phase obeys the following order: benzoic acid > acetic acid > phenol. The same order of the constants of the reaction equilibrium of the solute (equal to the quotient of the dissociation constants of acid and water) values at 25\(^\circ\)C [18], can be seen in Table 4.

3.4 Effect of stripping phase concentration

The extraction results are presented in all Figures below in terms of remaining fraction of the organic acid (\( C_t/C_0 \)) vs. extraction time, \( t \), which gives a better illustration of the extraction results.
Figure 6. Effect of stripping phase concentration on organic acids extraction efficiency by emulsion liquid membrane (a) acetic acid, (b) benzoic acid, (c) phenol; concentration of span 80 =2%, $V_M/V_I=4:1$, $V_E/V_F=1:4$, agitation speed of feed solution =300 rpm, emulsification speed 10,000 rpm

The internal stripping agent concentration is an effective parameter for the experiment for liquid membrane extraction as it transfers the solutes from the membrane phase to the internal aqueous phase. A driving force for the extraction of organic acid in the ELM system is established from a pH difference between the feed and the stripping phase. The effect of NaOH concentration in the stripping solution was investigated and the results are shown in Fig. 6. The stripping phase concentrations of 0.3, 1, 0.5 M that gave high separation efficiency were selected for acetic acid, benzoic acid, and phenol extraction respectively. Mortaheb et al. [19] declared that a high concentration of NaOH increases the pH of the internal aqueous phase and osmotic swelling can occur under a high difference in pH between the feed phase and the internal phase. When NaOH concentration is low, the emulsion is stable; but, there is no enough NaOH to react with an organic acid in the internal phase because an excessive amount of the stoichiometric NaOH is required in order to neutralize the organic acid and achieve acid removal rate as high as possible. When NaOH concentration is high, the liquid membrane is unstable and hence the removal efficiency decreases.

3.5 Mixing speed of feed solution influence on removal of organic Acids

The mixing speed plays an important part in the transfer rate of the solute through the liquid membrane. Increasing the agitation level will increase the interfacial area and the coefficient of mass transfer, but emulsion droplets are likely to break at a certain level of agitation and thus reduce the overall enrichment and extraction of acids [20].

Figure 7. Effect of mixing speed of feed solution on organic acids removal (a) acetic acid, (b) benzoic acid, (c) phenol; concentration of span 80 =3%, $V_M/V_I=4:1$, $V_E/V_F=1:4$, emulsification speed 10,000 rpm

Figure 7. shows extraction of organic acids at mixing speeds 200, 300, and 400 rpm. It can be shown from Fig. 7 that stirring at 300 rpm provides maximum removal of the three organic acids. When the agitation speed decreased below 300 rpm, the rate of mass transfer for the organic acids was decreased due to the increase in the size of the emulsion globules. Increasing the mixing speed results in the creation of smaller globules of emulsion in the external phase, thereby greater mass transfer.
interfacial area, and results in increased extraction rate [21]. However, at the same time, the higher speed of mixing influences the stability of emulsion globules that can lead to a breakup of the globules, causing the leakage of strip agents into the external phase. A mixing speed of 300 rpm was therefore selected to be most suitable for the extraction experiments.

### 3.6 Influence of volume ratio of membrane phase to internal stripping phase (\(V_{M}/V_{I}\))

As the volume ratio of kerosene to internal phase increases, this increases the strength of the emulsion wall and can form more stable emulsion globules. Removal percentage of organic acids increases with the increase of the kerosene: internal phase ratio as can be seen from Fig. 8.

![Figure 8](image1.png)

**Figure 8.** Effect of volume ratio of membrane phase to internal phase on removal of organic acids (a) acetic acid, (b) benzoic acid, (c) phenol; : mixing speed of feed solution =300 rpm, concentration of span 80 =2\%, \(VE/VF=1:4\), emulsification speed 10,000 rpm.

As the ratio of kerosene: internal phase increased, adequate organic phase will be available for surrounding all the internal phase and W/O emulsion dispersion became easier [19]. However, it was also found that kerosene: internal phase ratio less than 4:1 did not improve the removal of organic acids. This phenomenon may be attributed to the resistance built up around the internal phase droplets at the high kerosene: internal phase ratio. The increase in membrane thickness provided resistance which slowed down the rate of permeation of organic acids.

### 3.7 Influence of Volume Ratio of Emulsion Phase to Feed Phase (\(V_{E}/V_{F}\))

The volume ratio of the emulsion phase to the external aqueous feed solution (treatment ratio) plays an important role in evaluating the efficacy of ELMs. The mass transfer rate in ELM systems is considered to be directly proportional to the specific area of mass transfer given in units of (m²/m³). The emulsion to feed ratio in traditional liquid-solvent extraction is the same as the solvent to feed ratio. It is a measure of the system's emulsion hold-up. An increase in the emulsion-to-feed ratio leads to an increase in the emulsion phase holdup increasing in the emulsion extraction capability. It also leads to an increase in the total surface area available for mass transfer in the system and therefore the performance of the extraction process.

![Figure 9](image2.png)

**Figure 9.** Effect of the volume ratio of membrane phase to feed phase (\(V_{M}/V_{F}\)) on removal of organic acids (a) acetic acid, (b) benzoic acid, (c) phenol; mixing speed of feed solution =300 rpm, conc. of span 80 =2\%, \(VM/VF=4:1\), emulsification speed 10,000 rpm.
The influence of changing the volume ratio of emulsion to the external phase on the removal efficiency was studied in the range 1/3 to 1/6, and the results obtained are plotted in Fig. 9. It was found that the extraction of organic acids from the external feed phase was high at a treatment ratio of 1/5 and that the increase in the efficiency of extraction was not significant in increasing the treatment ratio. Generally, with the increase in the treatment ratio, an increase in the rate of mass transfer is attained, because the internal phase capacity to act as an organic acid sink increases but requires higher emulsion volume. It was noted that there was no effect of the $V_E/V_F$ ratio on stability because the breakage of emulsion globule increases slightly as the $V_E/V_F$ ratio increases [22]. The small emulsion volume is always beneficial to make ELM less costly than the extraction of liquid solvents, as long as there is enough stripping agent exists to extract all of the organic acids from the external aqueous feed phase, for which a value of 1/5 for $V_E/V_F$ ratio was chosen as the best in all experiments.

3.8 Comparative extraction of organic acids

The extraction of organic acids from aqueous solution was found to be easily achieved using an emulsion liquid system with the membrane containing only an aliphatic solvent (kerosene) and an emulsifying agent (Span 80). The results obtained are presented in Fig. 10 in terms of the fraction of the organic acids remaining in the aqueous feed (net extracted), $C_t/C_0$.

![Figure 10. Extraction trends of organic acids](image)

Comparison of the extraction rates of acetic acid, benzoic acid, and phenol indicates that benzoic acid and phenol are extracted more rapidly than that of acetic acid in the early stages of the experiment or shorter residence contact time because the distribution coefficient ($m$) of benzoic acid and phenol shown in Table 2 is much larger than that of acetic acid due to their ability to dissolve in the membrane phase, and consequently they have higher extraction rates than acetic acid. However, at later stages i.e. longer residence contact time, the conversion efficiency of the stronger acetic acid to a non-transportable form in the inner aqueous droplets increases the degree of extraction of acetic acid. Similar behavior was observed by Patnaik [23].

4. Conclusions

In this research, the feasibility of ELM for the extraction of organic acids from wastewater was studied. The ELM technique was shown to be effective in the extraction and recovery of organic acids from wastewater. The effective diffusivities indicate that the mobility of organic acids in the membrane phase obeys the following order: benzoic acid > acetic acid > phenol. Comparison of the extraction rates of acetic acid, benzoic acid, and phenol indicates that benzoic acid and phenol are extracted more rapidly than that of acetic acid in the early stages of the experiment or shorter residence contact time because of the distribution coefficient ($m$) of benzoic acid and phenol.
Symbols

\( A \) — Area of the dispersed phase (m\(^2\))  
\( C_0 \) — NaOH concentration in the inner phase (M)  
\( C_e \) — Initial concentration of organic acids (ppm)  
\( C_r \) — Concentration of organic acids at time \( t \) (ppm)  
\( d_{12} \) — Sauter mean diameter (µm)  
\( d_t \) — globule diameter (µm)  
\( D_{sa} \) — Diffusion coefficient (cm\(^2\)/s)  
\( D_m \) — Diffusion coefficient of solute in the organic phase (cm\(^2\)/s)  
\( D_0 \) — Diffusion coefficient of solute in water phase (cm\(^2\)/s)  
\( K \) — Reaction equilibrium constant of Solute (–)

\( m \) — Distribution coefficient (–)  
\( M \) — Solvent Molecular weight (kg/kg.mol)  
\( t \) — Time (min)  
\( T \) — Temperature (k)  
\( V \) — total volume of the dispersed phase (m\(^3\))  
\( V_s \) — Molar volume of solute (m\(^3\)/kg mol)  
\( V_{si} \) — volume ratio of membrane phase to internal phase (–)  
\( V_{j}\text{/}V_{i} \) — volume ratio of emulsion phase to feed phase (–)  
\( \mu \) — Solvent Viscosity (kg/m.s)  
\( \Psi \) — Association factor of Solvent (–)

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